Article

Metal Corrosion in Polychrome Baroque Lead Sculptures: a Case Study

Dalva L. A. de Faria,*,a Thiago S. Puglieria and Luiz Antonio C. Souzab

*aInstituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748,
Cidade Universitária, 05508-000 São Paulo-SP, Brazil*

*bLaboratório de Ciência da Conservação (Lacicor), Escola de Belas Artes, Universidade Federal de
Minas Gerais, Av. Antônio Carlos, 6627, Pampulha, 31270-901 Belo Horizonte-MG, Brazil*

Esculturas policromadas de Pb do Museu do Oratório em Ouro Preto (Minas Gerais, Brasil), expostas em um mostruário de vidro foram severamente degradadas. Os produtos de corrosão foram analisados por difratometria de raios X (XRD), espectroscopia no infravermelho com transformada de Fourier (FTIR), microscopia eletrônica de varredura (SEM), fluorescência de raios X por dispersão de energia (EDX) e microscopia Raman, e constatou-se a formação majoritária de carbonatos e formiatos de Pb. Embora carbonatos sejam comuns na corrosão atmosférica de Pb, formiatos podem ser formados tanto pela ação de ácido fórmico quanto de formaldeído, sendo sua origem um ponto importante a ser investigado. Simulações ambientais com tiras de Pb expostas a possíveis fontes desses compostos orgânicos voláteis possibilitaram concluir que o processo de degradação foi causado principalmente pelo processo de cura da tinta utilizada na base do mostruário. Contudo, produtos de limpeza, que podem conter formaldeído como conservante, mostraram-se potencialmente capazes de causar danos a objetos de chumbo, acelerando sua corrosão.

Polychrome lead sculptures from Oratory Museum in Ouro Preto (Minas Gerais, Brazil) kept inside a glass showcase were severely degraded. The formed corrosion products were analyzed by X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray fluorescence (EDX) and Raman microscopy and proved to be mostly Pb carbonates and formates. Although carbonate is a very common finding in Pb atmospheric corrosion, Pb formates can be formed by the action of formic acid or formaldehyde, being their origin a key point to be investigated. Environmental simulations with Pb coupons exposed to possible sources of these volatile organic compounds led to the conclusion that the degradation process was caused mainly by the curing process of the painted showcase baseplate. However, cleaning products, which can also contain formaldehyde as preservative, proved to be potentially harmful to Pb, accelerating its corrosion.

Keywords: formaldehyde, formic acid, Pb corrosion, Raman, preventive conservation

Introduction

Material and immaterial heritages, essential in the composition of the culture of countries and human groups, are representative of their philosophical, artistic and scientific achievements. Thus, it is clear the necessity and importance of their transmission throughout the generations. Science and technology are key elements in dealing with material culture and the understanding of their vulnerabilities and respective agents of degradation.

Degradation of material heritage is a natural ageing process and, as such, has to be dealt with under a preventive conservation context in order to minimize its effects as the damage is generally an irreversible event. The understanding of the role played by temperature, relative humidity (RH) and microenvironment composition is essential for the correct preventive strategy to be adopted. Air pollutants, particularly volatile organic compounds (VOCs) released by industrial products, such as varnishes, resins, paints and adhesives are known to be harmful, particularly to metals.[1-10]

The chemical aspects of degradation are a key issue in the preventive conservation. Studies on the interaction

*e-mail: dlafaria@iq.usp.br

between materials and pollutants lead to the clarification of the chemical mechanisms involved in the degradation, thus allowing the choice of the best preventive methods. Lead objects develop an oxide patina that prevents corrosion[11] and it is known that such patina is not efficient when acids (mainly formic, acetic and carbonic acids)[5,12-16] or, as confirmed recently, formaldehyde are present in the environment.[3] The white powder formed at the corroded surface is composed of carbonates, acetates and formates. Concerning the VOC sources, formic acid is commonly released by wood and wood composites, paints, adhesives, varnishes, sealants and some silicones;[2] acetic acid has essentially the same sources[2] whereas formaldehyde is released mainly from materials containing urea-formaldehyde resins (some wood derivatives, glues, adhesives and some papers),[17] tobacco smoke,[18] some coating materials like paints and varnishes,[1] wood and their composites,[2] as well as from products containing formaldehyde in its composition.

Recently, an intense and accelerated degradation process on polychrome lead sculptures from the Oratory Museum (Ouro Preto, Minas Gerais, Brazil) was observed. Such sculptures were in glass showcases mounted over painted steel baseplates and the extensive corrosion showed that they were in a contaminated atmosphere. Figure 1 shows two corroded sculptures, in which the corroded areas are clearly depicted by the white powdered corrosion products.

Figure 1. Corroded polychrome lead sculptures from the Oratory Museum, Ouro Preto (Minas Gerais, Brazil). The white areas correspond to corrosion products.

The steel baseplates were treated with automotive paint and since it is known that the paint cure process releases VOCs, such as formic acid and formaldehyde and that such compounds are harmful towards several materials,[3,5,13-16] it was decided to investigate the effect of the paint used in the showcases. Both formic acid and formaldehyde react at the metal surface generating formates with composition largely dependent on the VOC concentration, RH and environmental CO_2 concentration.[3]

Another possible formaldehyde source to be considered is the glass cleaning product. The use of formaldehyde in household products was banned in Brazil only recently, in 2008,[19] but it is frequently found in street marketed products which are not under the government control and, although formaldehyde use is now prohibited, it was largely employed for decades in sanitizing products.

Thus, this work aims the identification of the corrosion products formed on the polychrome sculptures from the collection of the Oratory Museum and the investigation on the sources and nature of the harmful agents.

Experimental

Materials and methods

The analyzed sculpture was part of a small (17 × 10 × 10 cm) bullet shaped oratory from the XIX century and supposedly represents Nossa Senhora da Conceição. It is a 5 cm Pb sculpture, originally painted in red, white and blue hues. Small amounts of the corrosion layer were collected directly from the artwork for analysis.

Lead foil used (0.125 mm thickness, 99.99%, Goodfellow Cambridge Ltd.) was cut in 1 cm × 2 cm coupons and cleaned with a fiber glass brush before exposing to the controlled environments. Formaldehyde (40% v/v, Carlo Erba, Milan, Italy) stabilized with methanol (10% v/v) was diluted with deionized water (USF Elga) to prepare a 1% v/v solution. Deionized water, 1% v/v formaldehyde solution, aluminum foil, synthetic blue paint (Dupont, code B9550.1437, lot 7390) and glass cleaning products (Veja Vidrex®, Reckitt Benckiser of Brazil, Cif®, Unilever of Brazil and a street marketed glass cleaning product) were used to prepare the controlled environments. Parafilm M® (Pechiney Plastic Packaging, Chicago, USA) was used as sealant. Relative humidity (RH) was 100% to speed up the ageing process and all experiments were run at least in duplicate. Lead formate $(Pb(HCO_2)_2)$ was prepared treating a saturated $PbCO_3$ solution with formic acid.

Lead exposure was carried out in 50 mL Erlenmeyer containing the components shown in Table 1. Lead coupons were kept suspended by parafilm thread and the Erlenmeyers were also sealed with parafilm. The flasks were kept on a laboratory bench at room temperature (ca. 23 °C) and illuminated.

Raman microscopy was used to characterize the corrosion products on the Pb surfaces and the corrosion

Table 1. Experimental data

System	Exposure time / days
Aluminum foil with a dry blue paint coating; the paint is the same used at the Oratory Museum and was dried for 10 days in open atmosphere[a]	10
Aluminum foil with a fresh blue paint coating; the paint is the same used at the Oratory Museum[a]	10
5 mL of the cleaning product Veja Vidrex®	24
5 mL of the cleaning product Cif®	20
5 mL of a street marketed cleaning product	15
5 mL of a 1% v/v formaldehyde solution	2

[a]2 mL of deionized water in a separated flask were added to ensure 100% RH.

solid formed on the sculpture. In some discussions, a sum of the spectra collected from the Pb coupons was used and identified as average Raman spectrum. Scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), FTIR and X-ray diffractometry (XRD) were also used to characterize the corrosion products on the sculpture.

Equipments

Raman spectra were obtained with a Renishaw inVia Reflex and with a Renishaw System 3000, both fitted with a Peltier cooled CCD camera (Renishaw, 600×400 pixels) and coupled to a Leica microscope. In the first equipment, the 632.8 and 785 nm laser lines (He-Ne laser and diode laser, respectively, both from Renishaw) were focused onto the sample by a × 50 Leica objective (NA 0.75) and the laser power was kept below 1 mW (632.8 nm) and 1.5 mW (785 nm). In the second equipment, a 632.8 nm laser line (He-Ne laser, Spectra Physics, mode 127) was used. In all cases, a visual inspection of the samples was performed to ensure that the sample was not affected by the laser illumination. From the optical and spectroscopic point of view, the Raman microscopes (System 3000 and inVia Reflex, both from Renishaw) are fully equivalent (same grating, focal distance, detector resolution, lenses, etc.), except for the fact that with System 3000, the 785 nm laser line is not available. Accordingly, and considering that the obtained spectra were the same irrespective of the equipment, the figure captions do not specify the instrument used to obtain each spectrum.

FTIR data were obtained with a Bomem MB100 equipment fitted with KBr optics and mercury cadmium telluride (MCT) quantum detector. The spectra were obtained by compressing a very small amount of sample with a diamond cell coupled to a beam condenser.

XRD data were collected with a Philips diffractometer (PW1710) using the Cu K_α radiation and a graphite monochromator. The compound identification was performed using the database PDF-2 from International Centre for Diffraction Data (ICDD).

Micrographies were obtained with a JEOL (6360LV model) microscope and EDX analysis was carried out with a Thermo Noran (Quest model) spectrometer.

Results and Discussion

Identification of the corrosion products from the degraded sculpture

The small lead sculpture was covered with a whitish material all over the paint surface. At a first glance, one would probably think of a *fungi* contamination because of the hair like aspect of the white powder. A careful examination under the stereomicroscope proved to be very effective in determining the nature of the whitish hair like structures, which were in fact microcrystals. It is noteworthy that the sculpture support, instead of being wood, as regularly found in polychrome baroque sculptures, was a bulk lead body.

Samples collected from the sculpture were first analyzed by SEM, EDX and XRD. SEM morphological analysis is generally useful for the determination of crystal habit. Since vibrational spectroscopy is a short range technique and XRD is a long range one, it is eventually important to access how crystalline the sample is and its external appearance. Particularly, the aspect is influenced by the conditions during crystal growth and, thus, adding extra information on the corrosion products. However, SEM micrographies (see Supplementary Information (SI) section) did not add new information on the corrosion products, whereas EDX revealed the presence of Pb, C and O. X-ray diffractogram (not shown), although with a poor signal-to-noise ratio, indicated the presence of basic lead carbonate ($Pb_3(CO_2)_2(OH)_2$, ICDD No. 10-0401). It is important to emphasize, however, that XRD is neither sensitive to amorphous compounds nor to chemical species present in small concentrations.

Concerning FTIR spectroscopy, a diamond cell was used due to the very small amount of sample available. This is not a problem for Raman microscopy since the laser footprint is typically ca. 2-3 μm in diameter and can be smaller in high confocal setups, but with FTIR, a beam condenser and a special accessory (diamond cell) are necessary. Even so, the tiny samples collected from the sculptures were difficult to analyze and the recorded spectra presented a poor signal-to-noise ratio (not shown), although the major peaks (assigned to basic lead carbonate) could be assigned. Furthermore, when compared to basic Pb

carbonate, the relative amount of Pb formate is small and the bands of the latter are easily hampered by the bands of the former due to accidental degeneration.

Raman microscopy was then chosen to investigate the fast degradation of the Pb sculptures, helping in understanding the corrosion process considering that, so far, there were no obvious reasons for such accelerated decay. Raman analysis confirmed the presence of basic lead carbonate (Figure 2, curve a), as indicated by the bands at 410, 1051 and 1385 cm^{-1}, assigned to in plane angular deformation and symmetric and antisymmetric carbonate C−O stretching vibrations,[20] respectively. Lead formate was also detected in some areas (Figure 2, curve b) with characteristic bands at 1343 and 1529 cm^{-1} assigned to the symmetric and antisymmetric carboxyl group stretching vibrations, respectively.[3] Figure 2, curve c, shows the Raman spectrum for the Pb formate ($Pb(HCO_2)_2$) which was included for comparison purposes.
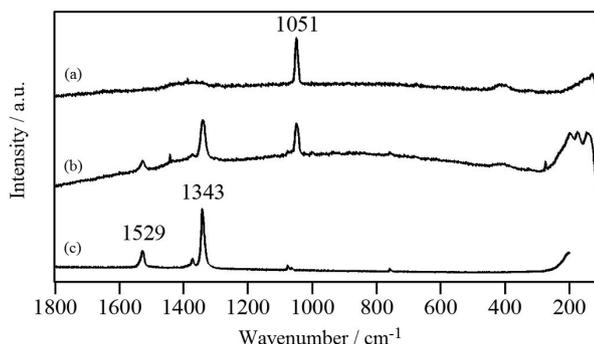

Figure 2. Raman spectra (632.8 nm) from different points of the corrosion product formed on the polychrome lead sculpture from the Oratory Museum (a and b). A lead formate spectrum (c) was added for comparison purposes.

The differences in the Raman spectra obtained from different points of samples collected from the same sculpture indicated a heterogeneous composition, with different carbonate content (Figure 3). A broad background was present in most spectra, in a behavior that is frequently observed for Pb corrosion products.[21] It is important to emphasize that the spectra reveal not a mere mixture of carbonates and formates, but different chemical phases as confirmed by the bands in the low frequency region (below 500 cm^{-1}), characteristic of lattice vibrations.

Possible sources of degradation

As it was mentioned before, generally the presence of formate is associated with formic acid released by the wood degradation.[2] It was recently shown, however, that formaldehyde also originates formates on the
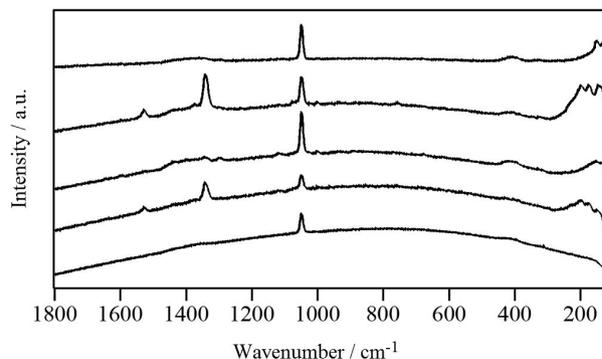

Figure 3. Raman spectra (632.8 nm) from different points of samples collected from the analyzed polychrome lead sculpture.

metal corrosion layer.[3] In the current case, all the wood objects had been removed from the exhibition hall and the sculptures were inside glass displays mounted on a painted steel baseplate. It is known that paint cure process releases formaldehyde[1] and formic acid[2] and, since these two compounds are harmful to metals, the presence of a painted steel baseplate in the showcase was the first possible source of damage.

Other plausible source of formaldehyde was glass cleaning product that could contain such compound as preservative. Although the Brazilian regulatory agency ANVISA (National Agency for Sanitary Surveillance) banned in 2008 the use of this aldehyde in cleaning products, street marketed products frequently contain a substantial amount of H_2CO.

The paint effect was investigated using lead coupons exposed to environments containing the same product (fresh and cured) used by the Oratory Museum, which kindly made available a sample of the paint used on the baseplates. The exposure periods (in days) were enough to produce a detectable visual change on the metal surface.

The average Raman spectra of the corrosion products formed on Pb coupons exposed for 10 days to the volatiles released by cured paint (Figure 4, curve b) are similar to the spectra obtained from Pb coupons exposed for 2 days to vapors of a 1% v/v formaldehyde solution (Figure 4, curve a), when formates were detected (characteristic band at 1354 cm^{-1}) together with carbonates (band at 1050 cm^{-1}). Furthermore, comparing Figure 4, curves b and d, it is clear that the formate produced by the paint volatiles is not $Pb(HCO_2)_2$. It is necessary to emphasize here that the spectra obtained from Pb coupons exposed to very low formic acid and formaldehyde concentrations (3 and 100 ppbv, respectively) are very similar (spectra not shown) and, thus, the possibility that the formate shown in Figure 4, curve b, results from formic acid and not from formaldehyde cannot be discarded.
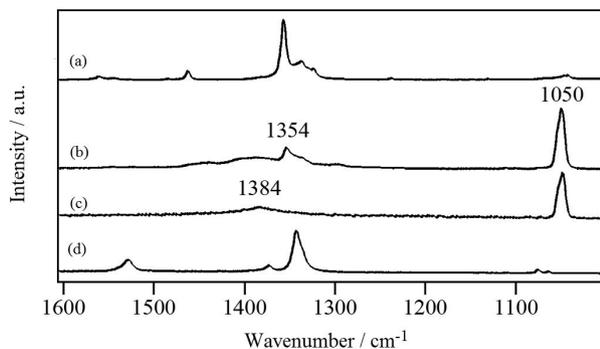
Figure 4. Average Raman spectra of Pb corrosion products formed during exposure of Pb coupons to: vapors of a 1% v/v formaldehyde solution for 2 days (a) and volatiles released from the cured (b) and fresh (c) paint used by the Oratory Museum (exposure time of 10 days). A Pb formate spectrum (d) was included for comparison purposes. All spectra were obtained using a 785 nm laser line, except curve b, in which the 632.8 nm laser line was used.

When lead coupons were exposed to environments containing fresh paint at 100% RH, a mixture of carbonates was detected in the corrosion layer (Figure 4, curve c, main bands at 1050 and 1384 cm^{-1}) and formate bands were not observed, as can be confirmed comparing Figure 4, curves c and d.

To investigate the possibility of formaldehyde release by glass cleaning products, Pb coupons were exposed to the atmosphere generated by the glass cleaning product used in that particular museum (Veja Vidrex®). The Raman spectra (Figure 5, curve b) did not show the presence of formates as can be seen in Figure 5, that also includes two formate reference spectra (Figure 5, curves a and e).
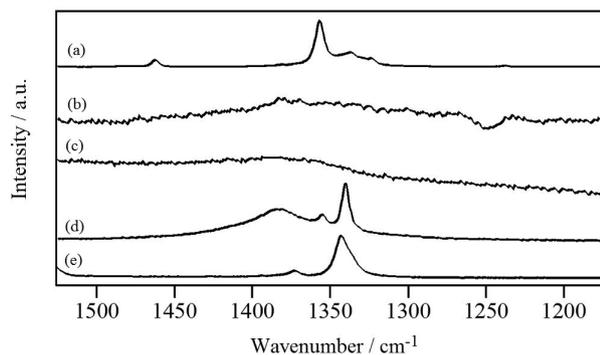

Figure 5. Average Raman spectra of Pb corrosion products formed during exposure of Pb coupons to: vapors of a 1% v/v formaldehyde solution after 2 days (a) and compounds released from Veja Vidrex® after 24 days (b), Cif® after 20 days (c) and a street marketed cleaning product after 15 days (d). A Pb formate spectrum (e) was included for comparison purposes. All spectra were obtained using a 785 nm laser line, except curve e, in which the 632.8 nm laser line was used.

Aiming to emphasize the effect of cleaning products on indoor air quality, Pb coupons were exposed to vapors released by another popular commercial glass cleaning

product (Cif®) and to a street marketed glass cleaning product, with exposure times of 20 and 15 days, respectively. In the first case (Cif®), the average Raman spectrum of the Pb corrosion layer did not show the presence of formates (Figure 5, curve c). However, the same was not true for the street marketed cleaning product (Figure 5, curve d), which led to the formation of carbonates and of a Pb formate. The spectrum shown in Figure 5, curve d, is clearly different from the characteristic spectrum of Pb(HCO$_2$)$_2$, as occurred in the case of the cured paint. So far, the exact chemical composition of this formate is unknown but experiments are being carried out to clarify this point.

Although the relative intensities of the average Raman spectrum of the corrosion products generated by the street marketed cleaning product are not the same observed when Pb coupon was exposed to formaldehyde, there is a clear agreement in terms of band position, indicating that this aldehyde is responsible for the accelerated corrosion. Furthermore, formic acid (the other plausible formate source) is not expected in the chemical composition of glass cleaning products contrarily to formaldehyde.

The results highlight the importance of a careful evaluation of commercial products, such as cleaning products and paints, aimed to be used inside museums or other institutions that keep artworks or cultural heritage items, considering the potential risk of harmful volatile compounds release that can cause significant damage in the artworks and objects in general.

Conclusions

Basic lead carbonate (Pb$_3$(CO$_2$)$_2$(OH)$_2$) and lead formates (Pb(HCO$_2$)$_2$) and other phases, so far unknown, were detected as corrosion products of a polychrome lead sculpture from the Oratory Museum, Ouro Preto (Minas Gerais, Brazil). Environmental simulations showed that the source of this corrosion process was the volatile organic compounds released in the cure process of the paint used on the steel baseplate of the showcases that exhibited the sculptures. From the chemical point of view, paint drying and curing are not necessarily the same phenomenon. Drying may imply in the mere release of solvents, whereas curing indicates that cross linking reactions are occurring. The coupon behavior clearly indicated that in the present case, drying and curing involve the release of different compounds and the literature confirms that formaldehyde is more significantly released during the paint cure.[22]

Finally, it was shown that Pb formate was detected in the corrosion layer when Pb coupons were exposed to a street marketed glass cleaning product, indicating the potential risk to artworks represented by the use of irregular products.

Thus, it is here emphasized the importance of a careful evaluation of commercial products to be used indoors prior to their use. Specifically in the case of metals, such concern is the object of the well-known Oddy tests[2] and the necessity of a continuous monitoring of the indoor air quality is a current issue in the most important museums all over the world[23] and built-on-purpose devices are increasingly being used[21] in the prevention or mitigation of the harmful effects of undesired, although sometimes unavoidable, atmospheric compounds.

Supplementary Information

Supplementary information (Figure S1) is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

References

1. Salthammer, T.; Mentese, S.; Marutzky, R.; *Chem. Rev.* **2010**, *4*, 2536.

2. Thickett, D.; Lee, L. R.; *The Selection of Materials for the Storage or Display of Museum Objects*; The British Museum: UK, 2004.

3. Faria, D. L. A.; Cavicchioli, A.; Puglieri, T. S.; *Vib. Spectrosc.* **2010**, *54*, 159.

4. Raychaudhuri, M. R.; Brimblecombe, P.; *Stud. Conserv.* **2000**, *45*, 226.

5. Niklasson, A.; Johansson, L.-G.; Svensson, J.-E.; *Corros. Sci.* **2008**, *50*, 3031.

6. Tetreault, J.; Sirois, J.; Stamatopoulou, E.; *Stud. Conserv.* **1998**, *43*, 17.

7. Niklasson, A.; Johansson, L.-G.; Svensson, J.-E.; *J. Electrochem. Soc.* **2005**, *152*, B519.

8. Lopez-Delgado, A.; Cano, E.; Bastidas, J. M.; Lopez, F. A.; *J. Mater. Sci.* **2001**, *36*, 5203.

9. Cano, E.; Bastidas, J. M.; Polo, J. L.; Mora, N.; *J. Electrochem. Soc.* **2001**, *148*, B431.

10. Bastidas, D. M.; La Iglesia, V. M.; *Corros. Eng., Sci. Technol.* **2007**, *42*, 272.

11. Black, L.; Allen, G. C.; *Br. Corros. J.* **1999**, *34*, 192.

12. Allen, G. C.; Black, L.; *Br. Corros. J.* **2000**, *35*, 39.

13. Niklasson, A.; Langer, S.; Arrhenius, K; Rosell, L.; Bergsten, C. J.; Johansson, L.-G.; Svensson, J.-E.; *Stud. Conserv.* **2008**, *53*, 24.

14. Chiavari, C.; Martini, C.; Prandstraller, D.; Niklasson, A.; Johansson, L.-G.; Svensson, J.-E.; Aslund, A.; Bergsten, C. J.; *Corros. Sci.* **2008**, *50*, 2444.

15. Niklasson, A.; Johansson, L.-G.; Svensson, J.-E.; *J. Electrochem. Soc.* **2007**, *154*, C618.

16. Tétreault, J.; Cano, E.; Van, B. M.; Scott, D.; Dennis, M.; Barthes-Labrousse, M.-G.; Minel, L.; Robbiola, L.; *Stud. Conserv.* **2003**, *48*, 237.

17. Hatchfield, P. B.; Carpenter, J. M.; *Int. J. Museum Manage. Curator.* **1986**, *5*, 183.

18. Li, S.; Banyasz, J. L.; Parrish, M. E.; Lyons-Hart, J.; Shafer, K. H.; *J. Anal. Appl. Pyrolysis* **2002**, *65*, 137.

19. Ministério da Saúde, Agência Nacional de Vigilância Sanitária (ANVISA); Resolução-RDC No. 35, de 3 de junho de 2008, dispõe sobre *Conservantes Permitidos para Produtos Saneantes*; Diário Oficial da União, Brasil, 2008.

20. Ciomartan, D. A.; Clark, R. J. H.; McDonald, L. J.; Odlyha, M.; *J. Chem. Soc., Dalton Trans.* **1996**, 3639.

21. Bergsten, C. J.; Odlyha, M.; Jakiela, S.; Slater, J. M.; Cavicchioli, A.; de Faria, D. L. A.; Niklasson, A.; Svensson, J. E.; Bratasz, L.; Camuffo, D.; Valle, A. D.; Baldini, F.; Falciai, R.; Mencaglia, A.; Senesi, F.; Theodorakopoulos, C.; *e-PS* **2010**, *7*, 116.

22. Osemeahon, S. A.; Barminas, J. T.; *Int. J. Phys. Sci.* **2007**, *2*, 169.

23. Bacci, M.; Cucci, C.; Mencaglia, A. Z.; Mignani, A. G.; *Sensors* **2008**, *8*, 1984.