



MASS SPECTROMETRY FOR STRUCTURAL CHARACTERIZATION OF NON-CYANIDE GOLD COMPLEX

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ABSTRACT

In this work, the possibilities of a mass spectrometry approach towards the characterizations of the electrolyte for decorative gold plating based on mercaptotriazole were studied. All mass spectra were obtained using laser desorption ionization (LDI) method on a commercial matrix assisted laser desorption ionization – time of flight (MALDI-TOF) mass spectrometer. The LDI MS spectra of chloroauric acid gave evidence of the presence of a variety of monomeric and polymeric complexes. LDI MS spectra of the electrolyte obtained from chloroauric acid, glycine and mercaptotriazole revealed existence of the ion at m/z 472 which indicated that the complex $[Au(NH_2CH_2COOH)(C_2H_2N_3S)_2]^+$ has been formed.

Keywords: MALDI-TOF MS, gold, mercaptotriazole, decorative plating

1 INTRODUCTION

In this paper, the laser desorption ionization (LDI) on a commercial matrix assisted laser desorption ionization - time of flight mass spectrometric instrument is used for characterization of the electrolyte for decorative gold plating based on mercaptotriazole. The electrolyte, based on the gold complex with mercaptotriazole, was obtained from chloroauric acid, $HAuCl_4$ (2.5 gAu/dm³), glycine (6%) and mercaptotriazole (6%), at pH=7 [1-4]. Generally, the advantages of using LDI MS for detection of low-mass molecules are: the absence of signals from matrices in the low-mass range, the absence of formation the *analyte-matrix adducts*, and high tolerance toward increased concentrations of inorganic salts [5,6]. $HAuCl_4$ is a fairly strong UV absorber, which makes easier the utilization of N₂ laser in the analysis of the gold plating complex with mercaptotriazole.

2 EXPERIMENTAL

Mass spectra were acquired on a MALDI-TOF mass spectrometer (Voyager-DE PRO, AB Sciex, USA) with delayed extraction. Ions are generated in the source region by means of a nitrogen laser (337 nm, laser repetition rate 20.0 Hz, input bandwidth 500 MHz). All mass spectra were acquired in the negative reflector mode using delayed extraction (extraction delay time 100ns). An extraction voltage of 20 kV was typically used. For the LDIMS experiments, a 0.5 μ L aliquot of solution sample was loaded in a well (i.e., sample spot) of a

stainless steel MALDI target plate having 100 wells (V700666, SCIEX, Framingham, MA, USA) and allowed to dry. In this experiment, the following samples were used: solution of chloroauric acid with gold concentration of 2.5 g/dm³ (pH 1.25) and gold complex based on mercaptotriazole with gold concentration of 2.5 g/dm³. A MALDI target plate with samples on it was inserted into the machine. The instrument was equipped with a video camera to display the sample image on a monitor and permit the laser to be focused on a specific well. Mass calibration was conducted using fragments produced from a CHCA standard at m/z 172.0393.

2.1 Reagents

For the synthesis of the gold complex with mercaptotriazole the following chemicals were used: gold powder (99.99%, Mining and Metallurgy Institute Bor – MMI Bor); hydrochloric acid p.a. (Zorka, Šabac); nitric acid p.a. (Zorka, Šabac), glycine (min. 99%, Alkaloid Skopje), potassium hydroxide (Merck, Germany), distilled water (5 μS/cm) and mercaptotriazole. Mercaptotriazole was synthesized in MMI laboratory. Thiosemicarbazide, CH₃N₃S (min 98%, Merck, Germany) and formamide p.a. (Alkaloid, Skopje) were used in this synthesis [1, 2].

3 RESULTS AND DISCUSSION

Figure 1 presents the negative-ion mode LDI mass spectra for aqueous HAuCl₄ solutions.

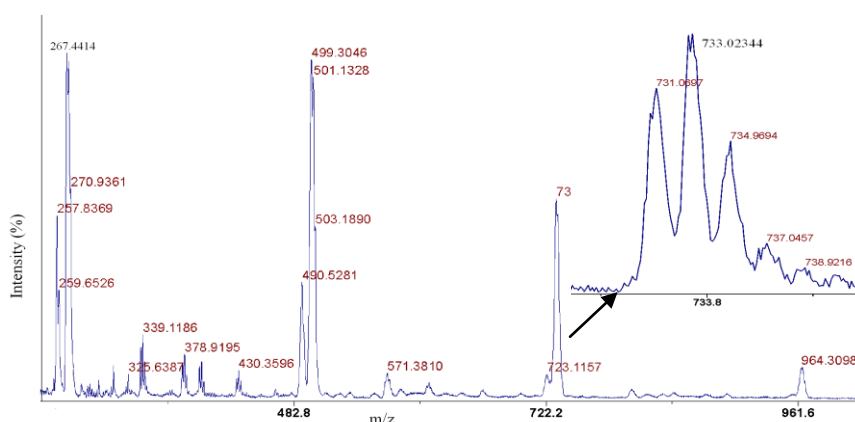


Figure 1 Negative-ion mode LDI mass spectra for the solution of chloroauric acid with gold concentration of 2.5 g/dm³ (pH 1.25)

Three mononuclear complexes have been observed in the mass range m/z 260–420, a m/z of 267.44 Da (calcd 266.90 Da) may correspond to AuCl₂⁻ ion, m/z 429.91 Da (calcd 429.89 Da) may correspond to AuCl₃⁻(HCl)x(H₂O)₅ ion, and m/z of 339.11 Da (calcd 338.83 Da) may correspond to AuCl₄⁻ ion. In addition to mononuclear gold, Figure 1 also presents mass spectra of two possible dinuclear gold clusters with m/z 499.30 Da (calcd 498.84 Da) assigned to [Au₂Cl₃]⁻, and 571.0210 Da (calcd 570.77 Da), assigned to [Au₂Cl₅]⁻. One possible three-nuclear gold cluster [Au₃Cl₄]⁻ detected at m/z of 733.02 Da (calcd 732.77 Da), is shown in the form of zoomed MALDI-TOF MS spectra of this cluster in the insert of Fig. 1.

The ion signal seen in Figure 1 at m/z 964.30 Da (calcd 963.94 Da) may correspond to $[\text{Au}_4(\text{OH})_4] \times (\text{H}_2\text{O})_6$. The experimental and theoretical isotopic peak distributions are matched each other for each complex. For example in Fig. 2, the experimental and theoretical isotopic peak distributions of $[\text{Au}_2\text{Cl}_5]^-$ are shown.

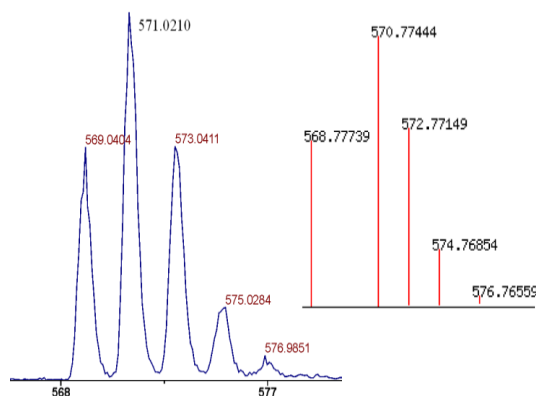


Figure 2 The experimental (left panel) and theoretical (right panel) isotopic peak distributions for $[\text{Au}_2\text{Cl}_5]^-$ ion

The ions detectable in the mass spectra at m/z about 267, 339, 499, 570, 732 (Figure 1) correspond to the negative ions generated of the solution of dichloride (pyridine) gold(III) chloride [6]. However, some authors have revealed that transition metal complexes are not detectable as negative ions. [7].

The LDI mass spectra of the electrolyte obtained from HAuCl_4 (2.5 gAu/dm³), glycine (6%) and mercaptotriazole (6%) were recorded in negative-ion mode (Figure 3).

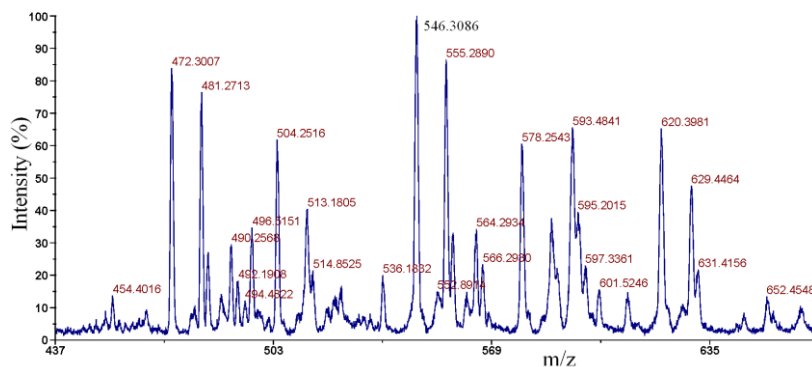


Figure 3 Negative-ion mode LDI mass spectra of gold complex based on mercaptotriazole

The ion signals seen in the spectrum may correspond to the following species:
 $[\text{Au}(\text{NH}_2\text{CH}_2\text{COOH})(\text{C}_2\text{H}_2\text{N}_3\text{S})_2]^-$ (expt 472.30, calcd 471.99 Da),
 $[\text{AuCl}(\text{NH}_2\text{CH}_2\text{COOH})_2(\text{C}_2\text{H}_2\text{N}_3\text{S})]^-$ (expt 481.27 and 483.24 calcd 481.99 and 483.99),
 $[\text{Au}(\text{C}_2\text{H}_2\text{N}_3\text{S})_2(\text{OH})(\text{H}_2\text{O})_5]^-$ (expt 504.25 calcd 504.01 Da),
 $[\text{Au}_2(\text{C}_2\text{H}_2\text{N}_3\text{S})(\text{OH})_2(\text{H}_2\text{O})]^-$ (expt 546.30 calcd 545.94 Da),
 $[\text{Au}_2\text{Cl}(\text{CH}_2\text{NH}_2\text{COOH})(\text{OH})(\text{H}_2\text{O})_2]^-$ (expt 555.28 and 557.25 calcd 555.95 and 557.95 Da)

$[\text{Au}_2\text{Cl}(\text{C}_2\text{H}_2\text{N}_3\text{S})(\text{HO})(\text{H}_2\text{O})]^-$ (expt 564.29 and 566.29 calcd 563.91 and 565.90 Da)
 $[\text{Au}_2(\text{C}_2\text{H}_2\text{N}_3\text{S})(\text{OH})_5]^-$ (expt 578.25 calcd 578.94 Da),
 $[\text{Au}_2\text{Cl}_2(\text{NH}_2\text{CH}_2\text{COOH})(\text{H}_2\text{O})_3]^-$ (expt 593.48, 595.20 and 597.33 calcd 593.94, 595.93, and 597.93 Da),
 $[\text{Au}_2(\text{NH}_2\text{CH}_2\text{COOH})(\text{C}_2\text{H}_2\text{N}_3\text{S})(\text{OH})_2(\text{H}_2\text{O})]^-$ (expt 620.39, calcd 619.97 Da)
 $[\text{Au}_2\text{Cl}(\text{NHCH}_2\text{COOH})_2(\text{OH})_2(\text{H}_2\text{O})]^-$ (expt 629.44 and 531.41 calcd 628.96 and 63.96Da).

The results show that the single isotopic ion at m/z 472.30 Da may originate from the gold complex based on glycine and mercaptotriazole, such as $[\text{Au}(\text{NH}_2\text{CH}_2\text{COOH})(\text{C}_2\text{H}_2\text{N}_3\text{S})_2]^-$, which is in analogy with the structure of corresponding palladium complex [2].

CONCLUSION

In this experiment, the LDI has proved reasonably effective as a characterization tool for the electrolyte for decorative gold plating based on mercaptotriazole. The LDI MS spectra of chloroauric acid gave evidence of presence the variety of monomeric and polymeric complexes. LDI MS spectra of the electrolyte obtained from chloroauric acid, glycine and mercaptotriazole at pH=7 revealed the existence of ion at m/z 472 which indicated that the complex $[\text{Au}(\text{NH}_2\text{CH}_2\text{COOH})(\text{C}_2\text{H}_2\text{N}_3\text{S})_2]^-$ was formed.

ACKNOWLEDGEMENTS

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LASER DESORPTION IONISATION TIME-OF-FLIGHT MASS SPECTROMETRY OF ANODIC FILM ON Ag₄₃Cu₃₇Zn₂₀ ALLOY

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ABSTRACT

The laser desorption/ionization (LDI) and mass spectra of the anodic film on Ag₄₃Cu₃₇Zn₂₀ alloy are reported. The ion signals are identified by both m/z values and distinctive isotope patterns. Layers were found to be complex composites of various chemical entities such as copper chlorides (CuCl, CuCl·H₂O), zinc hydroxide chlorides (β-Zn(OH)Cl and Zn₃(OH)₆Cl₂·H₂O), copper oxide/hydroxide (Cu₂O and Cu(OH)₂) and silver chloride (AgCl). The results presented here illustrate the LDI TOF MS with a sufficiently high resolution, enabling the observation of isotopic patterns of peaks and can be a powerful tool for the identification of the anodic film on Ag₄₃Cu₃₇Zn₂₀ alloy.

Keywords: LDI MS, Alloy, Anodic film, Potentiostatic polarization.

1 INTRODUCTION

The Raman spectroscopy and X-ray crystallography for characterization of anodic film on metals and alloys after potentiostatic polarization have been used routinely. The Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) is one of the latest laser ionization methods used in the mass spectrometric analysis. Generally, in order for mass spectrometry to provide useful molecular weight information, analytes need to be in the gas phase and ionized. MALDI categorized as a “soft” and indirect ionization where matrices (such as α-cyano-4-hydroxycinnamic acid - CHCA) absorb the energy of the laser light firstly, and then the energy, released proton, and/or charge is transferred to the analytes. To date, MALDI is successfully used in studying the biological macromolecules and, to a somewhat lesser extent, in the polymer chemistry and routine characterization of polar organic molecules. In defiance of the fact that there are reports of its use in the analysis of inorganic species; MALDI is yet to become influential method in coordination, organometallic chemistry, and inorganic chemistry. Spectra detected by MALDI method are very sensitive of the choice of matrix. The lower limit of the practical detection range is restricted when matrix peaks hide ion signals in the region of interest [1].

Matrix-free laser desorption ionization LDI-MS has been widely used during the last 15 years for the analysis of inorganic materials such as chalcogenide glasses and nano-layers, and for characterisation the hydrolysis products of some complex in aqueous solution [2, 3].

LDI represents very rapid heating of the sample or sample substrate to vaporise molecules so quickly that they do not have time to decompose, due to this method is good for low- to medium-molecular weight compounds and surface analysis.

The aim of this work was to elucidate the chemical structures of anodic film on Ag₄₃Cu₃₇Zn₂₀ alloy after potentiostatic polarization and to evaluate the possibilities and limitations of LDI method for this purpose.

2 EXPERIMENTAL

Mass spectra with (MALDI) and without a matrix (LDI) were collected on a Voyager-DE PRO, AB Sciex, USA TOF mass spectrometer equipped with a N₂ laser (337 nm operating at 20.0 Hz) to desorb and ionize the samples, and video camera, allowing to aim the laser at a specific spot within the area of the target. In all cases 20 kV total acceleration voltage with an extraction delay time of 150 ns was used. All spectra were taken in the linear mode with the laser power just above the threshold of ion formation/ desorption. Laser desorption/ionization mass spectra acquired for this work were obtained from at least 200 laser pulses per spectrum and the recorded spectra of all the laser shots were summed. In this work, a sample was film on Ag₄₃Cu₃₇Zn₂₀ alloy after potentiostatic polarization. The sample was dissolved in 10 µl of deionized water or propanol. A volume of 0.5 µl of these solutions was deposited onto the sample plate (stainless steel), and allowed to air-dry.

3 RESULTS AND DISCUSSION

All of the species discussed in this paper desorb without a matrix. The positive mode of LDI mass spectra provides valuable information. For this reason, Figure 1 and Figure 2 show LDI mass spectra recorded in the positive ion mode of the sample dissolved in deionized water and the sample dissolved in propanol, respectively.

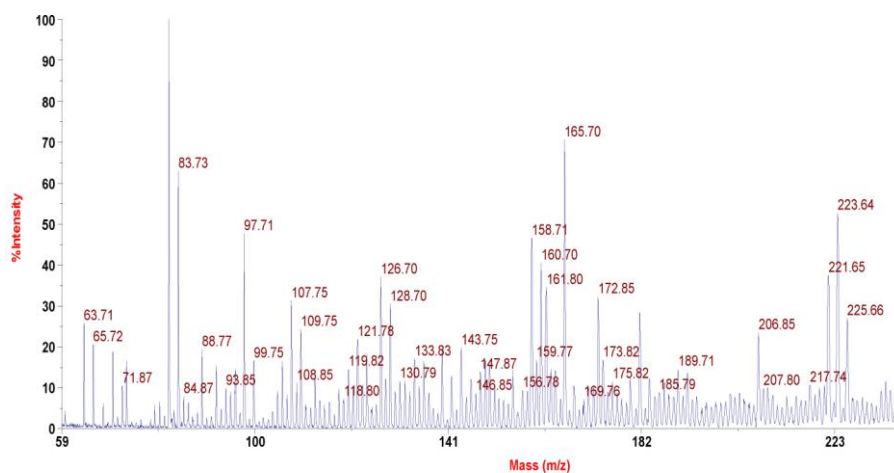


Figure 1 LDI mass spectrum of the sample dissolved in deionized water (without any matrix) recorded in the positive ion mode

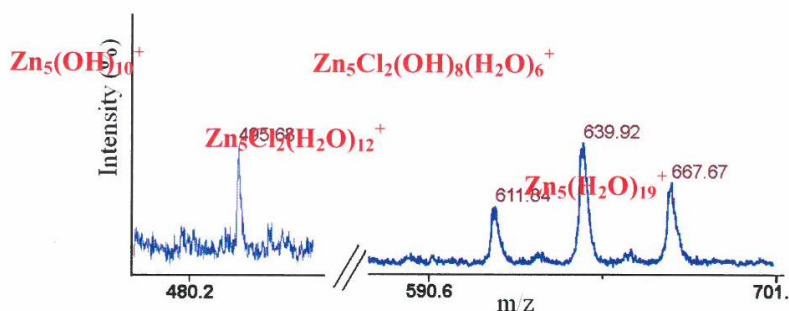


Figure 2 LDI mass spectrum of the sample dissolved in propanol (without any matrix) recorded in the positive ion mode

Ion signals for each species give a distinctive envelope of peaks due to the isotopes and the isotopic abundances of zinc, copper, silver and chlorine. For example, the pattern at approximately m/z 63 can be explained by the overlap of isotopic patterns for Zn^+ and CuH^+ . For this reason, Figure 3 shows the experimental mass spectra about m/z 63 and theoretical isotopic peak distributions of Zn and Cu.

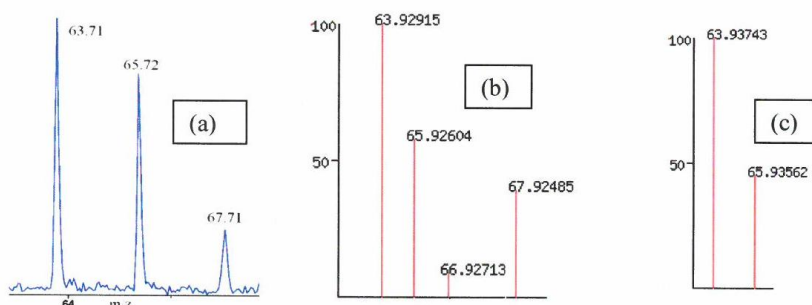


Figure 3 LDI mass spectrum of the sample dissolved in deionized water (without any matrix) recorded in the positive about m/z 63(a) and theoretical isotopic peak distributions of Zn (b) and Cu (c)

All signals observed in the positive ion mode mass spectra in all figures of this work are listed in Table 1. The use of propanol as solvent for these samples leads to improving the detection of the ions at m/z above 400 Da. These data correspond to the data obtained for from XRD analysis and Raman spectroscopy. X-ray diffractogram of the same material shows presence of nantokite ($CuCl$), zinc hydroxide chloride ($\beta-Zn(OH)Cl$), simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$) and cuprous oxide (Cu_2O). All compounds on diffractogram could be identify in the LDI-TOF mass spectra which also suggests that $AgCl$, $AgCl$ hydrates or silver chloride complexes are also part of the surface film on Ag-Cu-Zn alloy.

Table 1 Signals detected in the LDI-TOF mass spectra of the anodic film on Ag₄₃Cu₃₇Zn₂₀ alloy after potentiostatic polarization observed in all mass spectra acquired in this work

| Experimental peak position m/z | Peak identity | Calculated m/z | Experimental peak position m/z | Peak identity | Calculated m/z |
|--------------------------------|--|----------------|--------------------------------|---|----------------|
| 63.71 | Zn and CuH ⁺ | 63.9/63.93 | 158.71 | Cu ₂ O(OH) | 158.85 |
| 65.72 | | 65.92/65.90 | 160.70 | | 160.86 |
| 67.71 | | 67.92 | 162.77 | | 162.85 |
| 81.73 | Zn(H ₂ O) | 81.93 | 159.77 | AgCl(H ₂ O) | 159.88 |
| 83.73 | | 83.93 | 161.80 | | 161.88 |
| 85.93 | | 85.93 | 163.73 | | 163.88 |
| 97.71 | CuCl | 97.89 | 170.75 | Cu(HCl) ₃ | 170.85 |
| 99.75 | | 99.89 | 172.85 | | 172.85 |
| 101.79 | | 101.89 | 174.83 | | 174.85 |
| 107.75 | AgH | 107.91 | 176.84 | | 176.85 |
| 109.75 | | 109.91 | 179.68 | | 179.86 |
| 126.70 | Cu ₂ H | 126.86 | 181.67 | Ag(HCl) ₂ H | 181.86 |
| 128.70 | | 128.86 | 183.70 | | 183.86 |
| 130.79 | | 130.86 | 185.79 | | 185.86 |
| 133.83 | ZnCl(OH)(H ₂ O)/ CuCl(H ₂ O) ₂ | 133.91/133.91 | 221.65 | Cu ₃ O(OH) | 221.79 |
| 135.83 | | 135.90/135.91 | 223.64 | | 223.78 |
| 137.83 | | 137.90/137.91 | 225.66 | | 225.78 |
| 141.72 | AgCl | 141.87 | 639.92 | Zn ₅ Cl ₂ (OH) ₈ (H ₂ O) ₆ | 639.66 |
| 143.75 | | 143.87 | 611.84 | Zn ₅ Cl ₂ (H ₂ O) ₁₂ | 611.70 |
| 145.84 | | 145.87 | 667.67 | Zn ₅ (H ₂ O) ₁₉ | 667.83 |

4 CONCLUSION

LDI-TOF MS is a simple and fast technique that requires very little sample. Spectra recorded with sample dissolved in propanol in this study exhibit less fragmentation than spectra recorded with sample dissolved in deionized water. Mass spectrometry lack as LDI TOF MS with a sufficiently high resolution, enabling the observation of isotopic patterns of peaks, can be a powerful tool for the identification of the complex structures like anodic films of the ternary alloys, obtained by potentiostatic polarization in chloride solutions.

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