



Determination of a typical additive in zinc electroplating baths



I. Sciscenko, I. Pedre, A. Hunt, H. Bogo, G.A. González *

INQUIMAE, Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas, 1428 Buenos Aires, Argentina

ARTICLE INFO

Article history:

Received 17 January 2016

Received in revised form 23 March 2016

Accepted 23 March 2016

Available online 28 March 2016

Keywords:

MnO₂ nanoparticles
Chlorobenzaldehyde
Colorimetric method
Electroplating

ABSTRACT

Determining commercial additives contained in zinc electroplating baths is critical for quality control and process management in order to obtain better results in zinc coatings, monitor the use of chemicals and establish safe forms of treatment and reuse of wastewater. In this work, the conditions for the quantification by oxidation with potassium permanganate of a commercial brightener mainly composed of chlorobenzaldehyde, were optimized. The signal generation consisted in the formation of MnO₂ nanoparticles with a characteristic surface plasmon resonance band (SPRB) at around 400 nm. The results showed that it is viable to apply this method to direct measurements of brightener in electroplating processes.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Electroplated zinc and its alloys coatings have been widely used for the corrosion protection of steel [1] by virtue of their low standard reduction electrode potential. The use of zinc plating baths containing zinc sulfate and chloride have been cited in the literature and are employed on industrial scale as an alternative to cyanide containing baths. The popularity of this kind of baths has been increasing due to its relatively low cost and eco-friendliness [2]. The primary requirement of these baths is to produce smooth, compact, bright deposits of improved properties over a large range of current densities (1–100 A cm⁻²). These properties depend on the nature and concentrations of bath constituents. The main components of these baths are metal ions, conducting salts, buffers and addition agents [3].

The commonly used additives in electroplating baths are classified as levelers and brighteners. These additives affect the plating process to yield electrodeposits with the appropriate properties for their given applications. During plating, these additives gradually decompose and the sensitivity of the electrodeposition process to the concentration of additives makes it difficult to maintain control of the plating process [4,5]. The brighteners are mixtures of organic compounds usually added in small quantities (10⁻⁴–10⁻² M) to the bath solution, and the levelers are generally used in relatively higher concentrations, around 10⁻² M. Carbonyl compounds like o-chlorobenzaldehyde, benzylideneacetone, vanillin, glycyl-glycine, etc. were reported as brighteners for zinc deposition [6], while surfactants like cetyltrimethylammonium bromide (CTAB), sodium dodecylsulfate (SDS), polyethylene glycol (PEG) and Triton X-100 were used as levelers for zinc electroplating [3]. Some

additives simultaneously act as levelers and brighteners, but in most cases, suitable combinations of different additives give satisfactory results [3].

Typically, replenishment of organic additives is based on amp-hours. However, the consumption rate of additives may depend on the operating conditions and even the geometry of the plated parts. Therefore, amp-hour control must be supplemented by analytical determination of additive level. Traditionally, the effective concentration of electroplating additives was obtained by using a Hull Cell test. The interpretation of the results of a Hull Cell test is subjective and requires extensive personnel training. Since the Hull Cell test is a qualitative, overall performance test, it is not suitable for the separate determination of individual components of additives [4,5]. Normally, the quantification and characterization of commercial additives requires sophisticated and expensive instrumentation such as GC–MS, HPLC, and UV spectrophotometer, not common in industrial laboratories.

The use of nanoparticles as colorimetric probes has received a great deal of attention because of the color changes associated with the surface plasmon resonance band (SPRB), which is very sensitive to a number of parameters, such as particle size and shape, adsorbed species (stabilizer), medium dielectric properties, and the distance between particles [7]. Changes in the SPRB have been successfully used for the detection of analytes such as proteins [8] and other ligands and compounds [9–12]. As for MnO₂ nanoparticles, there are some papers reporting their preparation and characterization, and the most general method is the chemical reduction of Mn(VII) salts with an appropriate reducing agent. In reported experiments, the three peaks centered at 315, 525 and 545 nm, corresponding to KMnO₄, gradually disappear with the occurrence of a new peak centered at 370 nm which indicates the formation of MnO₂ nanoparticles [13,14]. This new surface plasmon band gradually grows in intensity, which is

* Corresponding author.

assigned to a considerable increase in the amount of MnO_2 nanoparticles, and shifts to larger wavelengths, which is attributed to the growth of the nanoparticles [13].

In this work, we optimized the conditions for the quantification of a commercial brightener added to zinc electroplating baths. The chosen strategy consisted in the generation of MnO_2 nanoparticles by a reaction between potassium permanganate and oxidizable organic compounds, mainly chlorobenzaldehyde (see Fig. 1), which is the main component of the analyzed additive. This method allows to follow the evolution of the additive, in an industrial matrix in the concentration range of interest, in a simple and inexpensive manner. The reaction conditions enable their quantification by absorbance measurements, employing a simple photometer at 400 nm, or a semi-quantitative determination by simple visualization of a colorimetric scale.

The development of simple methods such as the one reported here, for typical components that permit the measurement of the commercial formulation contained in the bath, will enable the quality control of the process, which is critical in order to obtain high quality zinc coatings, monitoring the use of chemicals, and establishing safe forms of treatment and reuse of wastewater.

2. Experimental

2.1. Apparatus and reagents

Potassium permanganate, p-chlorobenzaldehyde, ethyl ether and hydrochloric acid (36%) were analytical grade reagents, and were used without further purification. Zinc chloride, boric acid and potassium chloride were industrial grade reagents. An industrial commercial additive was employed as brightener. All solutions were prepared with Milli-Q water. Measurements were carried out in $HCl\ 10^{-4}$ M solution or in an artificial bath for zinc electroplating (see composition in Table 1). The mentioned range of brightener concentration is the one recommended by the manufacturer in order to obtain high quality zinc coatings.

Visible absorption spectra were recorded on an Ocean Optics spectrophotometer using a 1 cm path length plastic cell.

GC–MS determinations were performed on a GC Agilent Technologies 7890A–MSD Agilent Technologies 5975C instrument. The injection volume was 1 μ l in the Split mode (100:1). The total flow was 164 ml/min, and the oven program, 5 min at 50 °C, then 8 °C/min to 300 °C. The column was an Agilent Technologies HP-5, 350 °C. All experiments were performed at room temperature ((25 ± 2) °C). The particle morphology and size were observed with a Field Emission Scanning Electron Microscope (FE-SEM).

3. Results and discussion

3.1. Additive characterization

Usually, commercial additive formulations remain unknown to ordinary users. This makes it difficult to quantify additives in industrial baths to optimize their use and particularly the treatment of effluents.

In order to characterize the commercial brightener employed in this work, 5 ml of the additive were extracted with ethyl ether (two times

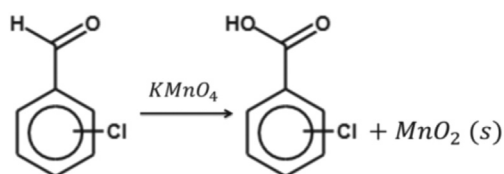


Fig. 1. Scheme of the reaction between $KMnO_4$ and chlorobenzaldehyde to give MnO_2 nanoparticles in aqueous medium.

Table 1
Composition of a typical electrolytic bath for zinc electroplating.

Compound	Concentration
H_3BO_3	25 g/l
$ZnCl_2$	70 g/l
KCl	180 g/l
Brightener	0.3–0.7 ml/l (0.34–0.8 mM in o-chlorobenzaldehyde)
HCl 36%	Drops until pH 5

2.5 ml). The extracts were evaporated until 1.5 ml. The obtained solution was analyzed by GC–MS in the conditions described above.

The major components (>5%) present in the additive were o-chlorobenzaldehyde (160 mg/ml), 4-phenyl-3-buten-2-one, 2-(2-butoxyethoxy)-ethanol and 1-(1-naphthalenyl)-ethanone. p-chlorobenzaldehyde was used as standard for o-chlorobenzaldehyde, since it is solid and easy to manipulate.

Chlorobenzaldehyde is a typical additive employed as a brightener in commercial products and in our case, it is the major component of the used formulation. In this work we used its concentration as an indicator of the amount of compounds oxidizable by permanganate in a commercial additive in a typical electroplating bath solution in a suitable range of concentrations.

3.2. Spectrophotometric determination in water

Potassium permanganate, $KMnO_4$, is probably the most common, and also the most applicable oxidizing agent and can be utilized to oxidize a wide range of organic molecules. The products that are obtained can vary depending on the conditions, but because $KMnO_4$ is such a strong oxidizing agent, the final products are often carboxylic acids. Under acidic conditions, alkene double bonds are cleaved to give the appropriate carboxylic acids and potassium permanganate oxidizes aldehydes to carboxylic acids.

For the analytical determination, several solutions were prepared in the range of 0.1 to 0.9 ml/l brightener (equivalent to 0.113 to 1.02 mM chlorobenzaldehyde) in $HCl\ 10^{-4}$ M solution. Then 150 μ l of a 3.2 mM $KMnO_4$ solution (pH = 4 with HCl) were added to 5 ml of each solution, and left to react for 10 min at room temperature without stirring. After that, the solution showed an appreciable color change to be measured or observed by the naked eye. In Fig. 2 we present a picture of the reaction vessels for different concentrations of brightener in water (0, 0.3, 0.5 and 0.7 ml/l brightener, equivalent to 0, 0.34, 0.57 and 0.79 mM in o-chlorobenzaldehyde respectively). Similar measurements were performed at pH 2 and pH 6 but with less satisfactory results (data not shown).

The UV–vis spectra of the brightener show a well defined peak at around 300 nm. However, measuring in this region of the spectrum is not practical, since it is not a selective measurement, given the fact that many compounds absorb in that region.



Fig. 2. Reaction of brightener in $HCl\ 10^{-4}$ M solution with MnO_4^- . 150 μ l of a 3.2 mM $KMnO_4$ solution (pH = 4 with HCl) was added to 5 ml of the standards and left to react for 10 min. From left to right: 0, 0.3, 0.5 and 0.7 ml/l brightener, equivalent to 0, 0.34, 0.57 and 0.79 mM in o-chlorobenzaldehyde, respectively.

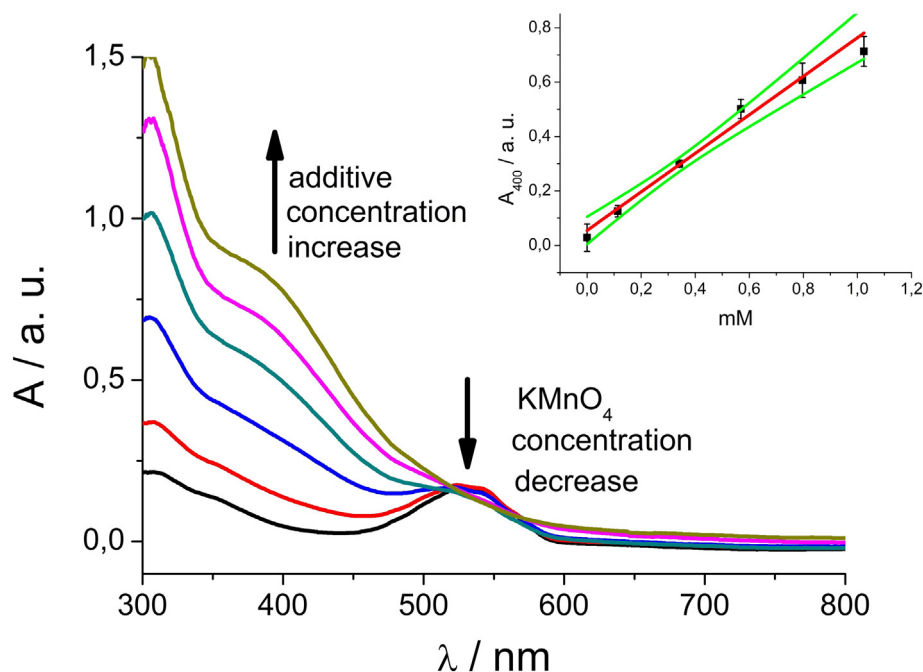


Fig. 3. Reaction of 5 ml of each standard (brightener in $\text{HCl } 10^{-4} \text{ M}$) with $150 \mu\text{l}$ of a 3.2 mM KMnO_4 solution. Reaction time = 10 min, light path = 1 cm. UV-vis spectra for 0, 0.1, 0.3, 0.5, 0.7 and 0.9 ml/l (0, 1.13, 3.4, 5.7, 7.9 and 10.2 mM *o*-chlorobenzaldehyde). (inset) Calibration curve. Wavelength for the construction of the calibration curve: 400 nm, calibration curve: slope $(0.70 \pm 0.05) \text{ a. u./mM}$, intercept $(0.05 \pm 0.02) \text{ a. u.}$, R^2 0.978. Error bars represent the standard deviation from 3 independent experiments. Linear fitting: red line, confidence bands: green line.

Fig. 3 shows the changes in the UV-vis absorption spectra as a result of the reaction with KMnO_4 solutions, where the effects of brightener concentration were investigated. As seen in Fig. 3, with 0 ml/l, KMnO_4 has a characteristic absorption peak in the range of 450–600 nm. It could be observed that this absorption peak gradually decreased with increasing additive concentration. On the other hand, a new broad peak at around 400 nm emerged. Based on the literature, the new peak can be attributed to colloidal MnO_2 particles [13–17]. The formation of MnO_2 nanoparticles was confirmed by SEM microscopy as seen in Fig. 4. The nanoparticles presented no uniform morphology and their size varies between 10 and 100 nm. This result is consistent with the broad peak seen in Fig. 3.

In a first approach, a calibration curve was constructed plotting the absorbance at 400 nm against the concentration of *o*-chlorobenzaldehyde.

The absorbance values as a function of *o*-chlorobenzaldehyde coming from the additive were evaluated in water and they were fitted for 0, 0.1, 0.3, 0.5, 0.7 and 0.9 ml/l (0, 1.13, 3.4, 5.7, 7.9 and 10.2 mM *o*-chlorobenzaldehyde) showing a linear correlation, with an average sensitivity of $(0.70 \pm 0.05) \text{ a. u./mM}$, and R^2 0.978. The intercept value was $(0.05 \pm 0.02) \text{ a. u.}$ Three independent experiments were performed for each concentration (see inset Fig. 3).

3.3. Spectrophotometric determination in real samples

A similar procedure was applied to a zinc plating bath. In this case, the reaction time was 15 min in order to have noticeable color changes. In Fig. 5 we present the colorimetric scale corresponding to the measurements of the commercial brightener in this bath.

Fig. 6 shows the UV-vis absorption spectra as a result of the reaction of 5 ml of each standard (brightener in electroplating bath) adjusted to pH 4, with $150 \mu\text{l}$ of a 3.2 mM KMnO_4 solution. Composition of the bath: see Table 1. As seen in Fig. 6, the characteristic absorption peak of KMnO_4 decreased as a function of brightener concentration as in water (Fig. 3). On the other hand, the absorbance around 400 nm showed less pronounced changes for the same range of concentration, evidencing that in this condition of higher ionic strength, the evolution of the reaction to the MnO_2 nanoparticle formation is less favorable. The average of three independent absorbance values as a function of *o*-chlorobenzaldehyde from brightener additive, was evaluated in zinc electroplating bath and they were fitted for 0, 0.1, 0.3, 0.5, 0.7 and 0.9 ml/l (0, 1.13, 3.4, 5.7, 7.9 and 10.2 mM *o*-chlorobenzaldehyde) showing a linear correlation, with an average sensitivity of $(0.56 \pm 0.01) \text{ a. u./mM}$, intercept $(-0.001 \pm 0.008) \text{ a. u.}$ and R^2 0.998 (see inset Fig. 6).

3.4. pH influence

In order to evaluate the reaction directly in zinc electroplating bath, the experiments related in Fig. 6 were repeated without additional pH

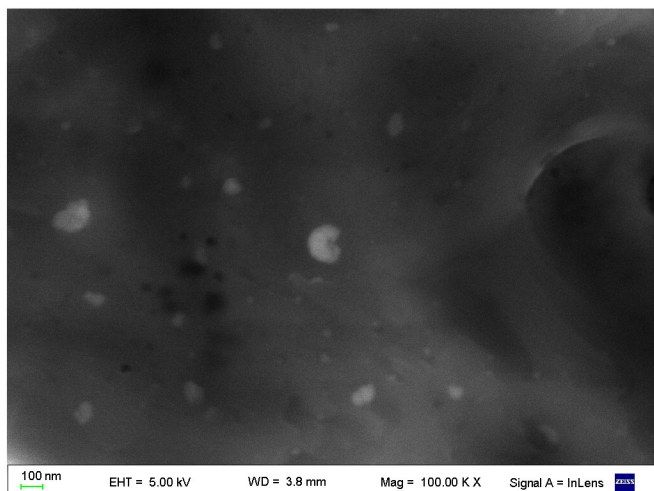


Fig. 4. FE-SEM micrograph of the obtained MnO_2 nanoparticles.



Fig. 5. Reaction of brightener in zinc electroplating bath with MnO_4^- . 150 μl of a 3.2 mM KMnO_4 solution was added to 5 ml of the standards and left to react for 15 min. Composition of the bath: see Table 1. From left to right: 0, 0.1, 0.3, 0.5, 0.7 and 0.9 ml/l (0, 1.13, 3.4, 5.7, 7.9 and 10.2 mM o-chlorobenzaldehyde).

modification (electroplating bath at pH 5). In Fig. 7 we can observe that the characteristic absorption peak of KMnO_4 decreased more markedly with increasing additive concentration than in Fig. 6, showing that the KMnO_4 reduction is more favorable at pH 5 than at pH 4. Also in Fig. 7, the absorbance around 400 nm showed less pronounced changes for the same range of concentration than at pH 4, evidencing that in this condition of pH, the evolution of the reaction to the MnO_2 nanoparticle formation is much less favorable than in the electroplating bath at pH 4. This situation can be observed in the calibration curve in the inset of Fig. 7, where the average of three independent absorbance values as a function of o-chlorobenzaldehyde from brightener additive, was evaluated in the zinc electroplating bath and they were fitted for 0, 0.1, 0.3, 0.5, 0.7 and 0.9 ml/l (0, 1.13, 3.4, 5.7, 7.9 and 10.2 mM o-chlorobenzaldehyde) showing a linear correlation, with an average sensitivity of (0.33 ± 0.04) a. u./mM, intercept (0.01 ± 0.02) a. u. and R^2 0.995.

Despite the fact that in the electroplating bath the formation of MnO_2 nanoparticles is less pronounced than in water, and a reduced sensitivity is obtained, the results show that it is viable to apply the method to samples with this matrix even without adjusting the pH value. The proposed system provides a simple and reliable measurement tool for the direct monitoring of brightener in electroplating process, allowing the reconditioning of baths and reducing its environmental impact.

4. Conclusions

In this work we optimized the conditions for the quantification of a brightener consisting mainly of chlorobenzaldehyde used in zinc plating cells. The principle of the method is the reaction of the o-chlorobenzaldehyde present in the additive with KMnO_4 , to yield brown MnO_2 nanoparticles. The KMnO_4 reduction proceeds more

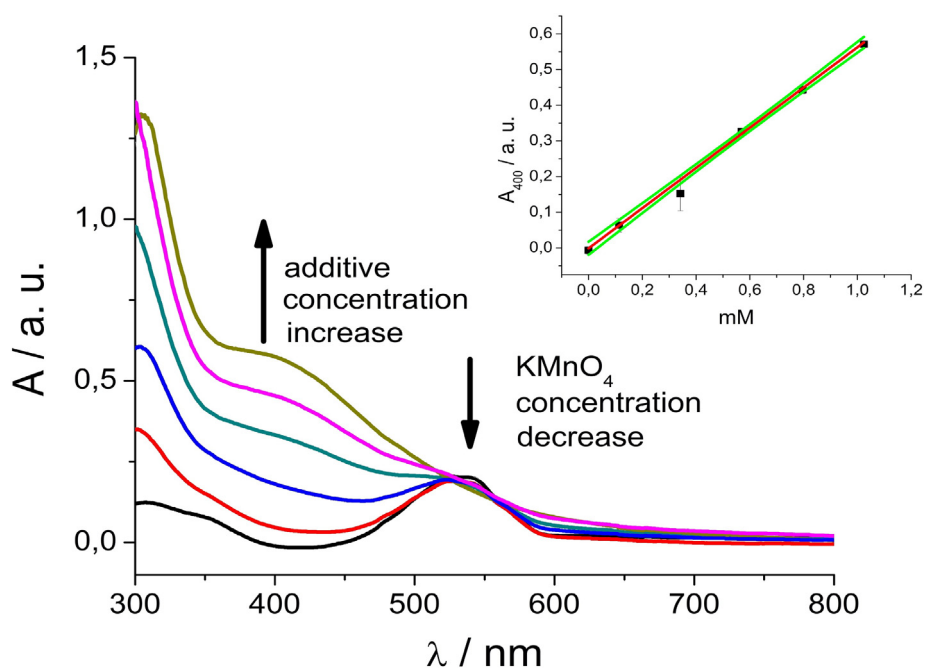


Fig. 6. Reaction of 5 ml of each standard (brightener in bath at pH 4) with 150 μl of a 3.2 mM KMnO_4 solution. Reaction time = 15 min, light path = 1 cm. Composition of the bath: see Table 1. UV-vis spectra for 0, 0.1, 0.3, 0.5, 0.7 and 0.9 ml/l (0, 1.13, 3.4, 5.7, 7.9 and 10.2 mM o-chlorobenzaldehyde). (inset) Calibration curve: wavelength for the construction of the calibration curve: 400 nm, slope (0.56 ± 0.01) a. u./mM, intercept (-0.001 ± 0.008) a. u., R^2 0.998. Error bars represent the standard deviation from 3 independent experiments. Linear fitting: red line, confidence bands: green line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

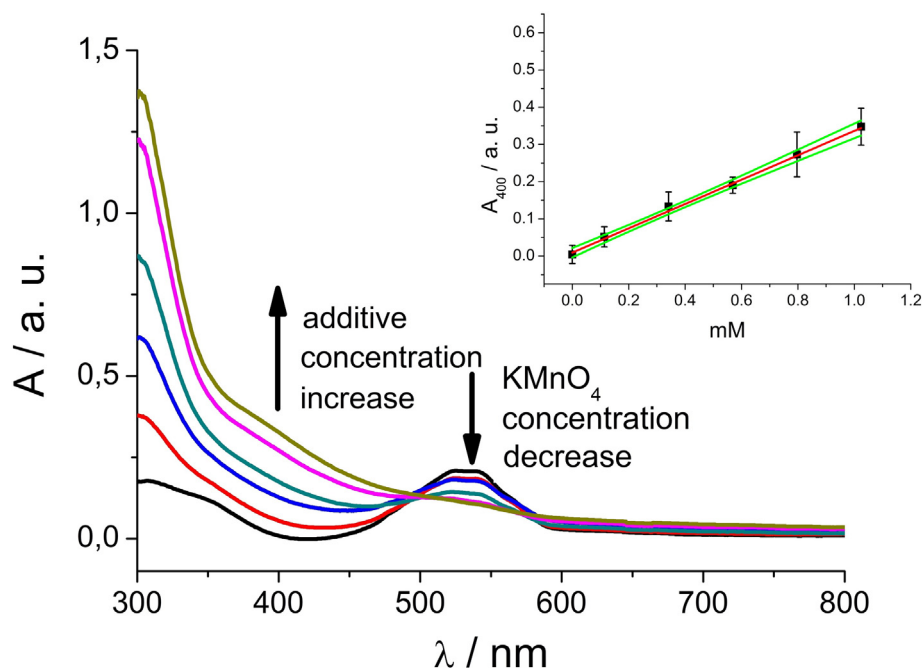


Fig. 7. Reaction of 5 ml of each standard (brightener in bath at pH 5) with 150 μ l of a 3.2 mM KMnO_4 solution. Reaction time = 15 min, light path = 1 cm. Composition of the bath: see Table 1. UV-vis spectra for 0, 0.1, 0.3, 0.5, 0.7 and 0.9 ml/l (0, 1.13, 3.4, 5.7, 7.9 and 10.2 mM *o*-chlorobenzaldehyde). (inset) Calibration curve: wavelength for the construction of the calibration curve: 400 nm, slope (0.33 ± 0.04) a. u./mM, intercept (0.01 ± 0.02) a. u., R^2 0.995. Error bars represent the standard deviation from 3 independent experiments. Linear fitting: red line, confidence bands: green line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

efficiently in the industrial bath but with less formation of nanoparticles. According to that, the reaction conditions for the reported method have been adjusted so that it is useful in this matrix.

This method allows the quantification of the additive in the visible region of the spectrum in a simple and economic way, being this determination applicable to the range of concentrations of interest.

Acknowledgments

This work was partially supported by the Universidad de Buenos Aires, CONICET, and by the ANPCYT (PICT2012-3081). A. H., H. B. and G. A. G. are research staff of CONICET, I. P. acknowledges CONICET for his doctoral fellowship. I. S. is an undergrad student of the Universidad de Buenos Aires. The authors would like to thank Comisión de Seguridad, Medio Ambiente y Salud Ocupacional de ADIMRA (Asociación de Industrias Metalúrgicas de la República Argentina) and Obdulio Pennella S.A. for the information about additives and industrial baths.

References

- [1] H.B. Muralidhara, Y. Arthoba Naik, Electrochemical deposition of nanocrystalline zinc on steel substrate from acid zincate bath, *Surf. Coat. Technol.* 202 (2008) 3403–3412, <http://dx.doi.org/10.1016/j.surfcoat.2007.12.012>.
- [2] B. Kavitha, P. Santhosh, M. Renukadevi, A. Kalpana, P. Shakkthivel, T. Vasudevan, Role of organic additives on zinc plating, *Surf. Coat. Technol.* 201 (2006) 3438–3442, <http://dx.doi.org/10.1016/j.surfcoat.2006.07.235>.
- [3] K.O. Nayana, T.V. Venkatesha, Synergistic effects of additives on morphology, texture and discharge mechanism of zinc during electrodeposition, *J. Electroanal. Chem.* 663 (2011) 98–107, <http://dx.doi.org/10.1016/j.jelechem.2011.10.001>.
- [4] R.B. Ross, *Handbook of Metal Treatments and Testing*, second ed. Chapman & Hall, London; New York, 1988.
- [5] H. Geduld, *Zinc Plating*, Finishing Publications, Teddington, England, 1988.
- [6] J.-C. Hsieh, C.-C. Hu, T.-C. Lee, The synergistic effects of additives on improving the electroplating of zinc under high current densities, *J. Electrochem. Soc.* 155 (2008) D675, <http://dx.doi.org/10.1149/1.2967343>.
- [7] G.-L. Wang, Y.-M. Dong, X.-Y. Zhu, W.-J. Zhang, C. Wang, H.-J. Jiao, Ultrasensitive and selective colorimetric detection of thiourea using silver nanoparticles, *Analyst* 136 (2011) 5256, <http://dx.doi.org/10.1039/c1an15613f>.
- [8] H. Wei, C. Chen, B. Han, E. Wang, Enzyme colorimetric assay using unmodified silver nanoparticles, *Anal. Chem.* 80 (2008) 7051–7055, <http://dx.doi.org/10.1021/ac801144t>.
- [9] A. Taheri, M. Noroozifar, M. Khorasani-Motlagh, Investigation of a new electrochemical cyanide sensor based on Ag nanoparticles embedded in a three-dimensional sol-gel, *J. Electroanal. Chem.* 628 (2009) 48–54, <http://dx.doi.org/10.1016/j.jelechem.2009.01.003>.
- [10] J.-S. Lee, P.A. Ulmann, M.S. Han, C.A. Mirkin, A DNA-gold nanoparticle-based colorimetric competition assay for the detection of cysteine, *Nano Lett.* 8 (2008) 529–533, <http://dx.doi.org/10.1021/nl0727563>.
- [11] C.L. Schofield, A.H. Haines, R.A. Field, D.A. Russell, Silver and gold glyconanoparticles for colorimetric bioassays, *Langmuir* 22 (2006) 6707–6711, <http://dx.doi.org/10.1021/la060288r>.
- [12] I. Pedre, F. Battaglini, G.J.L. Delgado, M.G. Sánchez-Loredo, G.A. González, Detection of thiourea from electrorefining baths using silver nanoparticles-based sensors, *Sensors Actuators B Chem.* 211 (2015) 515–522, <http://dx.doi.org/10.1016/j.snb.2015.01.074>.
- [13] Y. Luo, Preparation of MnO_2 nanoparticles by directly mixing potassium permanganate and polyelectrolyte aqueous solutions, *Mater. Lett.* 61 (2007) 1893–1895, <http://dx.doi.org/10.1016/j.matlet.2006.07.165>.
- [14] P. Mulvaney, R. Cooper, F. Grieser, D. Meisel, Kinetics of reductive dissolution of colloidal manganese dioxide, *J. Phys. Chem.* 94 (1990) 8339–8345, <http://dx.doi.org/10.1021/j100384a063>.
- [15] T. Fujimoto, Y. Mizukoshi, Y. Nagata, Y. Maeda, R. Oshima, Sonochemical preparation of various types of metal nanoparticles in aqueous solution, *Scr. Mater.* 44 (2001) 2183–2186, [http://dx.doi.org/10.1016/S1359-6462\(01\)00900-9](http://dx.doi.org/10.1016/S1359-6462(01)00900-9).
- [16] J.Z. Sostaric, P. Mulvaney, F. Grieser, Sonochemical dissolution of MnO_2 colloids, *J. Chem. Soc. Faraday Trans.* 91 (1995) 2843, <http://dx.doi.org/10.1039/ft9959102843>.
- [17] A. Abulizi, G.H. Yang, K. Okitsu, J.-J. Zhu, Synthesis of MnO_2 nanoparticles from sonochemical reduction of MnO_4^- in water under different pH conditions, *Ultrason. Sonochem.* 21 (2014) 1629–1634, <http://dx.doi.org/10.1016/j.ultsonch.2014.03.030>.