Food Chemistry 130 (2012) 1105–1107

Contents lists available at SciVerse ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Conductive polymer gas sensor for quantitative detection of methanol in Brazilian sugar-cane spirit

Laura O. Péres [a,*], Rosamaria W.C. Li [b], Elaine Y. Yamauchi [b], Renata Lippi [b], Jonas Gruber [b,*]

[a] Instituto de Ciências Ambientais, Químicas e Farmacêuticas, Universidade Federal de São Paulo, Diadema, SP, Brazil
[b] Instituto de Química, Universidade de São Paulo, C.P. 26077, 05513-970 São Paulo, SP, Brazil

ARTICLE INFO

Article history:
Received 31 January 2011
Received in revised form 19 March 2011
Accepted 4 August 2011
Available online 9 August 2011

Keywords:
Gas sensor
Electronic nose
Conductive polymer
Sugar-cane spirit
Alcoholic beverages
Methanol

ABSTRACT

A low-cost chemiresistive gas sensor is described, made by the deposition of a thin film of a conductive polymer, poly(2-dodecanoylsulfanyl-*p*-phenylenevinylene), doped with dodecylbenzenesulfonic acid (10%, w/w), onto interdigitated electrodes. The sensor exhibits linear electrical conductance changes in function of the concentration of methanol present in sugar-cane spirit in the range between 0.05% and 4.0%. Since the sensor is cheap, easy to fabricate, durable, presents low power consumption, and is not sensitive to ethanol, acetic acid or water, it can be used in portable equipments for monitoring methanol levels in distilled alcoholic beverages such as Brazilian sugar-cane spirit (*cachaça*).

1. Introduction

Methanol, the simplest alcohol, is toxic to humans (Blinder, Voges, & Lauge, 1988). In small amounts it may cause headache, vertigo, nausea and vomiting. The consumption of ~20 mL can cause blindness while ~60 mL is usually lethal if not treated. Small amounts of methanol may be present in alcoholic drinks, formed as a secondary product of the fermentation process (Badolato & Duran, 2000). This quantity may increase due to storage in inadequate conditions and also by some methoxyl pectines and other enzymes present in the drink (Blinder et al., 1988). There are several studies concerning the presence of methanol in various fermentation products such as ciders (Mangas, Gonzales, & Blanco, 1993) and wine (Revilla & Gonzalez-San Jose, 1998).

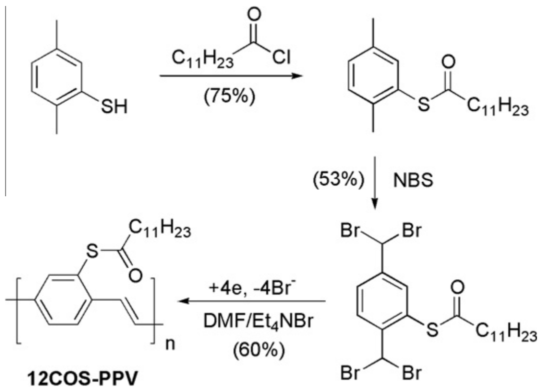
Cachaça (ca·sha·sa) or Brazilian sugar-cane spirit is the most popular spirit in Brazil. It is produced by distillation of sugar-cane juice, previously fermented by *Saccharomyces cerevisae*, and its ethanol content is in the range of 38–54% (Boscolo, Bezerra, Cardoso, Lima Neto, & Franco, 2000). Unfortunately, methanol is a possible fermentation by-product and its presence should not exceed 0.25 mL (200 mg)/100 mL of *cachaça*, according to Brazilian regulations (Badolato & Duran, 2000). The consumption of beverages from unreliable sources, containing higher concentrations of methanol, has been responsible for severe poisonings leading to central nervous system disorders, particularly blindness, and even death (Badolato & Duran, 2000). Especially dangerous are *cachaças* to which illicit additions of ethanol used as fuel were made, since it may had been adulterated with methanol (Carneiro et al., 2008).

There are several analytical methods described for the detection and quantification of methanol in the presence of ethanol being chromatography (Wang, Wang, & Choong, 2004; Zenebon et al., 1996) the most common. Other techniques are, for instance, surface plasmon resonance (SPR) (Manera et al., 2004), multi-enzyme system with chemiluninescence detection (Sekine, Suzuki, Takeuchi, Tamiya, & Karube, 1993), Fourier Transform Infrared Spectrometry (Bangalore, Small, Combs, Knapp, & Kroutil, 1994), and whole-cell biosensing (Naessens & Tran-Minh, 1998). These methods are expensive or need to be performed in a laboratory, normally far from the site where the analysis is needed.

The development of chemiresistors sensitive to organic vapours, based on metal-oxide semiconductors (MOS) (Gardner & Bartlett, 1999; Stephan, Bücking, & Steinhart, 2000), MOS field-effect transistors (MOSFET) (Naessens & Tran-Minh, 1998; Gardner & Bartlett, 1999), and electrically conductive polymers has been described (Benvenho, Li, & Gruber, 2009; Gardner & Bartlett, 1999; Gruber, Yoshikawa, Bao, & Geise, 2004; Li, Ventura, Gruber, & Carvalho, 2009; Li, Ventura, Gruber, Kawano, & Carvalho, 2008; Péres & Gruber, 2007; Rosa, Szulc, Li, & Gruber, 2005; Vanneste, De Wit, Eyckmans, & Geise, 1998). The advantages of the latter are that they operate at room temperature with very low power

* Corresponding authors. Tel.: +55 11 3091 1103 (J. Gruber).
E-mail addresses: lauraoperes@gmail.com (L.O. Péres), jogruber@iq.usp.br (J. Gruber).

0308-8146
doi:10.1016/j.foodchem.2011.08.014



Scheme 1. Synthetic route to poly(2-dodecanoylsulfanyl-*p*-phenylenevinylene) (12COS-PPV). NBS, *N*-bromosuccinimide; DMF, *N*,*N*-dimethylformamide (% Yield).

consumption, do not require expensive equipment and are portable. In the particular case of methanol vapours the sensors described so far are based on MOS (Bangalore et al., 1994; Patel, Patel, & Vaishnav, 2003) and do not show any selectivity towards methanol when mixed with ethanol.

In the present work, we describe a low-cost, rapid and accurate method for the determination of methanol in *cachaça*, based on a chemiresistive polymeric gas sensor, whose active layer is a thin film of a conducting polymer, poly(2-dodecanoylsulfanyl-*p*-phenylenevinylene) (12COS-PPV) (Scheme 1), doped with camphorsulfonic acid. Since the sensor is sensitive to methanol, but not to ethanol, it can be used for detecting methanol in *cachaça* or in any other alcoholic beverage.

2. Materials and methods

2.1. Synthesis of the polymer

Poly(2-dodecanoylsulfanyl-*p*-phenylenevinylene) (12COS-PPV), was synthesised from commercial 2,5-dimethylbenzenethiol (Aldrich, 98%) in three steps as previously described in the literature (Gruber et al., 2004). The polymerisation step was carried out electrochemically (Utley & Gruber, 2002) at a controlled potential of 1.41 V *vs*. Ag/AgBr.

2.2. Preparation of the sensor

The sensor substrate consisted of a flat 23 mm × 9 mm fibreglass printed circuit board with a pair of tin-coated copper interdigitated electrodes having a gap of ca. 200 µm between them (Fig. 1). Onto this substrate a thin layer (ca. 25 µm) of 12COS-PPV doped with dodecylbenzenesulfonic acid (DBSA) was deposited by drop-casting a solution containing 4.4 mg of 12COS-PPV, 0.5 mg of DBSA, and 5.0 mL of chloroform.

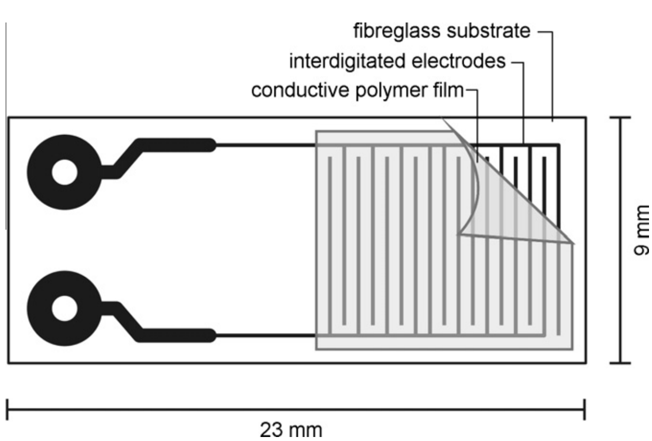


Fig. 1. Top view of the sensor.

2.3. Measurements

A sample of *cachaça* of the brand "Pirassununga 51" fabricated by Companhia Müller de Bebidas was tested for methanol by gas chromatography. Since no methanol was detected it was used for the preparation of the analytical samples of this study, which consisted of 10 *cachaça* samples containing 0.05%, 0.1%, 0.2%, 0.4%, 0.6%, 0.8%, 1.0%, 1.5%, 2.0%, and 4.0% (v/v) methanol.

The sensor was exposed in closed vessels to the headspace of the above samples, kept at 30 °C, for 10 s (exposure period), then to dry air, at the same temperature, for 50 s (recovery period). The tests were repeated 10 times for each of the 10 samples. The conductance over the sensor's contact pairs was continuously monitored with an accurate conductivity metre (Da Rocha, Gutz, & Do Lago, 1997), operating with 80 mV peak-to-peak 2 kHz triangle wave ac voltage, and connected *via* a 10 bit analog to digital converter to a personal computer.

3. Results and discussion

The electrical behaviour of doped 12COS-PPV films upon exposure to several organic solvents and to water had been already studied (Gruber et al., 2004). A very interesting behaviour was then observed, which included no sensitivity to water, acetic acid, and ethanol vapours while the sensor exhibited high sensitivity to methanol. This is an intriguing fact, since methanol and ethanol are closely related from a chemical point of view. The mechanism of the electrical response of conductive polymers towards volatile compounds is not fully understood at present. It may involve swelling of the polymers caused by absorption of the analyte molecules causing changes in the extrinsic conductivity, and/or changes in the intrinsic conductivity due to charge-transfer interactions between the analytes and the polymers (Slater, Watt, Freeman, May, & Weir, 1992). The molecule approximate diameters of water, methanol and ethanol are 2.75, 3.90 and 4.71 Å, respectively (Sakale et al., 2011). Possibly, ethanol molecules are too big to fit in the free volume cavities of the polymer matrix, while water molecules, although smaller, are too lipophobic. Further structural investigations are being carried out in our group to elucidate the observed behaviour.

The particular response pattern of this polymer makes it an excellent candidate for a gas sensor capable of measuring methanol concentration in alcoholic beverages as, for instance, *cachaça*, since the presence of ethanol, water and even acetic acid does not interfere.

Repetitive exposure/recovery cycles of the sensor to 10 *cachaça* samples containing different concentrations of methanol ranging from 0.05% to 4.0% were performed. The sensor exhibited fast response and recovery times and no drift of the background conductance even after hundreds of tests carried out over a period of 8 months.

Thus, relative responses (Ra), defined as Ra = $(G_f–G_o)/G_o$, where G_f is the conductance at the end of the exposure period and G_o is the initial conductance, were calculated for all the measurements. The average values of Ra and their relative errors were plotted against the methanol concentration of the samples (Fig. 2).

The plot of Fig. 2 reveals a linear relationship between Ra and the concentration of methanol. A linear fit (linear regression) gave

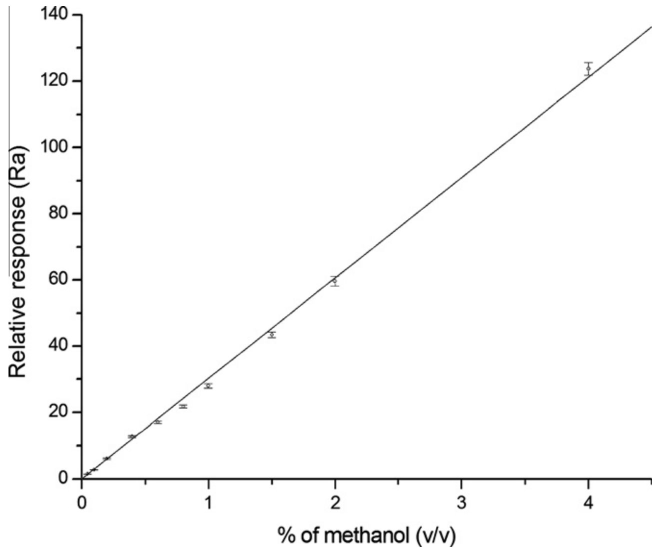


Fig. 2. Plot of the relative response (Ra) of the sensor *vs.* the concentration of methanol in *cachaça* (v/v).

a correlation coefficient of 0.9993 and the following equation: Ra = (30.31 ± 0.32) × (% conc. of MeOH).

Finally, it is worth noting that advantages such as (i) very low power consumption of the sensor (<1 μW), (ii) low production cost (<1 US$), (iii) short analysis time (1 min), (iv) reproducibility, and (v) durability make this sensor suitable for use in cheap portable equipments that could be present in distilleries located far from big urban centres, where accidents with methanol containing *cachaças* have been more likely to occur.

4. Conclusion

Poly(2-dodecanoylsulfanyl-*p*-phenylenevinylene) (12COS-PPV) doped with dodecylbenzenesulfonic acid (DBSA) and deposited onto interdigitated electrodes formed a highly selective chemiresistive sensor that can be used for methanol detection and quantification in Brazilian sugar-cane spirit (*cachaça*). The sensor is cheap, easy to fabricate, operates at room temperature, has low power consumption and can be used also for the analysis of other alcoholic beverages that may contain small, but yet dangerous, amounts of methanol.

Acknowledgements

The authors would like to thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) (Grant No.: 06/59464-2) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) (Grant Nos.: 303717/2010-6 and 472297/2007-4) for their financial support.

References

Badolato, E. S. G., & Duran, M. C. (2000). Risco de intoxicação por metanol pela ingestão de bebidas alcoólicas. *Revista de Psiquiatria Clínica, 27*(2), 1–4.

Bangalore, A. S., Small, G. W., Combs, R. J., Knapp, R. B., & Kroutil, R. T. (1994). Automated detection of methanol vapor by open-path Fourier-Transform Infrared Spectrometry. *Analytica Chimica Acta, 297*(3), 387–403.

Benvenho, A. R. V., Li, R. W. C., & Gruber, J. (2009). Polymeric electronic sensor for determining alcohol content in automotive fuels. *Sensors and Actuators B-Chemical, 136*(1), 173–176.

Blinder, F., Voges, E., & Lauge, P. (1988). The problem of methanol concentration admissible in distilled fruit spirits. *Food Additives and Contaminants, 5*(3), 343–351.

Boscolo, M., Bezerra, C. W. B., Cardoso, D. R., Lima Neto, B. S., & Franco, D. W. (2000). *Journal of the Brazilian Chemical Society, 11*(1), 86–90.

Carneiro, H. S. P., Medeiros, A. R. B., Oliveira, F. C. C., Aguiar, G. H. M., Rubim, J. C., & Suarez, P. A. Z. (2008). Determination of ethanol fuel adulteration by methanol using partial least-squares models based on Fourier transform techniques. *Energy & Fuels, 22*(4), 2767–2770.

Da Rocha, R. T., Gutz, I. G. R., & Do Lago, C. L. (1997). A low-cost and high-performance conductivity meter. *Journal of Chemical Education, 74*(5), 572–574.

Gardner, J. W., & Bartlett, P. N. (1999). *Electronic Noses–Principles and Applications*. New York: Oxford University Press, Inc..

Gruber, J., Yoshikawa, E. K. C., Bao, Y., & Geise, H. J. (2004). Synthesis of a novel poly(*p*-phenylene vinylene) derivative and its application in chemiresistive sensors for electronic noses with an unusual response to organic vapours. *e-Polymers*, article number 014.

Li, R. W. C., Ventura, L., Gruber, J., & Carvalho, L. R. F. (2009). Low cost selective sensor for carbonyl compounds in air based on a novel conductive poly(*p*-xylylene) derivative. *Materials Science and Engineering C-Biomimetic and Supramolecular Systems, 29*(2), 426–429.

Li, R. W. C., Ventura, L., Gruber, J., Kawano, Y., & Carvalho, L. R. F. (2008). A selective conductive polymer-based sensor for volatile halogenated organic compounds (VHOC). *Sensors and Actuators B-Chemical, 131*(2), 646–651.

Manera, M. G., Leo, G., Curri, M. L., Cozzoli, P. D., Rella, R., Siciliano, P., et al. (2004). Investigation on alcohol vapours/TiO_2 nanocrystal thin films interaction by SPR technique for sensing application. *Sensors and Actuators B-Chemical, 100*(1–2), 75–80.

Mangas, J., Gonzales, M. P., & Blanco, D. (1993). Influence of cider-making technology of low-boiling-point volatile compounds. *Zeitschrift für Lebensmittel Untersuchung und Forschung, 197*(6), 522–524.

Naessens, M., & Tran-Minh, A. (1998). Whole-cell biosensor for direct determination of solvent vapours. *Biosensors & Bioelectronics, 13*(3–4), 341–346.

Patel, N. G., Patel, P. D., & Vaishnav, V. S. (2003). Indium tin oxide (ITO) thin film gas sensor for detection of methanol at room temperature. *Sensors and Actuators B-Chemical, 96*(1–2), 180–189.

Péres, L. O., & Gruber, J. (2007). The use of block copolymers containing PPV in gas sensors for electronic noses. *Materials Science and Engineering C-Biomimetic and Supramolecular Systems, 27*, 67–69.

Revilla, I., & Gonzalez-San Jose, M. L. (1998). Methanol release during fermentation of red grapes treated with pectolyticenzymes. *Food Chemistry, 63*(3), 307–312.

Rosa, R. M., Szulc, R. L., Li, R. W. C., & Gruber, J. (2005). Conducting polymer-based chemiresistive sensor for organic vapours. *Macromolecular Symposia, 229*, 138–142.

Sakale, G., Knite, M., Teteris, V., Tupureina, V., Stepina, S., & Liepa, E. (2011). The investigation of sensing mechanism of ethanol vapour in polymer-nanostructured carbon composite. *Central European Journal of Physics, 9*(2), 307–312.

Sekine, Y., Suzuki, M., Takeuchi, T., Tamiya, E., & Karube, I. (1993). Selective flow-injection determination of methanol in the presence of ethanol based on a multienzyme system with chemiluminescence detection. *Analytica Chimica Acta, 280*(2), 179–184.

Slater, J. M., Watt, E. J., Freeman, N. J., May, I. P., & Weir, D. J. (1992). Gas and vapour detection with poly(pyrrole) gas sensors. *Analyst, 117*(8), 1265–1270.

Stephan, A., Bücking, M., & Steinhart, H. (2000). Novel analytical tools for food flavours. *Food Research International, 33*(3–4), 199–209.

Utley, J. H. P., & Gruber, J. (2002). Electrochemical synthesis of poly(*p*-xylylenes) (PPXs) and poly(*p*-phenylene vinylenes) (PPVs) and the study of xylylene (quinodimethane) intermediates; an underrated approach. *Journal of Materials Chemistry, 12*(6), 1613–1624.

Vanneste, E., De Wit, M., Eyckmans, K., & Geise, H. J. (1998). Arylene alkenylenes as chemiresistors in an electronic nose. *Seminars in Food Analysis, 3*, 107–113.

Wang, M. L., Wang, J. T., & Choong, W. M. (2004). A rapid and accurate method for determination of methanol in alcoholic beverage by direct injection capillary gas chromatography. *Journal of Food Composition and Analysis, 17*(2), 187–196.

Zenebon, O., Badolato, E. S. G., Nagato, L. A. F., Duran, M. C., Aued-Pimentel, S., & Vasconcelos, D. D. A. (1996). Metanol–avaliação da ocorrência de intoxicações causadas pela ingestão de bebidas alcoólicas no estado de São Paulo. *Boletim da Sociedade Brasileira de Ciência e Tecnologia de Alimentos, 30*(1), 71–74.