Supporting information

Rapid detection of metal impurities on surfaces of intact objects with irregular shapes using electrochemical mass spectrometry

Lili Song, Jiaquan Xu, Dacai Zhong, Konstantin Chingin, Ying Qu and Huanwen Chen*

Jiangxi Key Laboratory for Mass Spectrometry and Instrumentation, East China University of Technology, Nanchang, P. R. China.

Corresponding author: Dr. Huanwen Chen
Post address: East China University of Technology, 418 Guanglan Road, Nanchang, Jiangxi P.R. China
ZIP Code: 330013
Email: chw8868@gmail.com
Tel: (+86)791-8389-6370
Fax: (+86)791-8389-6370

Experimental Section

1. Materials and instruments

Ethylenediaminetetraacetic sodium (EDTA-2Na), $Fe(NO_3)_3$, $Ni(NO_3)_2$, $Pb(NO_3)_2$, $Pb(CH_3COO)_2$, $Cu(NO_3)_2$, $Al(NO_3)_3$ were purchased from Sinopharm Chemical Reagent Co., Ltd. Acetonitrile and methanol were both HPLC grade and purchased from Fisher Scientific and Merck, respectively. The ultrapure water used for the experiments was produced by Millipore ultrapure water system. All chemicals unless specified were reagent grade and were used as received. Pt wire, Ag wire and carbon rod were purchased from JianYi Company (Wenzhou, Chain). Ag/AgCl reference electrode was homemade. Gold necklace (> 99.9%) was purchased form Chow Tai Fook company. Fuel nozzle was purchased from BOSCH company. Polyvinyl chloride water pipe was purchased from local market.

Mass spectrometric experiment was carried out on Orbitrap Fusion MS (Orb-MS, Thermo Scientific) and linear trap quadruple MS (LTQ-MS, Thermo Scientific, San Jose, U.S.A.). Electrolysis of metal was performed on a high voltage power supply (10 - 5000 V, BOHER HV-71010P) or CHI 660d electrochemical workstation (CH instruments Inc.). Scanning electron microscope-Energy dispersive spectra (SEM-EDS) results were obtained on Oxford Inca Energy X-Max20 (Oxford instruments). Inductively coupled plasma optical emission spectrometer (ICP-OES) was obtained on iCAP7400 (Thermo Fisher, U.S.A.). The operation conditions and the wavelengths were summarized in Table S1.

Table S1 Instrumental and operating conditions for ICP-AES measurements

Parameter	Type or amount
Nebulizer	Concentric glass
Spray chamber	Cyclonic
RF power (KW)	1.15
Carrier gas (Ar) flow rate (L/min)	0.7
Auxiliary gas (Ar) flow rate (L/min)	0.5
Pump rate (rpm)	50
Integration time (s)	
On-axis	15
Off-axis	5
Wavelength (nm)	Cu (I) 324.754, Ni (II) 231.604, Pb (II) 220.353

2. Preparation of Ni, Cu and Pb doped gold jewelry

The gold jewelry (purity > 99.9%) was washed with ultrapure water, ethanol and ultrapure water in order. Ni, Cu and Pb doped gold jewelry was prepared by electrodeposition in 0.5 mL electrolyte containing 100 ppm Ni^{2+}, 100 ppm Cu^{2+} and 100 ppm Pb^{2+}. Gold jewelry, platinum wire and Ag/AgCl was using as working electrode, counter electrode and reference electrode, respectively. A -1.2 V potential was applied for 50 s to deposite the Ni, Cu and Pb onto gold jewelry. The amount of the Ni, Cu and Pb deposited on the gloden jewelry was calculated by the concentration difference of electrolyte before and after electrodeposition detected by MS.

3. Preparation of Pb doped fuel nozzle

The fuel nozzle was washed with ultrapure water, ethanol and ultrapure water in order. 0.1 mL electrolyte containing 100 ppm Pb^{2+} was infused into the pipe of fuel nozzle, and a drop was generated at the outlet of

the pipe which was used as electroytic cell. Then, fuel nozzle, platinum wire and Ag/AgCl was using as working electrode, counter electrode and reference electrode, respectively. After applied a -1.2 V potential for 50 s, Ni, Cu and Pb was electrodeposited in the inner wall of the fuel nozzle.

4. Calculation equations for sample consumption

$$m_{M-L} = V_{M-L} \times C_{M-L} \qquad (S1)$$

Where m_{M-L} is the mass of the metal-organic compound. V_{M-L} is the volume of the metal-organic solution. C_{M-L} is the concentration of the metal-organic compound, which was obtained by the method.

$$m_M = m_{M-L} \times (M_M / M_{M-L}) \qquad (S2)$$

Where m_M is the mass of the metal detected by the method. M_M is the molecular mass of the metal. M_{M-L} is the molecular mass of the metal-organic compound.

$$m_{consumed} = m_{M1} + m_{M2} + ... + m_{Mn} \qquad (S3)$$

$m_{consumed}$ is the total mass of the metals consumed.