Low power electrocorrosion for sample preparation: Identification of metals in alloys

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Abstract

Rapid surface oxidation of a metal was carried out using a low voltage (9–18 V dc) power supply to examine the feasibility of low power electrocorrosion as an alternative to current metal sampling techniques such as acid digestion. Potential was applied between a metal alloy and a cellulose electrode that was made conductive using an aqueous solution (NH_4NO_3, KCl). Metal ions diffuse into the cellulose as rapid surface oxidation of the metal occurs. The metal ions can then be extracted and analyzed using atomic spectroscopy (e.g. GFAAS). Steel (316L, SRM 663), brass and aluminum alloys were electro-corroded using constant potential. At short intervals (<2 min) the mass of corroded metal increased linearly with time. Corrosion rates for Cr, Ni, Cu and Mn ranged from 870 to 34 pg s^{-1}. The mass of metal corroded increased as applied potential/current increased and depends on the surface area of the cellulose–metal contact. Experiments showed that preferential metal corrosion does not occur in steel samples. SEM images show that there is a relatively large area ($\sim$1 mm^2) of homogenous corrosion and that the most damage occurs closest to the edge of filter paper/metal contact. Low power electrocorrosion was used to identify metals in a fork of unknown composition. Multiple techniques (GFAAS, FAAS and SN-ICP-MS) were used for analysis and it was found that Ag and Cu were the primary metals in the alloy, in a ratio of 3:1. Trace amounts of other metals (<1%) were found but not quantified.
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1. Introduction

Metal analyses can be carried out using spectroscopic methods such as flame atomic absorption spectroscopy (FAAS), graphite furnace atomic absorption spectroscopy (GFAAS) and inductively coupled plasma atomic emission spectroscopy/mass spectrometry (ICP-AES/MS), which typically require the target analyte to be dissolved in a dilute aqueous solution. Therefore, sample dissolution, usually in acid, may be required prior to analysis. Apart from traditional acid digestion, many sample preparation methods are useful for sample dissolution including: acid digestion [1,2], microwave digestion [1,3–7], pressure ashing [3,8,9], ultrasonication [10,11], high and low power spark ablation [2,12–15], and high power electrocorrosion [16]. The major drawback of all of these methods is that they will damage the object under investigation and may not be suitable for valuable samples, such as cultural objects, where the integrity of the object must be maintained.

Several analytical techniques are available to the analyst that minimize sample damage such as: proton-induced X-ray emission (PIXE) [17–23], neutron activation analysis (NAA) [24,25] and X-ray fluorescence (XRF) [17,26–29]. External beam PIXE is minimally destructive, is capable of multi-element analysis and applicable to many types of materials [17–23]. One drawback of using PIXE analysis for cultural objects is that it has low sensitivity (ppm) and the size, shape or nature of the object may not be compatible with the vacuum and the small sample enclosures of the instrument [17]. Neutron activation analysis (NAA) has also been used to characterize cultural objects [24,25]. Neutron activation offers very good sensitivity and accuracy and is especially useful for the determination of some trace elements (e.g. Pb and Fe). It is a multi-element technique that can

be used with or without sample preparation, however, routine applications of NAA are limited by the availability of a reactor [25].

X-ray fluorescence is one of the most common methods for analysis of cultural objects; it does not require sample preparation and portable instruments are available. In general, XRF can have low measurement sensitivity for lighter elements (i.e. Al) [26]. Quantification errors also occur when XRF is applied on curved metal surfaces and the use of conventional XRF instruments (large beam diameter) for quantitative analysis is limited. Micro-XRF offers similar capabilities as external beam PIXE but with better lateral resolution. Small beams allow sampling on locations that resemble flat surfaces [17]. Surface sampling techniques (<100 μm depth), such as XRF, may also be affected by the presence of surface corrosion and contamination because the depth of analysis is usually less than the patina thickness [19,28]. For example, over time silver can develop a patina with a thickness ranging from a few micrometers to hundreds of micrometers. This can be a result of artificial enrichment with silver after the minting process, or due to naturally selective corrosion phenomena [29]. The presence of a patina makes it very difficult to achieve quantitative results through direct, non-destructive surface analysis because it is not always possible to remove the patina due to curatorial concerns. However, in many cases exhaustive quantitative analysis is not required in order to achieve material identification (brass, bronze, silver alloy or tin) [28].

Low power electrocorrosion can be an alternative approach for rapid metal dissolution for the purpose of identifying surface metals in alloys. Several groups have used anodic dissolution for rapid metal analysis [16,30–32]. In anodic dissolution the conductive metal sample acts as the anode. The metal sample is immersed in an electrolytic solution, usually 0.5–1.5 M HNO_3, with the cathode and typically 2–5 A (current density 1.6–5 A cm^{-2}) is applied. Sampling intervals are short, usually being less than 10 s. After electrolysis the electrodissolved sample can be determined using either voltammetry or spectroscopy.

The objective of this study was to investigate some of the properties and to examine the feasibility of using low power (3–18 V) electrocorrosion for identifying metals in alloys. A low voltage potential (9 V dc), is applied between the metal sample and a cellulose electrode, which has been made conductive by an aqueous solution. Rapid oxidation of the alloy surface occurs and the metal ions diffuse into the cellulose, prior to analysis by GFAAS or ICP-MS.

2. Experimental

2.1. Chemicals

All solutions were prepared using de-ionized water (18 MΩ^{-1} cm Milli-Q). Standard metal solutions were prepared by appropriate dilution from 1000 μg mL^{-1} standards (SCP Science). High purity AR Select® Plus HNO_3 (Mallinckrodt) was used for acid dissolution and solution matrix matching; KCl (Aldrich) and NH_4NO_3 (Aldrich), were reagent grade and used without purification. All glassware and Petri dishes were pre-

soaked in 50% HNO_3 for at least 24 h and rinsed with de-ionized water prior to use.

For the cellulose electrode, filter paper (VWR 5.5 cm) was sectioned into approximately 1 cm × 2 cm pieces using tweezers wrapped in Parafilm® wax to minimize metal contamination. Filter paper was chosen because it is flexible and was found to be relatively free of transition metals. Flexibility was required to sample curved surfaces and small spaces. Metals were extracted in disposable 1.5 mL polystyrene cups, cups were not pre-treated prior to use. Several 9–1.5 V (AA) batteries were used in series to generate 3–27 V of applied potential. Alloys that were used for studying corrosion properties included two stainless steels (304L and 316L), aluminum (6061), brass and the standard reference material SRM 663 stainless steel.

2.2. Methods

The filter paper (anode) was saturated with aqueous solution and then placed on the bottom of a Petri dish and the metal (cathode) was contacted to the paper, typically for 10–120 s. Metals were extracted from the cellulose with concentrated HNO_3 and diluted to 2 mL prior to analysis (GFAAS or ICP-MS). Hydrochloric acid was avoided as the presence of large amounts of Cl$^-$ in the sample can cause matrix effects for some elements [33] with GFAAS and with ICP-MS analysis, it can also cause a spectral interference $^{40}Ar^{35}Cl^+$ with $^{75}As^+$.

2.3. Instrumentation

Absorption spectroscopy was carried out using a Perkin-Elmer 3100 flame atomic absorption spectrophotometer (FAAS) and a Perkin-Elmer AAnalyst 800 graphite furnace atomic absorption spectrophotometer (GFAAS) equipped with an AS80 autosampler. Recommended optical and lamp conditions were used for both the FAAS and GFAAS. For GFAAS, Zeeman effect background correction was used for all measurements with the recommended temperature program for each element. A Pd modifier (500 ppm Pd(NO$_3$)$_2$) was also used for the determination of Mn. External calibrations and method of standard addition were used for quantitative analysis.

A Perkin-Elmer Elan DRC II inductively coupled plasma mass spectrometer (ICP-MS) with solution nebulization was also used for the analysis of the fork. Experimental parameters for the ICP-MS are indicated in Table 1. A Cambridge

Table 1
SN-ICP-MS instrumental operating and data acquisition parameters

ICP mass spectrometer	
RF power	1100 W
Coolant Ar flow	15.0 L min^{-1}
Auxiliary Ar flow	1.4 L min^{-1}
Carrier Ar flow	1.0 L min^{-1}
ICP-MS data acquisition	
Dwell time	50 ms
Scan mode	Peak hopping
Signal measurement	Average counts
Resolution	0.7 amu at 10% peak height