Anodic electrodisolution: A low cost alternative for carbon steel sample preparation for quantification of metals by ICP-MS

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Abstract

A fast and low-cost method using electrolysis for sample preparation of carbon steel present in weld electrodes aiming to quantification of heavy metals by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was developed. Conditions of the electrolysis, such as pH and electrical charge were investigated to higher the solubility and concentration for the analytes in the electrolyte. The method showed high reproducibility, with a relative standard deviation (RSD) of less than 3.05% and the recovery from 88.6% to 108.9% for the analytes demonstrate the accuracy of the developed method.

Introduction

Acid digestion is widely employed to dissolve steel samples before spectrometric quantification of metals.¹⁻³ The acid digestion on a hot plate (ADHP) is a conventional and simple method of dissolution,⁴⁻⁹ which has several disadvantages, such as excessive consumption of reagents, pre-concentration of impurities, and the long digestion time.^{3,10} The use of electrolysis, named anodic electrodisolution (AE) to dissolve steel samples can be an alternative to minimize these problems.

The AE uses electrons for dissolving metallic samples,¹¹ by applying direct current (DC) between the sample used as an anode and an inert cathode immersed in an electrolyte.¹² In this arrangement, the anode undergoes oxidation and the analytes migrate to the solution.^{2,13} Several examples that employing the AE for dissolving steels and other alloys are reported in the literature showing good results, which makes the use of this method feasible.¹⁴⁻¹⁹

This note describes a low-cost method of dissolution for carbon steel alloys presents in AWS A5.1 E6013 electrode employing AE into plastic syringes operated as container electrolytic and posterior quantification of Co, Cr, Cu, Ni, and Pb by ICP-MS. These samples are employed in the arc electric welding and the metals evaluated are normally added to the electrode for increases in strength, thermal conductivity, and hardening of the welded joint.²⁰⁻²³

Experimental

Samples

Samples of four different manufacturers (E1, E2, E3 and E4) carbon steels presents in AWS A5.1 E6013 welding electrodes were purchased from local ironmongery shops and stored in plastic bags to avoid contaminations.

Reagents and chemicals

HNO₃ (65% ww⁻¹, suprapur), HCl (37% ww⁻¹, ultra pure), KNO₃ (99% purity), KCl (99% purity) were acquired from Sigma-Aldrich (Rio de Janeiro, Brazil). Standard metals solutions were prepared by dilution of 1000 mg L⁻¹ standards acquired from SpecSol (São José dos Campos, Brazil). Disposable syringes (5.00 mL), acquired from local pharmacies, were used as electrolytic containers. Platinum rod (5.00 cm, 1.6 mm diameter) acquired from Sigma-Aldrich (Rio de Janeiro, Brazil) was used as cathode. All glassware and syringes were pre-soaked in 10% vv⁻¹ of HNO₃ in deionized water for at least 24 h and rinsed with deionized water prior to use.

All solutions were prepared using deionized water (Milli-Q-Quantum EX, with resistivity equal to 18.0 MΩ cm).

Instrumentation

An ICP-MS model 7700 (Agilent Technologies) was employed for the quantification of the present analytes in the steel samples. Instrumental parameters are shown in Table S1.

Stabilized power supply (RadioNave R-3562) was employed to supply DC for AE. A hot plate model SP-140/D was purchased from SP labor (Presidente Prudente, Brazil) and used for ADHP.

Preparation of samples by AE

AE was conducted in disposable plastic syringes of 5.00 mL (Fig. 1). The steel samples were accommodated at the top of the syringe while the cathode of platinum was docked at the other end, closing a circuit on the electrodes after adding the electrolyte. The amount of electrodisolved mass (EM) was determined by the weighing of the steel samples before and after the electrodisolution process.

The pH effect was investigated to increase AE efficiency. For that, approximately 1 cm of the sample E1 was cut and polished with commercial 80/100 mesh granulation sandpaper for removing oxides. Solutions of HNO_3 1.0 (pH = 0), 0.01 (pH = 2) and $0.0001 \text{ mol L}^{-1}$ (pH = 4) were used. The effect in pH equal to 7 was rated using solution 1.0 mol L^{-1} of KNO_3 . An electrical charge equal to 240 C was used. In summary, the effect that the presence of chloride ions causes in the amount of EM employing the AE was rated using an electrolyte containing $\text{HCl } 0.1 \text{ mol L}^{-1}$ and $\text{HNO}_3 1.0 \text{ mol L}^{-1}$.

A study of the effect of the electrical charge in increase to EM was investigated by the application of 240, 300, 600, 900, 1200, and 1500 C between the samples and the cathode in the syringe.

Preparation of samples by ADHP

The ADHP was performed using open flasks. In about 0.1 g of the carbon steel samples were added 3 mL of concentrated HNO_3 and 1 mL of concentrated HCl at a

temperature of 80 °C under reflux. The mixture of HNO₃: HCl (3:1) is used for the rapid dissolution of metal alloys since it favors the formation of strongly oxidizing and complexing products.^{24,25}

Analysis by ICP-MS

The dissolved samples from AE and ADHP preparations were transferred to 10- and 25-mL volumetric flasks, respectively, and diluted with deionized water. For analysis by ICP-MS, the samples were diluted an additional 20 times with deionized water to ensure that the concentration of the analytes in the samples adjust to the external calibration curve.

For the quantification of the metals by ICP-MS, external calibration curves were constructed by diluting the metal standards 1000 mg L⁻¹ in HNO₃ medium (2% vv⁻¹). The concentration of the standards ranged from 0.1 to 100.0 µg L⁻¹ and the linear regressions were provided by the software itself.

For the recovery study, a final concentration de 1.8 mg L⁻¹ of the standards of Co, Cr, Cu, Ni, and Pb was adding to one of the samples before dissolutions using AE and ADHP.

Results and Discussion

Optimization of AE conditions:

As presented in Fig. 2 amount of EM decreases with the increase of pH, making the HNO₃ 1.0 mol L⁻¹ the electrolyte more efficient. This acid is also known to form soluble metallic nitrates.²⁶

The presence of HCl in the electrolyte resulted in an increase of 21.6 % in the

amount of EM. The addition of chloride ions favors the solubility of the analytes, once these ions are good complexing agents.²⁵ The combination of HNO₃ (1.0 mol L⁻¹) with HCl (0.1 mol L⁻¹) was chosen like electrolyte for dissolution of the samples by AE.

A linear relationship between the amount of EM and the electric charge supplied to AE was observed, evidencing that the process is governed by Faraday laws of electrolysis (Fig. 3).^{27,28} This relationship makes it possible to control the dissolved mass through monitoring the supplied electric charge.

An electric charge of 900 C (3A for 300 s) was employed in the dissolution by AE because it provided a good trade-off between efficiency and accuracy required. In the ADHP the dissolution time was from 30 minutes.

The dissolution by AE resulted in adequate repeatability, obtaining RSD equal to 3.05% for 10 measurements of electrodisolution. The samples E1, E2, E3, and E4 were electrodisolved in triplicate and the EM ranged from 30.3 to 35.1 mg.

Sample analysis by ICP-MS.

The limits of quantification (LOQ) for each analyte were determined based on the IUPAC definition²⁹ and were equal to 0.034 µg L⁻¹ for Co, 0.070 µg L⁻¹ for Cr, 0.086 µg L⁻¹ for Cu, 0.065 µg L⁻¹ for Ni and 0.070 µg L⁻¹ for Pb.

The results of the quantification of Co, Cr, Cu, Ni, and Pb by ICP-MS employing the AE and ADHP are presented in Table S2. The accuracy study of the AE showed values > 88% evidencing that the method has adequate accuracy. The t-test (95% confidence) was used to compare the results obtained by the two methods of dissolution, where was observed that the averages obtained by AE are equal to those obtained by ADHP (conventional method).

Conclusions

A low-cost method for dissolution of carbon steel samples presents in the weld electrode AWS A5.1 E6013 using electrodisolution was proposed. The process was carried out on disposable syringes, using diluted acids and in a dissolution time of only 300 s. Recovery values above 88% were obtained for all analytes indicating proper accuracy, making the method AE a viable alternative to the dissolution of steel alloy.

Acknowledgements

We are grateful for the financial support of the CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior), CNPQ (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and FAPEMIG (Fundação de Amparo à Pesquisa do Estado de Minas Gerais).

Supporting Information

Tables S1 and S2 is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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Figure Captions

Fig. 1 Disposable plastic syringes of 5.00 mL used as electrolytic container.

Fig. 2 Relationship between the amount of EM and the pH of the electrolyte in the AE process.

Fig. 3 Relationship between electrical charge supplied for AE and amount of the EM of the samples E1 (■), E2(●), E3(▲) and E(▼).

Fig. 1

Fig. 2

Fig. 3

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