Chemical Profiling of Bulk Alloys Using Micro-Electrochemical Probe Mass Spectrometry

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Supporting Information

ABSTRACT: Micro-electrochemical probe mass spectrometry (µECP-MS) is demonstrated as a method for the direct profiling of chemical composition of bulk alloy samples without tedious sample pretreatment. The spatial distribution of Zn and Cu components of a Cu/Zn alloy sample was successively identified by scanning the electrolysis potential from −0.6 V to 0.6 V. The lateral resolution of alloy chemical profiling was ≤10 μm, and the depth resolution was ≤0.5 nm. Besides metal components, the method also allows the simultaneous detection of organic molecules on the sample surface. The limit of detection for Rhodamine B, Zn, and Cu depositions was 4.47, 9.58, and 24.25 aq per μm², respectively. The method is particularly useful for high-throughput (<2 min per single run) quality monitoring of industrial parts and conductive materials of irregular geometries, such as alloy, microchips, solder side, etc.

The worldwide consumption and applications of metal materials are steadily increasing.1–3 The alloy properties vary dramatically, with regard to their elemental composition and spatial distribution.4,5 Therefore, the rapid characterization of alloy materials and industrial parts with high chemical sensitivity, minimal destruction, and spatial resolution is increasingly demanded in many fields of modern industry and research.

Currently, analytical techniques including energy spectrometry, spectrometry, and mass spectrometry are available for the chemical characterization of metallic materials. For example, electron probe microanalysis (EPMA),5–7 X-ray fluorescence spectroscopy (XRFS),8–10 proton-induced X-ray emission spectroscopy (PIXRES),10,11 secondary ion mass spectrometry (SIMS),12,13 and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)14,15 have the advantages of high spatial resolution, high sensitivity, and high speed of analysis. However, most of these methods provide only elemental information or require operation in vacuum environment, which greatly limits the throughput of analysis. Ideally, soft ionization is preferable for mass spectrometry analysis of alloys, particularly in the cases where the sample is of irregular geometry and the organic deposited on the alloy surface must be molecularly characterized.16

Herein, a novel method combining micro-electrochemical probe (µECP) with nanoelectrospray ionization mass spectrometry (nano-ESI MS) is proposed for the simultaneous characterization of metallic and organic components in the microarea of an alloy surface (Figure 1). Localized electrolysis and extraction allows high spatial resolution of analysis for the chemical components of an alloy, including the organic and metal species. The formed ions are directly detected by online mass spectrometry analysis. The current method provides low limits of detection (LODs) of 4.47, 9.58, and 24.25 aq per μm² for Rhodamine B (RhB), Zn, and Cu, respectively, and high lateral and vertical resolutions for a Cu/Zn alloy covered by a thin layer of RhB. The method has been also demonstrated for the quality monitoring of alloys and industrial products, showing potential for the chemical analysis of microareas.

EXPERIMENTAL SECTION

Equipment, Materials, and Reagents. Chemical characterization of a microarea on the surface of metal material samples were performed using a commercial mass spectrometer (Orbitrap Fusion MS, Thermo Fisher Scientific) equipped with a homemade µECP device (Figure 1). The µECP device consisted of two parts, including a microarea sampling probe and nano-ESI MS. A µECP, which was prepared by inserting a platinum wire of 100 μm diameter into a micropipette with a

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sharp tip of 5 μm. The diameter of the micropipette is a crucial parameter for the sampling resolution. A micromanipulator (Eppendorf TransferMan 4r) and a microscope (AmScope) were used for precise control of μECP position. After microarea sampling, the μECP was positioned in front of the MS (Orbitrap Fusion MS, Thermo Fisher) inlet for nano-ESI MS analysis.

Metal materials copper, iron, zinc, aluminum, and brass (purity of >99.9%) were purchased from JianYi Company (Wenzhou, China). Platinum wire of 100 μm diameter was purchased from Junlilai Company (Jiangsu, China). Quartz capillary (No. B100-75-10, 0.75 mm i.d., 1.00 mm o.d., Sutter Instrument Company, USA) was used to prepare a micropipette with a defined tip size using a laser puller (Model P2000, Sutter Instrument Company, USA). Ethylenediaminetetraacetic acid (EDTA), phenanthroline (Phen), RhB, and FeCl₃ were purchased from Tianjin Guang Fu Technology Development Co., Ltd. Cu(NO₃)₂, FeCl₃, Zn(NO₃)₂, and Al(NO₃)₃ were purchased from Sinopharm Chemical Reagent Co., Ltd. CH₃COONH₄ and acetonitrile were both HPLC grade and purchased from Fisher Scientific and Merck, respectively. All chemicals unless specified were Analytical-grade and were used as received.

Electrochemical experiment was performed on a CHI 660D electrochemical workstation (CH Instruments, Inc.). Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) results were obtained on Oxford Inca Energy X-Max20 equipment (Oxford Instruments).

**Microarea Analysis.** As shown in Figure S1a in the Supporting Information, a piece of alloy was placed on a three-axis translation stage. The travel range of the translation stage is 20 mm, and the minimal increment is 0.5 μm. To prevent the tip of μECP from crashing to the alloy surface, the μECP was inserted into a glass tube (ID = 1.3 mm) that was fixed on the micromanipulator (Figure S1a), which had a travel range of 50 mm across three dimensions and a minimum incremental motion of 0.1 μm. Microscopy was used to view the analytical area and the movement of alloy sample and μECP. The sample image was displayed on the computer screen with a scale plate. For a typical microarea analysis experiment (Figure 1), an electrolyte (10 ppm Phen in 1:1 (v/v) CH₃CN/H₂O) at the nanoliter level was sucked into the μECP (5 μm tip) by a micro-injector (CellTTram 4r Air, Eppendorf, USA) (see Figure 2b). Then, the μECP was accurately moved to the metal sample surface by micromanipulator with the assistance of a microscope. Because of the hydrophobicity of metal, a liquid junction was formed between the μECP and metal sample when the μECP touched a metal surface. The transformation of metal to metal ions occurred upon applying a voltage of +0.6 V (Model CHI 660D) between the metal sample (anode) and the μECP (cathode). For imaging of the alloy, (1) the μECP was moved from the left to right (Y-axis) to sample the alloy along the scale plate (Figure S1b in the Supporting Information); (2) after a complete sampling process from left to right, the alloy sample was moved forward (along the X-axis) 25 μm; and (3) then, the μECP was moved from left to right again to sample the alloy. By repeating the process steps (1)–(3), the two-dimensional (2D) alloy sampling in the XY domain was completed.

After electrolysis, the μECP was placed at the front of the MS entrance. The distance between the MS inlet and the tip of the μECP was 1 cm. Then, a high voltage (+2 kV) was applied on the μECP to generate ions for MS analysis. A similar procedure was used for other metal materials or biochemical molecule analysis with a little change of electrolyte and electrolysis potential.

**Calibration curve preparation:** Analytical-grade Zn(NO₃)₂ and Cu(NO₃)₂ was used as the source of Zn²⁺ and Cu²⁺. Working solutions of Zn²⁺ and Cu²⁺ with different concentration (1 ppb, 10 ppb, 50 ppb, 100 ppb, 500 ppb, 1000 ppb) were prepared by dissolving Zn(NO₃)₂ and Cu(NO₃)₂ in 10 ppm Phen CH₃CN/H₂O solution. RhB working solutions (1 ppb, 10 ppb, 50 ppb, 100 ppb, 500 ppb, 1000 ppb) were prepared by dissolving RhB in CH₃CN/H₂O solution. Then, the working solution was analyzed by μECP-MS to prepare the calibration curve.

**RESULTS AND DISCUSSION**

**Concept of μECP-MS for Molecular Profiling.** The μECP-MS combined micro-electrochemical sampling with nano-ESI MS for trace analysis (Figure 1). The essential feature of the method was to sample the chemicals of a microarea by electrolysis of metal components and simultaneous extraction of organic species thereon. Before the micro-sampling, a nanoliter electrolyte was sucked into the capillary through the tip of μECP. The volume of the electrolyte was ~2.5 nL (see Figure S2 in the Supporting Information), which
was controlled by fixing the liquid height $h$ (Figure 1a) by a micro-injector under a microscope. Then, the $\mu$ECP was quickly moved forward to the alloy surface by micro-manipulator. After the $\mu$ECP was gently touched with the alloy and a liquid junction formed between the $\mu$ECP and the alloy, the extraction of organics occurred, and then the metal electrolysis would be triggered when the appropriate voltage was applied between the $\mu$ECP (used as a cathode) and alloy (used as an anode) (Figure 1b). After electrolysis/extraction for a short time (e.g., 20 s), which was determined by the intensity of MS signal, the electrolyte was enriched with the organics and metal ions. Then, the $\mu$ECP was moved away from the alloy, placed in front of the MS inlet, and used as a nano-ESI emitter. Upon applying a high voltage ($\pm$2 kV) to the $\mu$ECP, analyte ions were generated at the tip of $\mu$ECP for MS analysis (Figure 1c).

Characterization of Microarea Sampling Process by $\mu$ECP. The present configuration of $\mu$ECP device was prepared by inserting a platinum wire (100 $\mu$m) into a micropipette (Figure 1a). Depending on the required spatial resolution, the tip size of the $\mu$ECP was varied by controlling the parameters of laser puller. Figure 2a shows a typical micropipette with a tip $\sim$5 $\mu$m in diameter. Cyclic voltammetry method was used to characterize the electrochemical properties of $\mu$ECP. As shown in Figures 2b and 2c, the typical "S" curve of K$_3$[Fe(SCN)$_6$]$_6$ was obtained in both 0.01 M KCl (Figure 2b) and KCl/acetonitrile (Figure 2c), indicating that the $\mu$ECP has ordinary electrochemical performance.

The sampling process was also characterized by electrochemical methods. In a typical analysis process, the nanoliter injector, as viewed under a microscope. Then, a voltage above the metal electrolysis potential was applied between $\mu$ECP (cathode) and alloy sample (anode). Under the microscope and with the help of micromanipulator, the $\mu$ECP was accurately positioned toward the sample (step 1 in Figure 2d). When the $\mu$ECP probe touched the sample (Figure 2e), a liquid junction formed between the tip of $\mu$ECP and sample, thus making the entire setup a conductive circuit. The generation of current (step 2 in Figure 2d) indicated that the electrolysis of metal component had started. After electrolysis, the $\mu$ECP was removed away from the sample (Step 3 in Figure 2b), and the current was stopped to terminate the electrolysis/sampling process. Both the SEM images (the upper panel) of a Cu substrate after sampling with $\mu$ECP of different tip sizes (20, 10, and 5 $\mu$m) and the microscopy pictures (the lower panel) of an Rh-covered substrate after sampling by CH$_3$CN/H$_2$O with $\mu$ECP of different tip sizes (20 $\mu$m, 10 and 5 $\mu$m) are shown in Figure 2f. The black areas with diameters of 25, 16, and 10 $\mu$m in Figure 2f correspond to the sampling spots. Note that, because of the liquid spreading during the sampling, the size of the sampling area is larger than the $\mu$ECP tip. A minimal spatial resolution of 10 $\mu$m was obtained by using $\mu$ECP with a 5 $\mu$m tip.

Characterization of Analytical Performance of $\mu$ECP-MS. Several metal samples were used to investigate the analytical performance of $\mu$ECP-MS, such as Cu, Zn, Fe, Al. For example, in Cu analysis, 10 ppm Phen in CH$_3$CN/H$_2$O was used as the electrolyte, and 0.6 V potential was used to sample the Cu with a spatial resolution of 10 $\mu$m. After electrolytic sampling for 60 s, the $\mu$ECP was employed as nano-ESI for MS analysis. Typical analytical results for Cu are displayed in Figure 3a. Signals at m/z 181.0758, 211.5327, and 301.5668 correspond to [Phen+H]$^+$, [Cu+2(Phen)]$^{2+}$, and [Cu+3(Phen)]$^{2+}$, respectively. The strong signal for Cu-Phen complexes (Cu$^{2+}$ and Phen) indicates that the $\mu$ECP-MS method can be used for high-sensitivity and high-spatial-resolution analysis of Cu. Notably, only Cu$^{2+}$ was detected in this experiment, while no Cu$^{+}$ signal was detected, probably because the Cu$^{2+}$ ions were formed before the analytes were nanoelectrospayed under the experimental conditions, without the notable transient state of Cu$^{2+}$.

In addition, the microarea analytical results of Zn (Figure 3b) and Fe (Figure 3a in the Supporting Information) were also successfully obtained by $\mu$ECP-MS that employed Phen/CH$_3$CN/H$_2$O as electrolytes. Notable signal of [Zn+2(Phen)]$^{2+}$ (m/z 212.0335) and [Cu+2(Phen)]$^{2+}$ (m/z 301.5666) can be observed in the mass spectra. Furthermore, our results indicate the importance of organic ligand, which is consistent with previous reports. There were no characteristic signals in the analytical results of Al employed Phen/CH$_3$CN/H$_2$O as electrolytes, while an obvious signal can be observed using EDTA/CH$_3$CN/H$_2$O as electrolytes. This is because Al$^{3+}$ cannot form complexes with Phen, while [Al+EDTA-4H]$^-$ can be formed in EDTA/CH$_3$CN/H$_2$O (Figure S3b in the Supporting Information). Prominent signals of [Cu+EDTA-4H]$^-$ (Figure S3c in the Supporting Information), [Zn+EDTA-4H]$^-$ (Figure S3d in the Supporting Information), and [Fe+EDTA-4H]$^-$ (Figure S3e in the Supporting Information) were observed in the mass spectra.

Figure 3. Qualitative performance of $\mu$ECP-MS for the analysis of metal samples. (a) Mass spectrum of Cu sampled with +0.6 V electrolysis potential; (b) mass spectrum of Zn sampled with +0.6 V electrolysis potential; (c) relationship between the mass signal intensity of metal and the electrolysis potential; (d) mass spectrum of RhB/Zn/Cu sampled with an electrolysis potential of ~0.2 V; (e) mass spectrum of RhB/Zn/Cu sampled with an electrolysis potential of ~0.6 V. The tip of nano-ESI was 1 cm away from the entrance of MS. The spray voltage was +2 kV. The dominant peak assignments: m/z 181.0764 [Phen+H]$^+$; m/z 211.5330 [Cu+2(Phen)]$^{2+}$; m/z 301.5666 [Cu+3(Phen)]$^{2+}$; m/z 212.0330 [Zn+2(Phen)]$^{2+}$; m/z 302.0674 [Zn+3(Phen)]$^{2+}$; m/z 443.2329 [RhB-Cl]$^-$. DOI: 10.1021/acs.analchem.9b01056 Anal. Chem. XXXX, XXX, XXX.

$$[\text{Cu+3(Phen)}]^{2+}$$
Metal has characteristic electrolysis potential under the defined condition. Figure 3c illustrates the relationship between the electrolysis potential and the signal intensity of Zn and Cu. The electrolysis of Zn was triggered at −0.4 V and enhanced as the potential increased, while the electrolysis Cu was initiated at approximately +0.1 V and enhanced as the potential increased. Therefore, in the range from −0.4 V to +0.1 V, the electrolysis of Zn, rather than that of Cu, was started. Thus, by tuning the electrolysis potential, one can achieve successive detection of the components in Zn/Cu alloy. Both electrolysis processes reached a plateau at above +0.2 V and +0.4 V for Zn and Cu, respectively. Thus, the potential for the best signals of Zn and Cu was above 0.4 V.

Without applying potential on the µECP, molecular analytes such as RhB was extracted as neutral molecules and then analyzed by nano-ESI MS. Figure 3d shows the analytical results of RhB on a Cu foil using CH₃CH₂OH as the extraction solvent without applying a potential on the µECP. Characteristic signal of RhB ([RhB-Cl]+, m/z 443.2329), which was confirmed by the MS² spectra with the fragment of m/z 399 and m/z 355 (see Figure S4 in the Supporting Information), was dominantly observed in the mass spectrum, showing that the method could be easily adapted for microarea analysis of either metal materials and/or organic species. As shown in Figure S5 in the Supporting Information, a high extraction efficiency (≥99%) was obtained for RhB after extraction for ~30 s (the experimental process was detailed in Figure S5), suggesting that quantification of trace organic analytes could be implemented.

Using a sample of Zn/Cu alloy covered by RhB, a proof-of-principle experiment was performed to use µECP for sequential microarea analysis of organic species and metal materials. The characteristic signals [RhB-Cl]+ (m/z 443.2327) was obviously observed in the mass spectrum (Figure S6 in the Supporting Information), while no metal ion signal appeared, indicating that neutral RhB was selectively sampled without applying a voltage for electrolysis. When a potential of −0.2 V was applied to the µEC for extraction/sampling, the signals of [Zn+3(Phen)]²⁺ (m/z 212.0330), [Zn+3(Phen)]²⁺ (m/z 302.0674) were detected in the mass spectrum (Figure 3e), indicating that Zn was detectable with the appearance of [RhB-Cl]+ (m/z 443.2327). By altering the electrolysis potential to +0.4 V, Cu signal was successfully detected after Zn component and RhB component (Figure 3f). The results confirmed that sequential analysis of the RhB/Zn/Cu sample was achieved by controlling the electrolysis potentials using the µECP-MS.

The detection limit of µECP-MS was experimentally evaluated by detecting different concentrations of Zn²⁺, Cu²⁺, and RhB working solutions (1.0−1000 ppb). As shown in Figure 4, the signal intensities of [Zn+3(Phen)]²⁺, [Cu+3(Phen)]³⁺, and [RhB-Cl]+ linearly responded to Zn²⁺, Cu²⁺, RhB concentration levels (Figure 4, R² ≥ 0.99) over the range of 10−1000 ppb, 10−500 ppb, 5−1000 ppb, respectively. Based on the calibration curve (Figure 4), the LOD (solution) of the µECP-MS for Zn²⁺, Cu²⁺ and RhB solution were calculated to be 1.59, 4.03, and 1.24 ppb, respectively.

![Figure 4](image)

**Figure 4.** Intensity levels of the characteristic ions against the analyte concentrations. (a) intensity of [Zn+3(Phen)]²⁺ vs concentration of Zn²⁺; (b) intensity of [Cu+3(Phen)]³⁺ vs concentration of Cu²⁺; (c) intensity of [RhB-Cl]+ vs concentration of RhB. The Zn²⁺, Cu²⁺, and RhB were all dissolved in acetonitrile/ultrapure water (v/v = 1:1) solution and detected by nano-ESI MS.

$$\text{LOD (solution)} = \frac{3\sigma}{a}$$

where σ is the standard deviation of a blank solution and a represents the slope of the calibration curve. Since the volume of working solution (V) was ~2.5 μL (see Figure S1 in the Supporting Information), the LOD (mass) values of the µECP-MS for Zn²⁺, Cu²⁺, and RhB were calculated to be 3.98, 10.07, and 3.1 fg, using the formula

$$\text{LOD (mass)} = \text{LOD (solution)} \times V$$

Thus, the LOD values of µECP-MS for Zn, Cu, and RhB on an alloy surface were 9.58, 24.25, and 4.47 ag per μm², as determined using the formula

$$\text{LOD} = \frac{\text{LOD (mass)}}{S}$$

where S is the sampling area.

**Spatial Profiling of Cu/Zn Alloy by µECP-MS.** Mass spectrometry imaging (MSI) is widely used in many areas, including biomedical science, forensics, and food science. By now, many MSI methods have been developed. Most of the MSI methods are developed for biomolecular imaging, such as MALDI, DESI-MS, and LAESI-MS. These MSI methods are unsuitable for metal element imaging. On the other hand, LA-ICP-MS is suitable for the imaging of element distribution, but it is unsuitable for biomolecular imaging. To date, it is extremely challenging to achieve MSI of metal and biomolecule components at the same time.

Because of the high lateral resolution for metal and organic component analysis, µECP-MS has great potential in the molecular imaging of alloys. As a proof demonstration, an artificial sample was first prepared by chemical deposition of a “Cu” symbol on a Zn surface (Figure 5a). Then, µECP-MS was used to analyze the component point by point. The characteristic peak [Cu+3(Phen)]²⁺ was used for Cu imaging. The time duration for single pixel was ~2 min and the pixel number of the image was ~400. Figure 5b was a result of Cu component profile. Out of the “Cu” symbol area, there was no Cu component, while obvious signals were observed in the area of “Cu” symbol. As shown in Figures 5a and 5b, the molecular imaging of Cu obtained by µECP-MS coincided well with the optical image, indicating that µECP-MS is able to generate the metal component profile of alloys. Because the imaging of organic compounds has been demonstrated in many earlier works using liquid extraction mass spectrometry, the imaging of organics were not pursued in this study.
Besides surface analysis, depth profiling of metal materials is always required in the industry. Classical methods used for vertical analysis of metal materials include EDS, XPS, or LA-ICP-MS. However, EDS and XPS can only ablate a surface of several nanometers, while LA-ICP is a hard ionization technique that cannot be used for the analysis of organic molecules. The μECP-MS process allows simultaneous analysis of metal and organic components of a sample. Moreover, electrolysis can be used for etching the metal materials by transforming them into metal ions. To investigate the etching efficiency of electrolysis, a 50-nm-thick Cu foil was prepared via magnetron sputtering. A +0.6 V potential was applied between μECP and Cu foil to etch the Cu. Figure 5c shows SEM images of the Cu foil after etching for 30, 60, and 100 s, which showed that the etching began at the edge of sampling area and then proceeded toward the center, which probably was caused by the nonuniform profile of electric field. After electrolysis for 100 s, 50-nm-thick Cu almost disappeared inside the sampling spot (inset in Figure 5c), resulting in an average vertical resolution of 0.5 nm/s. The signal level for Cu increased with the etching time (see Figures 5d and 5e), showing that more Cu was sampled with lengthened etching time. The etching performance of the present method has great potential in the depth profiling of metal materials (e.g., layered materials, core–shell particles).

Applications of μECP-MS. Semiconductor chip or circuit board is widely used in the information industry. There are many conductive spots on the chip or board. For example, the inset of Figure 6a displays a portion of a computer chip. There are many conductive spots (the yellow spots) on the chip. The place between the yellow spots is insulated. The chip would go out of work if the gap between the yellow spot was conductive (e.g., covered by metal particles, conductive dusts). Thus, sensitive and nondestructive detection of the conductive species is essential to guarantee the performance of a chip. For a demonstration, a computer chip contaminated with Cu particles was used as a sample. Note that the small area marked by a red circle in the inset of Figure 6a is considered to be the analysis area. No conductive current was measured using a sensitive ammeter. Accordingly, strong single of Cu was observed in the spectrum (Figure 6a), indicating that μECP-MS was more sensitive than the ammeter to screen potential conductive tiny spots on chips.

Welding is an important metal material processing technology, which has been widely used in the petrochemical industry, equipment manufacturing, power system, aerospace, aviation, transportation, construction, military, metallurgy, etc. However, the welding quality is affected by many factors, and inapposite parameters will lead to the formation of pits, fissures, pores, and other defects. These defects may cause enormous harm to the product. Thus, analysis of the welding quality is of great significance to guarantee the machining quality of metal materials. By now, physical methods are normally used to test the welding quality, although the chemical information on the micro structure of weld defects is always desirable. As shown in the inset of Figure 6b, several black pits ~20 μm in diameter were observed on the welding surface. In the μECP-MS spectrum of the microarea marked by the red circle in Figure 6b, both signals of Pb and Cu were observed, while weak signals of Pb appeared in the white area. The results demonstrate that μECP-MS is a promising method for the chemical analysis of micro-weld spots.

Figure 5. Molecular profiling of Cu deposited on Zn using μECP-MS with a tip size of 20 μm: (a) optical image of Cu/Zn alloy; the black symbol “Cu” is chemical-deposited Cu; (b) ion image of [Cu +3(Phen)]2+; (c) SEM images of Cu membrane (thickness = 50 nm) etched at 0.6 V for different times; (d) mass spectrum of the Cu membrane after microarea sampling at 0.6 V for 30 s; and (e) mass spectrum of the Cu membrane after microarea sampling at 0.6 V for 100 s.

Figure 6. Application of μECP-MS for chip and welding quality testing: (a) application of μECP-MS in chip analysis and (b) application of μECP-MS in weld analysis. [Dominant peak assignments: m/z 175.4934 [Cu+EDTA-4H]2−; m/z 248.0171 [Pb+EDTA-4H]2−.]
CONCLUSION

In summary, μECP-MS was developed for the simultaneous molecular profiling of metal and organic components in metal alloys. This method features high sensitivity (LOD = 4.47 ag/μm²), high specificity, and high lateral resolution (10 μm) and depth resolution (0.5 nm). Proof-of-concept application of the present method in the analysis of solder side and organics covered alloy indicates that the present method is a promising analytical method for the microarea chemical profiling of alloys.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.9b01056.

Schematic diagram of experimental setup; measurements of the electrolyte volume in μECP; qualitative performance of μECP-MS for metallic materials analysis; MS² of RhB; RhB extraction efficiency of μECP; mass spectra of RhB deposited on the surface of the alloy (PDF)

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Notes

The authors declare no competing financial interest.

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