

Received:

26 July 2018

Revised:

10 October 2018

Accepted:

28 February 2019

Cite as:

Felipe de Moura Souza,
Fernanda Pollo Paniz,
Tatiana Pedron,
Mauro Coelho dos Santos,
Bruno Lemos Batista. A high-
throughput analytical tool for
quantification of 15 metallic
nanoparticles supported on
carbon black.

Heliyon 5 (2019) e01308.

doi: [10.1016/j.heliyon.2019.e01308](https://doi.org/10.1016/j.heliyon.2019.e01308)



A high-throughput analytical tool for quantification of 15 metallic nanoparticles supported on carbon black

Felipe de Moura Souza, Fernanda Pollo Paniz, Tatiana Pedron,
Mauro Coelho dos Santos, Bruno Lemos Batista*

Centro de Ciências Naturais e Humanas, UFABC – Universidade Federal do ABC, Rua Santa Adélia 166, Bairro Bangu, CEP 09.210-170, Santo André, SP, Brazil

* Corresponding author.

E-mail address: bruno.lemos@ufabc.edu.br (B. Lemos Batista).

Abstract

Metallic nanoparticles (NPs) have been widely used in different areas of science. Usually, they are immobilized on a low-cost support for catalysis purposes. However, there is a lack of studies for specific methods for analytical quantification since the extraction of these metallic NPs from the matrix is still a challenge. In this work, 15 metallic NPs were synthesized (Pt, Pd, Au, Ag, Rh, Ru, Nb, Mn, Co, Cu, Zr, Sn, Ce, Ni and W) supported on a commercial carbon black (Vulcan XC72). Then, six different methods were employed for sample preparation and further determination by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The results can be divided in three groups concerning the extraction of metallic NPs: the first group could be extracted from the matrix with nitric acid, for the second one it was necessary to employ a digestion at 25 °C (room temperature), and finally a third group which was found to be independent of acid and temperature. These findings can contribute to future research in the field of catalysis to improve their characterization regarding the metallic NPs.

Keywords: Materials chemistry, Analytical chemistry, Electrochemistry

1. Introduction

Noble metals such as platinum, palladium, and gold, and some non-noble metals such as tungsten and cerium have been used as constituents of different types of catalysts [1, 2, 3, 4, 5]. These metals have unique physical and chemical properties which are useful mainly in electrocatalysis, photocatalysis and chemical catalysis [6, 7, 8, 9, 10, 11, 12, 13, 14].

Their high costs when used as bulks bring them to the field of nanoparticle (NP) science, generally applied as metallic NP on top of a substrate or support [15, 16, 17, 18, 19]. Since these metals are dispersed as metallic NPs on a support, their chemical activity increases using a considerable small amount of metal. Furthermore, new properties are acquired when they are at the nanometer level [20, 21]. The support where the metallic NPs are located is typically a low-cost porous-conductive material with a high surface area. The most common are molecular structure materials of carbon [22, 23], nitrides [24], metal oxides [25], carbides [26], electronically conducting polymers [27, 28], sulfoxides [29, 30], among others. It is worthy to highlight that the chemical surroundings of the support may influence catalytic activity [23].

The most widely used carbon support for catalyst preparation is the commercial carbon black Vulcan XC72 (Cabot®). This material has a specific surface area in Brunauer, Emmet and Teller (BET) of about $250 \text{ m}^2 \text{ g}^{-1}$, an electric conductivity of 2.8 S cm^{-1} , and a particle size distribution ranging from 100 nm to 500 μm [23].

Although qualitative and quantitative physical-chemical characterizations of these materials are essential for the attribution of catalytic chemical activity or performance, many studies do not use suitable techniques or methods to determine the amounts of metallic NPs [31, 32, 33, 34, 35]. The use of energy dispersive spectroscopy (EDS) or X-ray photoelectron spectroscopy (XPS) techniques can be imprecise, even though they are commonly used to determine the metallic NP concentration in the catalysts [33, 35, 36, 37].

The use of analytical techniques such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) and Graphite Furnace Atomic Absorption Spectroscopy (GF AAS) provide more precise and accurate results regarding analyte concentration determination. However, these techniques are under-exploited for quantification of metallic NPs in electrocatalysts probably due to difficulties in sample preparation, which are time-consuming, the need of high cost standards, and the lack of specific methods for metallic NPs sample preparation.

Therefore, this study aimed to investigate different conditions for preparation of electrocatalysts based on carbon-supported metallic NPs (Pt, Pd, Au, Ag, Rh, Ru,

Ce, Zr, Nb, W, Cu, Ni, Co, Mn, and Sn) to be submitted to spectroscopy analysis (ICP-MS, ICP OES, GF AAS). Moreover, the results were compared with scanning electron microscope (SEM), XRD and EDS techniques.

2. Materials and methods

2.1. Preparation of the electrocatalysts

Electrocatalysts containing metallic NPs can be binary or ternary. In the present study, 15 different metals were mixed to evaluate the incidence of interferences in sample preparation and analysis by ICP-MS. The electrocatalysts were prepared using the traditional method of borohydride reduction. The borohydride is a directional reducing agent which stabilizes the formation of metallic NPs [38]. Briefly, a 20 mL isopropyl/water solution (50/50, v/v) was dispersed in 320 mg of carbon black Vulcan XC72 particles. After that, under stirring, quantities of 13, 12, 27, 10, 13, 19, 14, 18, 10, 12, 11, 26, 12, 23, and 10 mg of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich, Germany), $\text{Pt}(\text{acac})_2$ (Aldrich, USA), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, France), AgNO_3 (Synth, Brazil), $\text{AuCl}_3 \cdot 3\text{H}_2\text{O}$ (Aldrich, USA), Ammonium niobate(V) oxalate hydrate (Aldrich, Germany), ZrCl_4 (Aldrich, USA), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, Brazil), WCl_4 (Aldrich, USA), CuCl_2 (Aldrich, USA), RhCl_3 (Aldrich, USA), $\text{Mn}(\text{NO}_3)_2\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich, Spain), CoCl_2 (Vetec, Brazil), $\text{Ru}(\text{acac})_3$ (Aldrich, USA) and SnCl_2 (Sigma-Aldrich, Brazil), were added to the solution and then placed into an ultrasonic bath (Thorton, Brazil) for 15 minutes. Then 20 mL of a sodium borohydride solution ($4.2 \mu\text{mol NaBH}_4$ into 0.01 mol L^{-1} KOH) were added and kept under stirring for 120 min. The reaction mixture was then washed with 3 L of water using a vacuum filtered system with a 3-micron porosity paper filter (Nalgon®, São Paulo, Brazil). The washed material was oven-dried at $70 \text{ }^\circ\text{C}$ for 24 h (SX1.0 DTME, Sterilifer®, São Paulo, Brazil).

2.2. Experimental characterization

2.2.1. Elemental composition by ICP-MS

The elemental composition of the electrocatalysts was determined using an ICP-MS (Agilent 7900, Hachioji, Japan) with high-purity argon (99.9999%, White Martins, Brazil). All reagents were of analytical grade. Nitric acid and HCl were purified with a DST-1000 Teflon sub-boiling distillation system (Savillex, USA). High-purity deionized water type 1 (resistivity $18.2 \text{ M}\Omega \text{ cm}$) was generated with a Milli-Q water purification system (Millipore, Bedford, MA, USA). The method of extraction was carried out using a closed vessel system. Approximately 15 mg of the catalyst powder was placed into 50 mL Teflon tubes. Then, aqua regia (1 mL of HNO_3 + 3 mL of HCl) or nitric acid (4 mL of HNO_3) were added and the tubes were closed. The extractions were carried out for 2 h at three different temperatures ($25 \text{ }^\circ\text{C}$,

100 °C and 200 °C) for each acid composition, using a graphite-covered digester block (EasyDigest, Analab, France). The volume was made up to 50 mL with type 1 water. Finally, the solution was diluted 1000 times and the elements were determined by ICP-MS. All experiments were performed in triplicate and without pre-digestion. The ICP-MS operating parameters are summarized in Table 1.

2.2.2. X-ray diffraction analysis

All electrocatalysts were physically characterized using X-ray diffraction (XRD). The equipment was a Rigaku-MiniFlex X-ray diffractometer with a CuK α radiation source operating continuously (2° min⁻¹) from 20 to 90° (2 θ) to determine the crystalline phases. Samples of synthesized catalysts were analysed in the powder form and on a sample holder of poly(methyl methacrylate) from Bruker®.

2.2.3. Energy dispersive X-ray spectroscopy

The energy dispersive spectroscopy (EDS) analyses were performed using an EDS chemical microanalysis module that was coupled to a JSM-6010LA Compact Sweep Electron Microscope (JEOL), operating at an acceleration voltage of 5 kV. The EDS analyses were obtained using the map mode with twenty measurements, and the average concentration was acquired from each mapped part of the sample. Small

Table 1. Instrumental parameters used for ICP-MS operation.

| | |
|-------------------------|--|
| Monitored Isotopes | ⁵⁵ Mn, ⁵⁹ Co, ⁶⁰ Ni, ⁶³ Cu, ⁹⁰ Zr, ⁹³ Nb, ¹⁰¹ Ru, ¹⁰³ Rh, ¹⁰⁵ Pd, ¹⁰⁷ Ag, ¹¹⁸ Sn, ¹⁴⁰ Ce, ¹⁸² W, ¹⁹⁵ Pt, ¹⁹⁷ Au |
| Limit of Detection | 0.03 µg L ⁻¹ Mn, 0.002 µg L ⁻¹ Co, 0.051 µg L ⁻¹ Ni, 0.032 µg L ⁻¹ Cu, 0.006 µg L ⁻¹ Zr, 0.003 µg L ⁻¹ Nb, 0.001 µg L ⁻¹ Ru, 0.0002 µg L ⁻¹ Rh, 0.004 µg L ⁻¹ Pd, 0.009 µg L ⁻¹ Ag, 0.006 µg L ⁻¹ Sn, 0.002 µg L ⁻¹ Ce, 0.001 µg L ⁻¹ W, 0.0004 µg L ⁻¹ Pt, 0.007 µg L ⁻¹ Au. |
| Radio frequency power | 1550 W |
| Argon flow rate | 15 L min ⁻¹ |
| Sample uptake pump | 0.4 rps |
| Nebulizer gas flow rate | 1.03 L min ⁻¹ |
| Nebulizer | MiraMist™ (Teflon) |
| Nebulizer chamber | Scott (double pass) |
| Torch | 2.5 mm |
| Torch sample depth | 8 mm |
| Interface | Platinum cones |
| Sampling cone | 0.91 mm |
| Skimmer | 0.45 mm |

amounts of electrocatalysts (powder) were placed on a copper adhesive tape for analysis.

2.2.4. Scanning electron microscopy (SEM)

The morphology of the electrocatalysts was observed by field emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL) at an acceleration voltage of 1 kV and a current of 10 μ A. Small portions of the electrocatalysts' powder were placed on a carbon-adhesive tape for analysis.

2.3. Statistics

The one-way ANOVA statistical test was used to evaluate statistical differences between two or more independent groups (acids and temperature). Fisher test was performed to identify significant differences between groups. The software OriginPro (OriginPro 8, version 8.0724, Northampton, MA, USA) was used for mathematical calculations. Statistical significance was set at 5 %.

3. Results and discussion

3.1. Characterization of the electrocatalysts by traditional instruments

Fig. 1 shows X-ray diffractograms (XRD) of the electrocatalysts and Vulcan XC72 Carbon. Two peaks centred at approximately $2\theta = 25^\circ$ and 44° (Bragg angle) on the electrocatalysts X-ray spectra were attributed to reflection plane (002) of the hexagonal structure of the Vulcan XC-72 carbon support (red line, Fig. 1). The peaks at $2\theta = 38.1^\circ$, 64.5° and 77.3° refer to metallic Ag (JCPDS 87-0597) in the Miller (111), (220) and (311) indices, respectively. The peaks relative to the other metals were not observed in the diffractogram due to their low concentration (about 1.5 % wt).

Fig. 2 shows a micrograph of electrocatalysts supported on Vulcan XC-72 carbon. Irregularities on Vulcan XC-72 surface can be observed, which contribute to its increased area, as showed by Souza *et al.* [5]; Santos *et al.* [39]; and Neto *et al.* [40]. In addition, it is possible to consider that the metallic NPs are at the nanometer scale levels and they are randomly distributed on the surface of the Vulcan XC-72 carbon.

The determination of carbon-supported metallic NPs by EDS analysis was laborious, imprecise and did not detect all metals present in the samples. In addition, the concentrations were different from the nominal concentration (Table 2). Although the EDS is a qualitative rather than quantitative analysis, many authors have used only this simple feature for characterization of the electrocatalysts [41, 42, 43, 44, 45]. Discrepancies between the nominal and EDS concentration values can be

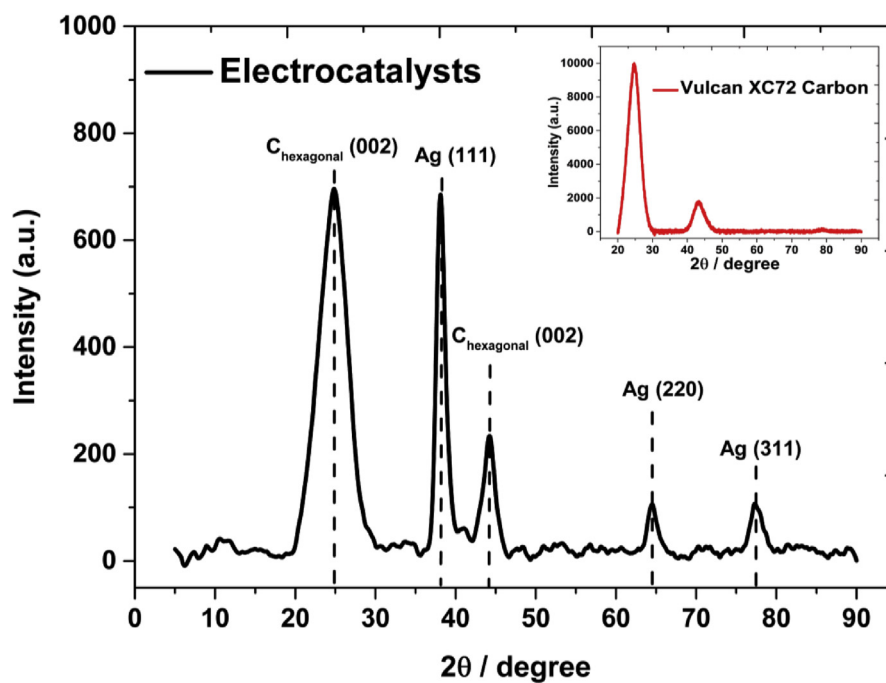


Fig. 1. X-ray diffractograms (XRD) of the electrocatalysts supported on Vulcan XC72 carbon (black line) and insert with the pure Vulcan XC72 carbon (upside right red line). The numbers in parentheses indicate the Miller index and dashed lines indicate the center of the peak for the crystalline faces.

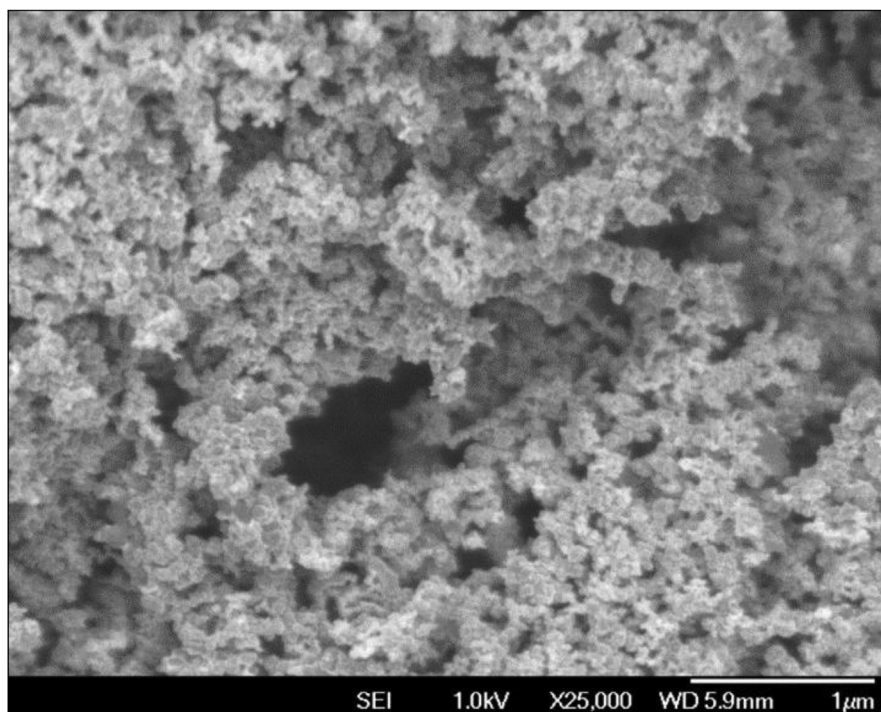


Fig. 2. Scanning electronic microscopy (SEM) image of the electrocatalysts supported on Vulcan-XC72 carbon. SEI: secondary electron imaging; WD: working distance. The measurement was performed using 1.0 kV of acceleration voltage and electric current of 10 μ A with a magnification of 25 thousand-fold.

Table 2. Metallic nanoparticle concentrations (mass ratio) obtained by using energy dispersive spectroscopy (EDS) and inductively coupled plasma mass spectrometry (ICP-MS) techniques.

| Metallic nanoparticle | Nominal (%) | EDS (%) | ICP-MS (%) |
|-----------------------|-------------|-----------|-------------------------|
| Pt | 1.3 | 2.5 ± 0.3 | 1.1 ± 0.2 ^a |
| Pd | 1.1 | 0.7 ± 0.2 | 1.0 ± 0.2 ^a |
| Au | 1.4 | n.d. | 0.5 ± 0.1 ^b |
| Ag | 1.5 | 0.2 ± 0.2 | 1.5 ± 0.1 ^b |
| Sn | 1.4 | 0.7 ± 0.4 | 1.4 ± 0.2 ^a |
| Nb | 1.2 | 0.7 ± 0.2 | 0.5 ± 0.1 ^a |
| Ru | 1.2 | 0.4 ± 0.1 | 0.4 ± 0.1 ^a |
| Cu | 1.2 | 0.4 ± 0.0 | 1.2 ± 0.2 ^a |
| Rh | 1.0 | 0.2 ± 0.1 | 0.3 ± 0.01 ^c |
| Ni | 1.2 | 1.8 ± 0.2 | 1.2 ± 0.2 ^a |
| Mn | 1.2 | n.d. | 1.2 ± 0.2 ^a |
| W | 1.0 | 0.6 ± 0.1 | 0.4 ± 0.1 ^a |
| Zr | 1.0 | n.d. | 0.9 ± 0.1 ^a |
| Ce | 1.4 | n.d. | 1.4 ± 0.2 ^a |
| Co | 1.2 | 3.2 ± 0.3 | 1.2 ± 0.2 ^a |

^a Aqua regia 25 °C.

^b Aqua regia 100 °C.

^c Aqua regia 200 °C.

probably due to: i) the low yield of the borohydride-synthesis; ii) the low concentration of metallic NPs used for EDS determination (approximately 1.3 % wt, compared to carbon) and; iii) the heterogeneous distribution of metallic NPs on the carbon surface. Even though the EDS analysis is performed in map mode, it still represents a partial analysis of the whole material. Considering a singular area of the catalyst, it is possible to observe a higher concentration than the nominal one. On the other hand, it was found in other areas much lower concentrations than the nominal, showing the imprecision and the inaccuracy of such technique. Furthermore, the EDS analysis showed limitations since it could not quantify Ce, Au, Mn, and Zr, due to their low concentrations and/or interferences.

3.2. Determination of metallic NPs by ICP-MS

The dissolution of noble metals is an issue for metallurgy, catalysis, organometallic chemistry, nanoscience and even recycling [46]. Electrocatalysts oxidizing agents with metallic NPs are complex matrices. The determination of trace and ultra-trace levels of metals in complex matrices is a great challenge, requiring advanced analytical techniques. Although analytical techniques such as ICP

OES could be used in this study, the ICP-MS was chosen because the interferences were easier controlled than for the ICP OES technique, in which may occur, for example, overlapping of emission lines [47]. Moreover, the ICP-MS is an interesting approach because it is versatile, robust, fast and presents high sensitivity and selectivity. Therefore, accurate and reliable information for quantification with the best resolution can be provided by ICP-MS [48]. Additionally, this work emphasizes the methods of sample preparation for determination of chemical elements supported on carbon. Although it was used the ICP-MS technique, the same sample preparation presented in this study can be also applied for determination of metals by other analytical techniques such as ICP OES and GF AAS.

In the present study, electrocatalysts were submitted to six different sample preparation methods (Figs. 3, 4, and 5) for quantification by ICP-MS. Closed Teflon vessels were used to avoid losses of acids and elements by volatilization (products of metal reactions such as oxides or chlorides) [49]. The choice of acid is also a critical step in the employment of digestion methods. Some acids such as HNO_3 , HCl , H_2SO_4 , HF , as well as acid mixtures (aqua regia, for example) are commonly used for digestion of organic samples, metallic alloys and silicates [50]. In this work, HNO_3 and HCl were used throughout the digestion procedures, once they are the most common acids used for sample preparation.

Nitric acid is a strong acid and a powerful oxidizing agent. Although HNO_3 oxidizes and dissolves several metals, other elements such as Al, B, Cr, Ga, In, Nb, Ti, Ta, Th, Zr, and Hf are oxidized to form acid-insoluble compounds [50]. Aqua regia is a powerful oxidizing agent for noble metals such as Pd, Pt and, Au. The reaction between both acids generates molecular chlorine, a complexing agent, and the NOCl (nitrosyl chloride) that helps on the dissolution [1, 50].

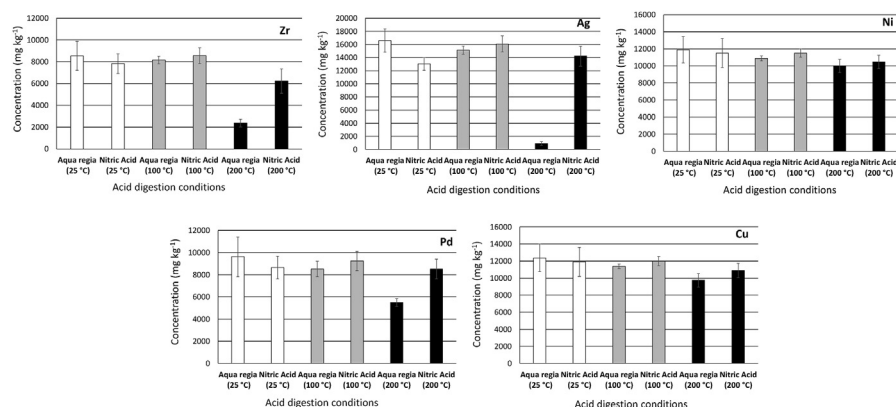


Fig. 3. Recoveries of Zr, Ag, Ni, Pd, and Cu after different acid digestion conditions. The determinations were carried out by ICP-MS. Statistics are presented in Table 3. Temperatures: 25 °C (white bars), 100 °C (gray bars); 200 °C (black bars).

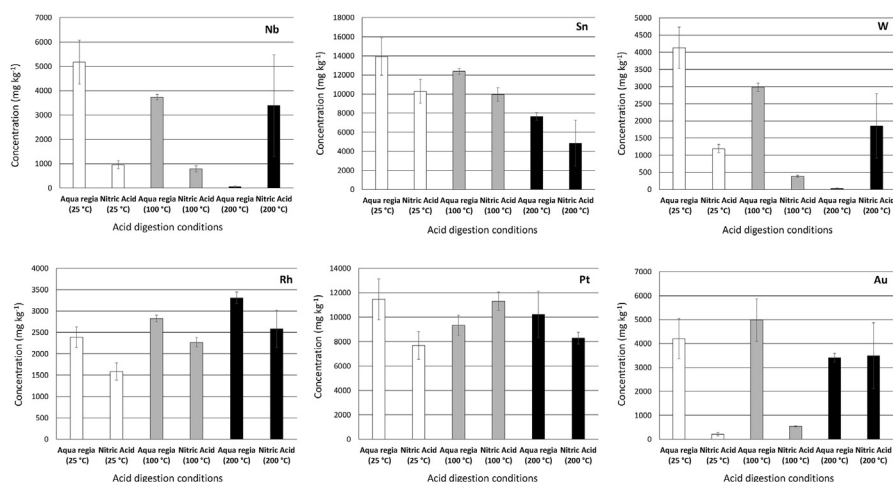


Fig. 4. Recoveries of Nb, Sn, W, Rh, Pt, and Au after different acid digestion conditions. The determinations were carried out by ICP-MS. Statistics are presented in Table 3. Temperatures: 25 °C (white bars), 100 °C (gray bars); 200 °C (black bars).

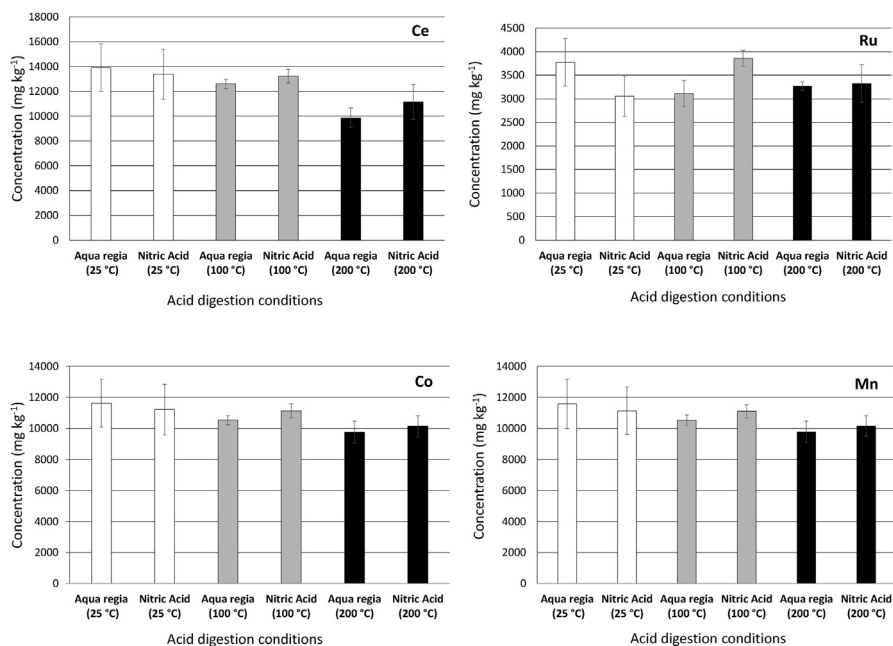


Fig. 5. Recoveries of Ce, Ru, Co, and Mn after different acid digestion conditions. The determinations were carried out by ICP-MS. Statistics are presented in Table 3. Temperatures: 25 °C (white bars), 100 °C (gray bars); 200 °C (black bars).

The results (Figs. 3 and 4) showed that aqua regia at 200 °C significantly decreased ($P < 0.05$) the mean recoveries for Zr, Ag, Pd, Nb, and W. In the case of Nb, Sn, W, Rh, and Au the digestion with aqua regia was necessary (Fig. 4). In general, higher temperatures decreased the recoveries regarding the elements Nb, Sn and, W. On the other hand, for Rh and Au the best temperatures to increase their recoveries were 200

°C and 100 °C, respectively. In respect of platinum, two preparation methods presented the best recoveries: HNO₃ at 100 °C or aqua regia at 25 °C (which have the highest standard deviations, Fig. 4). For Zr, Ag, Pd, Cu, and Ni the results showed that at temperatures of 100 and 200 °C these metallic NPs did not present an efficient matrix extraction (Fig. 3). This low recovery is more evident for Ag and Zr in aqua regia at 200 °C. Their low recoveries probably occur due to adsorption in the vessel's walls or due to the volatilization. Silver, As and Pb are known as metals that hydrochloric acid must be avoided due to the volatilization as metal-chloride [51]. In the case of Nb, W and Sn metallic NPs, low recoveries were observed by using HNO₃. Although HNO₃ is the most used acid for metal digestion, it promotes some water-insoluble oxides for metals such as Al, Ta, Sb, Ti and, Nb or volatile oxides for W and Sn (especially at 200 °C, Fig. 4) [52].

Balcerzak *et al.* [1] showed that Ru, Rh, Os, and Ir present high resistance to acid digestion mixtures, including aqua regia. In the present study, results indicated the highest recoveries for Rh and Ru using aqua regia at 200 °C and HNO₃ at 100 °C, respectively (Figs. 4 and 5). In general, some catalysts have Pt and Ru concomitantly in their composition [1]. In this case, the authors recommended the use of a mixture of HNO₃ and HCl (aqua regia for example) to increase the Pt-dissolution. Our results using catalysts supported on Vulcan XC72 carbon showed that aqua regia at 25 °C or even HNO₃ 100 °C are two simple treatments for best recoveries of metallic NPs (Figs. 4 and 5). In addition, samples present high superficial area (Fig. 2), thereby improving the contact between the analytes and, consequently, the recoveries. Fig. 5 shows the group of metallic NPs (Ce, Ru, Co, and Mn) in which the carbon matrix extraction (carbon black) was suitable under regardless of the acid and the digestion temperature in the experiment tested.

The metallic NPs determinations by ICP-MS were possible to its multi-elemental capacity to provide a faster and reliable quantification than EDS technique. In addition, the concentrations were close to the nominal amount expected for most of metallic NPs (Table 2). In contrast, Au, Nb, Ru, Cu, Rh, and W concentrations were not close to the expected nominal quantity. Probably these metals were not totally reduced in the synthesis reaction, being leached from Vulcan XC72 during the washing process. Table 3 shows the detailed ICP-MS results, associated with statistics results regarding the different methods.

Many works normalize the amperometric currents during the electrocatalytic processes considering the mass of metal quantified by techniques as EDS. They simply ignore that chemical reactions have never a 100% yielding. Pirez *et al.* [53], Yuanxin *et al.* [54], Jiann-Horng *et al.* [55], and other authors showed that more accurate results are provided by the ICP-MS, which helps on a higher precision characterization of a catalytic activity from materials containing metallic elements. Souza *et al.* [56] reported an accelerated durability test (ADT) using the ICP-MS technique to monitor

Table 3. ICP-MS results for different acid digestion conditions for preparation of the catalysts.

| Element (mg kg ⁻¹) | Temperature and acid conditions | | | | | |
|-----------------------------------|---------------------------------|-------------------------------|------------------------------|-------------------------------|---------------------------------|-------------------------------|
| | 25 °C | | 100 °C | | 200 °C | |
| | Aqua regia | HNO ₃ | Aqua regia | HNO ₃ | Aqua regia | HNO ₃ |
| <i>Mn</i> | 11577 ± 1590 | 11131 ± 1538 | 10521 ± 337 | 11097 ± 422 | 9775 ± 699 | 10148 ± 666 |
| <i>Co</i> | 11627 ± 1549 | 11208 ± 1627 | 10534 ± 296 | 11135 ± 440 | 9755 ± 723 | 10143 ± 686 |
| <i>Ni</i> | 11896 ± 1549 | 11503 ± 1708 | 10874 ± 299 | 11495 ± 485 | 10005 ± 781 | 10468 ± 779 |
| <i>Cu</i> | 12374 ± 1629 | 11902 ± 1707 | 11377 ± 254 | 11992 ± 536 | 9741 ± 796 | 10886 ± 836 |
| <i>Zr</i> | 8533 ± 1323 ^a | 7823 ± 906 ^b | 8153 ± 355 ^c | 8565 ± 740 ^d | 2373 ± 354 ^{a,b,c,d,e} | 6225 ± 1118 ^e |
| <i>Nb</i> | 5174 ± 907 ^{a,c,g} | 954 ± 162 ^{a,b,e} | 3739 ± 112 ^{b,d,h} | 789 ± 126 ^{e,d,f} | 52 ± 37 ^{e,f,i} | 3390 ± 2092 ^{g,h,i} |
| <i>Ru</i> | 3774 ± 507 | 3055 ± 429 | 3112 ± 278 ^a | 3860 ± 169 ^{a,b} | 3266 ± 90 ^{a,b} | 3329 ± 397 |
| <i>Rh</i> | 2386 ± 239 ^{a,c,g} | 1585 ± 200 ^{a,b,e} | 2824 ± 78 ^{b,d,h} | 2266 ± 111 ^{e,d,f} | 3307 ± 135 ^{e,f,i} | 2584 ± 436 ^{g,h,i} |
| <i>Pd</i> | 9620 ± 1796 ^a | 8649 ± 1025 ^b | 8511 ± 697 ^c | 9240 ± 878 ^d | 5489 ± 351 ^{a,b,c,d,e} | 8506 ± 893 ^e |
| <i>Ag</i> | 16595 ± 1773 ^{a,c,g} | 13036 ± 979 ^{a,b,e} | 15138 ± 647 ^{b,d,h} | 16089 ± 1222 ^{e,d,f} | 903 ± 298 ^{e,f,i} | 14234 ± 1530 ^{g,h,i} |
| <i>Ce</i> | 13914 ± 1919 | 13383 ± 2016 | 12601 ± 367 ^a | 13226 ± 546 ^b | 9870 ± 791 ^{a,b} | 11142 ± 1417 |
| <i>Sn</i> | 13927 ± 1949 ^{a,c,g} | 10284 ± 1248 ^{a,b,e} | 12380 ± 310 ^{b,d,h} | 9942 ± 712 ^{e,d,f} | 7645 ± 394 ^{e,f,i} | 4860 ± 2412 ^{g,h,i} |
| <i>W</i> | 4131 ± 602 ^{a,b,c,g} | 1190 ± 121 ^{a,d} | 2978 ± 121 ^{b,e} | 384 ± 28 ^{c,f} | 32 ± 14 ^{d,e,f,h} | 1854 ± 938 ^{g,h} |
| <i>Pt</i> | 11473 ± 1670 ^{a,c,g} | 7673 ± 1145 ^{a,b,e} | 9340 ± 801 ^{b,d,h} | 11307 ± 759 ^{e,d,f} | 10220 ± 1887 ^{e,f,i} | 8274 ± 485 ^{g,h,i} |
| <i>Au</i> | 4202 ± 836 ^{a,d,h} | 207 ± 68 ^{a,b,f} | 4972 ± 892 ^{b,e,i} | 541 ± 20 ^{d,e,g} | 3407 ± 186 ^{f,g,j} | 3494 ± 1374 ^{h,l,j} |

The same letter indicates that the means difference is significant at the 0.05 level; the absence of letter indicates no significant difference.

the decrease in electrocatalytic activity related to the dissolution of metallic NPs due to the intense and stressful use of the electrocatalysts.

Therefore, the best conditions for sample preparation presented in this study can contribute for future implementation in experiments involving electrocatalysts and the ICP-MS technique. In addition, highly relevant information regarding many conditions of the electrocatalysts, and even the stability experiments of electrocatalysts during long periods can be provided.

4. Conclusions

The results support that techniques, such as XRD, XPS or EDS are qualitative and semi-quantitative techniques only. These techniques are even more imprecise when used for evaluation of very low concentration levels of metals on a support. In order to achieve reliable experiments in catalysis, more consistent quantifications are necessary using specialized spectroscopic analytical techniques.

The acid digestion methods showed that for Zr, Ag, Pd, Cu, and Ni the use of temperatures closer to the ambient conditions is essential and independent of the type of acid. On the other hand, Nb, Sn, W, Rh, Pt, and Au exhibited better results with the

use of aqua regia. Some metallic NPs such Ag and Zr did not present good recoveries in aqua regia when submitted to temperatures above 100 °C. Finally, Ce, Ru, Co, and Mn demonstrated excellent results in all six acid digestion conditions performed. These results are important to support future investigations regarding the characterization of electrocatalysts containing metallic NPs.

Declarations

Author contribution statement

Felipe de Moura Souza, Fernanda Pollo Paniz, Tatiana Pedron, Mauro Coelho dos Santos, Bruno Lemos Batista: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This work was supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP projects/grants 2017/22976-0; 2017/21846-6; 2017/10118-0, 2016/10060-9, 2014/05151-0, 2016/19924-6 and 2018/06870-0).

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

- [1] M. Balcerzak, Sample digestion methods for the determination of traces of precious metals by spectrometric techniques, *Anal. Sci.* 18 (2002) 737–750.
- [2] P.S. Fernández, D.S. Ferreira, C.A. Martins, H.E. Troiani, G.A. Camara, M.E. Martins, Platinum nanoparticles produced by EG/PVP method: the effect of cleaning on the electro-oxidation of glycerol, *Electrochim. Acta* 98 (2013).
- [3] A.N. Geraldes, D. Furtunato Da Silva, J.C. Martins Da Silva, O. Antonio De Sá, E.V. Spinacé, A.O. Neto, M. Coelho Dos Santos, Palladium and palladium-tin supported on multi wall carbon nanotubes or carbon for alkaline direct ethanol fuel cell, *J. Power Sources* 275 (2015) 189–199.

- [4] X. Qiu, Y. Dai, Y. Tang, T. Lu, S. Wei, Y. Chen, One-pot synthesis of gold–palladium@palladium core–shell nanoflowers as efficient electrocatalyst for ethanol electrooxidation, *J. Power Sources* 278 (2015) 430–435.
- [5] F.M. Souza, L.S. Parreira, P. Hammer, B.L. Batista, M.C. Santos, Niobium: a promising Pd co-electrocatalyst for ethanol electrooxidation reactions, *J. Solid State Electrochem.* 22 (5) (2018) 1495–1506.
- [6] Y. Xu, B. Zhang, Recent advances in porous Pt-based nanostructures: synthesis and electrochemical applications, *Chem. Soc. Rev.* 43 (8) (2014) 2439–2450.
- [7] C. Wang, H. Daimon, Y. Lee, J. Kim, S. Sun, Synthesis of monodisperse Pt nanocubes and their enhanced catalysis for oxygen reduction, *J. Am. Chem. Soc.* 129 (22) (2007) 6974–6975.
- [8] C. Coutanceau, S. Brimaud, C. Lamy, J.-M. Léger, L. Dubau, S. Rousseau, F. Vigier, Review of different methods for developing nanoelectrocatalysts for the oxidation of organic compounds, *Electrochim. Acta* 53 (2008) 6865–6880.
- [9] D. Baldocchi, Y. Ryu, T. Keenan, Open peer review terrestrial carbon cycle variability [version 1; referees: 2 approved], *F1000 Fac Rev* (2016) 2371–2375, 8962189621.
- [10] X. Zhou, Y. Gan, J. Du, D. Tian, R. Zhang, C. Yang, Z. Dai, A review of hollow Pt-based nanocatalysts applied in proton exchange membrane fuel cells, *J. Power Sources* 232 (2013) 310–322.
- [11] F.C. Campbell (Ed.), *Elements of metallurgy and engineering alloys*, ASM International, 2008.
- [12] T. Ahuja, D. Kumar, Recent progress in the development of nano-structured conducting polymers/nanocomposites for sensor applications, *Sensor. Actuator. B Chem.* 136 (1) (2009) 275–286.
- [13] N.M. Rodriguez, M.S. Kim, R.T.K. Baker, Carbon nanofibers: a unique catalyst support medium, *J. Phys. Chem.* 98 (50) (1994) 13108–13111.
- [14] S. Sharma, B.G. Pollet, Support materials for PEMFC and DMFC electrocatalysts—a review, *J. Power Sources* 208 (2012) 96–119.
- [15] S.Y. Shen, T.S. Zhao, J.B. Xu, Carbon-supported bimetallic PdIr catalysts for ethanol oxidation in alkaline media, *Electrochim. Acta* 55 (2010) 9179–9184.

- [16] Z. Bai, P. Li, L. Liu, G. Xiong, Oxidative dehydrogenation of propane over MoO_x and PO_x supported on carbon nanotube catalysts, *ChemCatChem* 4 (2) (2012) 260–264.
- [17] J.M. Sieben, M.M.E. Duarte, Nanostructured Pt and Pt–Sn catalysts supported on oxidized carbon nanotubes for ethanol and ethylene glycol electro-oxidation, *Int. J. Hydrog. Energy* 36 (2011) 3313–3321.
- [18] W.T. Grubb, D.W. McKee, Boron carbide, a new substrate for fuel cell electrocatalysts, *Nature* 210 (5032) (1966) 192.
- [19] M.H.M.T. Assumpção, R.F.B. De Souza, R.M. Reis, R.S. Rocha, J.R. Steter, P. Hammer, I. Gaubeur, M.L. Calegari, M.R.V. Lanza, M.C. Santos, Low tungsten content of nanostructured material supported on carbon for the degradation of phenol, *Appl. Catal. B Environ.* 142 (143) (2013) 479–486.
- [20] I. Sameut Bouhaik, P. Leroy, P. Ollivier, M. Azaroual, L. Mercury, Influence of surface conductivity on the apparent zeta potential of TiO₂ nanoparticles: application to the modeling of their aggregation kinetics, *J. Colloid Interface Sci.* 406 (2013) 75–85.
- [21] A.S. Brady-Estévez, S. Kang, M. Elimelech, A single-walled-carbon-nanotube filter for removal of viral and bacterial pathogens, *Small* 4 (2008) 481–484.
- [22] U.A. Paulus, T.J. Schmidt, H.A. Gasteiger, R.J. Behm, Oxygen reduction on a high-surface area Pt/Vulcan carbon catalyst: a thin-film rotating ring-disk electrode study, *J. Electroanal. Chem.* 495 (2001) 134–145.
- [23] M.H.M.T. Assumpção, R.F.B. De Souza, D.C. Rascio, J.C.M. Silva, M.L. Calegari, I. Gaubeur, T.R.L.C. Paixão, P. Hammer, M.R.V. Lanza, M.C. Santos, A comparative study of the electrogeneration of hydrogen peroxide using Vulcan and Printex carbon supports, *Carbon N Y* 49 (2011) 2842–2851.
- [24] M.O. Thotiyl, T.R. Kumar, S. Sampath, Pd supported on titanium nitride for efficient ethanol oxidation, *J. Phys. Chem. C* 114 (41) (2010) 17934–17941.
- [25] B.C. Fitzmorris, J.Z. Zhang, Recent advances in metal oxide-based photoelectrochemical hydrogen production. *Photonics*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2015, pp. 343–370.
- [26] J.J. Patt, S.K. Bej, L.T. Thompson, Carbide-and nitride-based fuel processing catalysts, in: *Studies in Surface Science and Catalysis*, 147, Elsevier, 2004, pp. 85–90.
- [27] D.-L. Huang, R.-Z. Wang, Y.-G. Liu, G.-M. Zeng, C. Lai, P. Xu, B.-A. Lu, J.-J. Xu, C. Wang, C. Huang, Application of molecularly imprinted polymers in wastewater treatment: a review, *Environ. Sci. Pollut. Res.* 22 (2015) 963–977.

- [28] J. Jang, Conducting polymer nanomaterials and their applications. *Emissive Materials Nanomaterials*, Springer, Berlin, Heidelberg, 2006, pp. 189–260.
- [29] D.E. Curtin, R.D. Lousenberg, T.J. Henry, P.C. Tangeman, M.E. Tisack, Advanced materials for improved PEMFC performance and life, *J. Power Sources* 131 (2004) 41–48.
- [30] M. Ziolek, Niobium-containing catalysts—the state of the art, *Catal. Today* 78 (2003) 47–64.
- [31] O.O. Fashedemi, K.I. Ozoemena, Comparative electrocatalytic oxidation of ethanol, ethylene glycol and glycerol in alkaline medium at Pd-decorated FeCo@Fe/C core-shell nanocatalysts, *Electrochim. Acta* 128 (2014) 279–286.
- [32] F. Guo, D. Cao, M. Du, K. Ye, G. Wang, W. Zhang, Y. Gao, K. Cheng, Enhancement of direct urea-hydrogen peroxide fuel cell performance by three-dimensional porous nickel-cobalt anode, *J. Power Sources* 307 (2016) 697–704.
- [33] M.H.M.T. Assumpção, R.M. Piasentin, P. Hammer, R.F.B. De Souza, G.S. Buzzo, M.C. Santos, E.V. Spinacé, A.O. Neto, J.C.M. Silva, Oxidation of ammonia using PtRh/C electrocatalysts: fuel cell and electrochemical evaluation, *Appl. Catal. B Environ.* 174 (175) (2015) 136–144.
- [34] M.H.M.T. Assumpção, S.G. Da Silva, R.F.B. De Souza, G.S. Buzzo, E.V. Spinacé, M.C. Santos, A.O. Neto, J.C.M. Silva, Investigation of PdIr/C electrocatalysts as anode on the performance of direct ammonia fuel cell, *J. Power Sources* 268 (2014) 129–136.
- [35] M. Choun, D. Nauryzbayev, D. Shin, J. Lee, Polydimethylsiloxane treated cathode catalyst layer to prolong hydrogen fuel cell lifetime, *Catal. Today* 262 (2016) 155–160.
- [36] D. Zanchet, J.B.O. Santos, S. Damyanova, J.M.R. Gallo, J.M.C. Bueno, Toward understanding metal-catalyzed ethanol reforming, *ACS Catal.* 5 (2015) 3841–3863.
- [37] X. Yang, Q. Yang, J. Xu, C.-S. Lee, Bimetallic PtPd nanoparticles on Nafion–graphene film as catalyst for ethanol electro-oxidation, *J. Mater. Chem.* 22 (2012) 8057.
- [38] A.O. Neto, J. Nandenha, R.F.B. De Souza, G. Buzzo, J.C.M. Silva, E.V. Spinacé, M.H.M.T. Assumpção, Anodic oxidation of formic acid on PdAuIr/C-Sb₂O₅·SnO₂ electrocatalysts prepared by borohydride reduction, *J. Fuel Chem. Technol.* 42 (2014) 851–857.

- [39] V.S. Pinheiro, E.C. Paz, L.R. Aveiro, L.S. Parreira, F.M. Souza, P.H.C. Camargo, M.C. Santos, Ceria high aspect ratio nanostructures supported on carbon for hydrogen peroxide electrogeneration, *Electrochim. Acta* 259 (2018) 865–872.
- [40] A.O. Neto, M. Linardi, D.M. dos Anjos, G. Tremiliosi-Filho, E.V. Spinacé, Electro-oxidation of ethanol on PtSn/CeO₂-C electrocatalyst, *J. Appl. Electrochem.* 39 (7) (2009) 1153–1156.
- [41] A.N. Geraldes, D.F. da Silva, J.C.M. da Silva, O.A. de Sá, E.V. Spinacé, A.O. Neto, M.C. dos Santos, Palladium and palladium–tin supported on multi wall carbon nanotubes or carbon for alkaline direct ethanol fuel cell, *J. Power Sources* 275 (2015) 189–199.
- [42] E.V. Spinacé, R.R. Dias, M. Brandalise, M. Linardi, A.O. Neto, Electro-oxidation of ethanol using PtSnRh/C electrocatalysts prepared by an alcohol-reduction process, *Ionics* 16 (2010) 91–95.
- [43] C.A. Ottoni, S.G. da Silva, R.F.B. De Souza, A.O. Neto, PtAu electrocatalyst for glycerol oxidation reaction using a ATR-FTIR/single direct alkaline glycerol/air cell in situ study, *Electrocatalysis* 7 (2016) 22–32.
- [44] L.S. Parreira, J.C.M. Da Silva, M. D’Villa-Silva, F.C. Simões, S. Garcia, I. Gaubeur, M.A.L. Cordeiro, E.R. Leite, M.C. Dos Santos, PtSnNi/C nanoparticle electrocatalysts for the ethanol oxidation reaction: Ni stability study, *Electrochim. Acta* 96 (2013) 243–252.
- [45] J.C.M. Silva, B. Anea, R.F.B. De Souza, M.H.M.T. Assumpção, M.L. Calegari, O. Neto A, M.C. Santos, Ethanol oxidation reaction on IrPtSn/C electrocatalysts with low Pt content, *J. Braz. Chem. Soc.* 24 (10) (2013) 1553–1560.
- [46] W. Lin, R.W. Zhang, S.S. Jang, C.P. Wong, J II Hong, Organic aqua regia-Powerful liquids for dissolving noble metals, *Angew. Chem. Int. Ed.* 49 (2010) 7929–7932.
- [47] F.M. Dalla Nora, S.M. Cruz, C.K. Giesbrecht, G. Knapp, H. Wiltsche, C.A. Bizzi, J.S. Barin, E.M.M. Flores, A new approach for the digestion of diesel oil by microwave-induced combustion and determination of inorganic impurities by ICP-MS, *J Anal At Spectrom* 32 (2) (2017) 408–414.
- [48] A.A. Ammann, Inductively coupled plasma mass spectrometry (ICP MS): a versatile tool, *J. Mass Spectrom.* 42 (2007) 419–427.
- [49] E. De Oliveira, Sample preparation for atomic spectroscopy: evolution and future trends, *J. Braz. Chem. Soc.* 14 (2003) 174–182.

- [50] F.J. Krug, Métodos de preparo de amostras: Fundamentos sobre preparo de amostras orgânicas e inorgânicas para análise elementar, 1a Edição, Seção Técnica de Biblioteca-CENA/USP, Piracicaba, SP, Brazil, 2008.
- [51] R.M. Twyman, Wet Digestion, Elsevier Ltd, 2005, pp. 4503–4510.
- [52] D.E. Raynie, R.E. Majors, Trends in sample preparation, LC GC 29 (2016) 142–154.
- [53] C. Pirez, W. Fang, M. Capron, S. Paul, H. Jobic, F. Dumeignil, L. Jalowiecki-Duhamel, Steam reforming, partial oxidation and oxidative steam reforming for hydrogen production from ethanol over cerium nickel based oxyhydride catalyst, Appl. Catal. Gen. 518 (2016) 78–86.
- [54] Y. Du, K. Ni, Q. Zhai, Y. Yun, Y. Xu, H. Sheng, Y. Zhu, M. Zhu, Facile air oxidative induced dealloying of hierarchical branched PtCu nanodendrites with enhanced activity for hydrogen evolution, Appl. Catal. Gen. 557 (2018) 72–78.
- [55] J.H. Lin, V.V. Guliyants, Alumina-supported Cu@Ni and Ni@Cu core-shell nanoparticles: synthesis, characterization, and catalytic activity in water-gas-shift reaction, Appl. Catal. Gen. 445–446 (2012) 187–194.
- [56] F.M. Souza, J. Nandenha, B.L. Batista, V.H.A. Oliveira, V.S. Pinheiro, L.S. Parreira, et al., PdxNby electrocatalysts for DEFC in alkaline medium: stability, selectivity and mechanism for EOR, Int. J. Hydrog. Energy 43 (9) (2018) 4505–4516.