

Time-of-flight Static Secondary Ion Mass Spectrometry Analysis of Surface Contamination on Pt/Ir Standard Mass Material

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Static time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been used to characterize surface contaminants on a Pt–10% Ir alloy sample prescribed for fabrication of a prototype kilogram mass standard. The identification of various oxygenated and non-oxygenated hydrocarbon adsorbates on the Pt–Ir surface provides a scenario for the increase in mass observed after standard cleaning procedures, and as a function of time. Static TOF-SIMS analysis suggests the catalytic activity of Pt plays a key role in the adsorption of organic solvents used in standard cleaning procedures as well as adsorption of hydrocarbon species present in ambient laboratory air. © 1998 John Wiley & Sons, Ltd.

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The international prototype kilogram is a cylindrical piece of Pt–10% Ir alloy, stored at Bureau International des Poids et Mesures (BIPM), Paris. National prototype kilograms (such as the one at the National Institute of Standards and Technology, Gaithersburg, MD) are replicas of the international prototype kilogram. Periodically, the national prototype kilograms are compared to the international prototype kilogram to ensure mass accuracy. Due to the remarkable improvement in the mass resolution of balances, this type of verification has revealed a rapid increase in mass of a few micrograms after the standard cleaning procedure.^{1,2,3,4,5} The standard cleaning procedure employs rinsing the prototype kilogram mass standards with ethanol and water followed by drying in an oven. This cleaning process is performed before each comparison of the prototype kilogram mass standards.

Many laboratories have used surface analytical techniques, such as Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and thermal desorption spectroscopy (TDS), to examine the effects of different treatments used for the cleaning procedure and subsequent adsorption of contaminant species on the surface of the prototype kilogram mass standard.^{6,7,8,9,10} The phenomenon responsible for the increase in mass after cleaning is yet to be confirmed, due to limitations of the above techniques.

Secondary ion mass spectrometry (SIMS) was first used to examine the increase in mass of the Pt–Ir alloy mass material following different cleaning procedures by Sharma, *et al.*¹¹ However, the dynamic mode of SIMS used by the authors could only show the nature of the diffusion of atomic impurities, such as Na, Ca, and K, from the surface into the bulk material. To characterize both the atomic and molecular contaminants on the surface of the Pt–Ir alloy

material, static SIMS conditions are necessary. The low ion dose ($<10^{12}$ primary ions/cm²) of static SIMS results in sputtering less than 1% of the surface, yet all the atomic and molecular information is obtained.

In this report, results obtained from static time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis of a Pt–Ir alloy sample are discussed. The type of contaminants present on the surface before and after the standard cleaning procedure and as a function of time are identified, and the role of these contaminants in the mass gain phenomenon is also discussed.

EXPERIMENTAL

The Pt–10% Ir alloy disk-shaped (10 mm diameter, 0.5 mm thickness) sample was prepared by BIPM for the National Physical Laboratory, New Delhi, from material similar to the international prototype kilogram. Three treatments were performed on the Pt–Ir alloy sample to observe the behavior of the adsorption of contaminants on the surface. First, the Pt–Ir alloy sample was sputter-cleaned using a 25 kV Ga⁺ ion beam (1–2 nA) for 5 minutes. This procedure removed surface contaminants and some of the substrate to reveal a fresh substrate surface. Next, the sample was subjected to the standard cleaning procedure prescribed by BIPM. This was done by placing the sample in a stirred ethanol bath for approximately 30 minutes, followed by drying with a clean lint free cotton cloth. The sample was then rinsed in a de-ionized water bath for approximately 1 hour. Drying was accomplished by placing the sample on a clean, dry glass container inside an oven kept at 140°C for 45 minutes. Finally, to identify the accumulation of adsorbates on the surface as a function of time after the standard cleaning procedure, the sample was kept in ambient laboratory air for almost two years after cleaning. The surface contaminants were analyzed after each of the three treatments above using a reflectron-based TOF-SIMS instrument with a 40 ns pulse of Ga⁺ from a liquid metal ion gun as the primary ion source (probe size of approximately 0.1 μm).¹²

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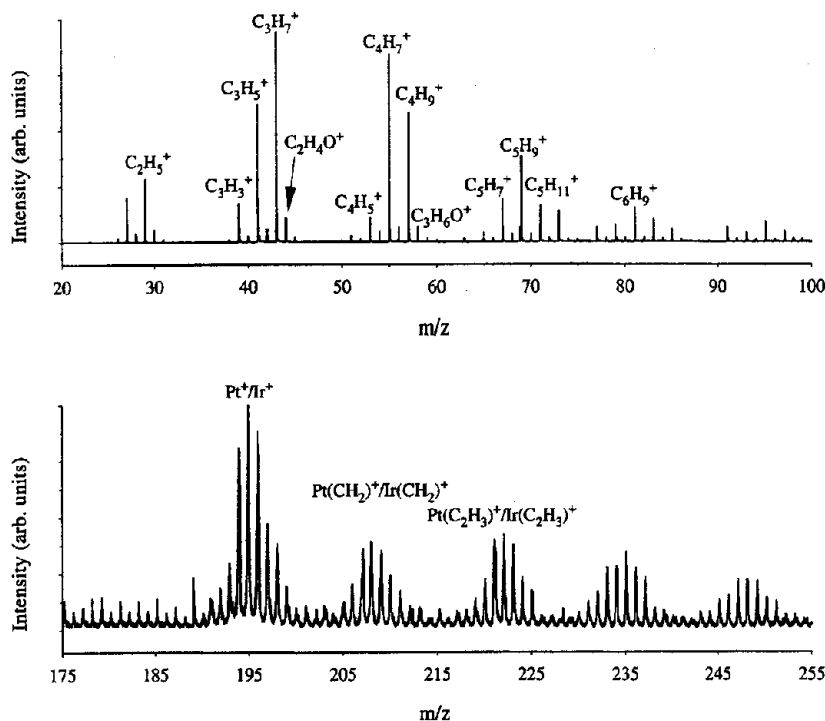


Figure 1. Positive ion static TOF-SIMS spectrum of the Pt-Ir sample after the BIPM cleaning procedure.

RESULTS AND DISCUSSION

The positive ion TOF-SIMS spectrum of the sputter-cleaned surface of the Pt-Ir alloy material shows some Na^+ and K^+ ions on the surface, which may be due to diffusion of these species from the surface into the bulk material as observed earlier by Sharma, *et al.*¹¹ Due to the high Ga^+ ion dosage

during the sputter cleaning, an intense Ga^+ ion signal is observed at m/z 69. The major and minor Pt^+ and Ir^+ isotopes are seen at and around m/z 195 and 192, respectively, and the isotope ratios observed are consistent with exact mass calculations for pure Pt and Ir.

The positive ion TOF-SIMS spectrum of the sample after the standard cleaning procedure prescribed by BIPM is

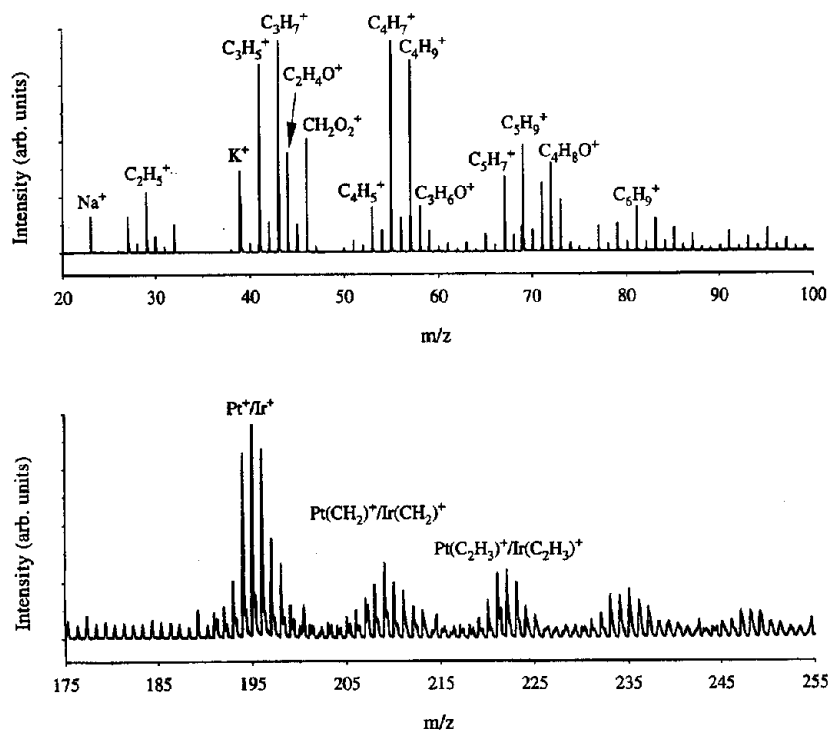


Figure 2. Positive ion static TOF-SIMS spectrum of the Pt-Ir sample exposed to ambient laboratory air for approximately two years.

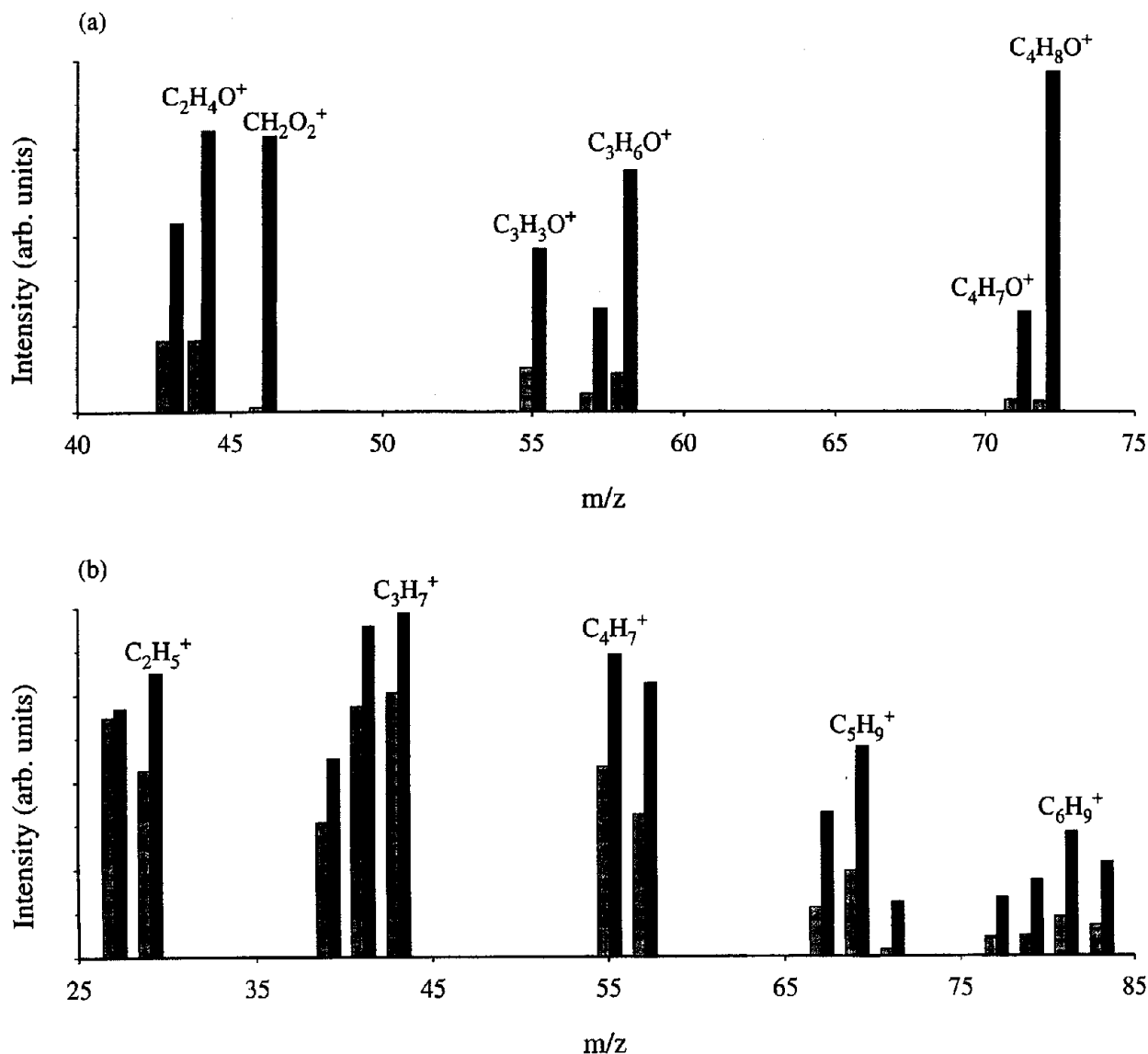


Figure 3. Normalized intensity comparison of (a) $C_xH_yO_z^+$ and (b) $C_xH_y^+$ contaminants on the Pt-Ir sample after long exposure to ambient laboratory air (dark gray) and after the BIPM cleaning procedure (light gray).

shown in Fig. 1. Na^+ and K^+ ions are not abundant, suggesting the cleaning procedure washes these species from the surface. A variety of hydrocarbon surface species of the form $C_xH_y^+$ are observed below m/z 100. Also noticeable are clusters of the form $C_xH_yO_z^+$ at m/z 44 and 58. Since TOF-SIMS provides high mass resolution, it is easy to discern between species such as CO_2^+ at m/z 43.99 and $C_2H_4O^+$ at m/z 44.03. Other $C_xH_yO_z^+$ species are present, but due to the scale of the x axis, the species are not apparent in this figure. For most oxygenated hydrocarbon species it is not currently possible to assign structures due to isobaric species, which consist of molecules such as aldehydes, alcohols, ethers and ketones. Organometallic species of composition $Pt(C_xH_y)^+$ and $Ir(C_xH_y)^+$ are centered around m/z 209 and higher.

The positive ion TOF-SIMS spectrum of the sample after approximately two years of exposure to ambient laboratory air after cleaning is shown in Fig. 2. The spectrum is similar to Fig. 1, except that, oxygenated hydrocarbon species are noticeably enhanced with respect to the non-oxygenated hydrocarbons. For instance, one can see that intensities of

$CH_2O_2^+$ and $C_4H_8O^+$ species are increased significantly. Intensities from Na^+ and K^+ have also increased with respect to the $C_xH_y^+$ species. These ions could either arise from bulk contaminants that have migrated to the surface or from adventitious sources.

The spectra in Figs 1 and 2 were normalized to the CH_3^+ peak, m/z 15, and selected peaks from both spectra are plotted in Fig. 3. Note the increase in intensity of the $C_xH_yO_z^+$ species as a function of time in Fig. 3(a). A similar, but less profound increase in intensity of $C_xH_y^+$ is seen in Fig. 3(b). From this it can be stated that contamination from both oxygenated and non-oxygenated hydrocarbon species increases as a function of storage time in ambient laboratory air after cleaning.

Expanded views from the spectra in Figs 1 and 2 at nominal masses of 43 and 55 are shown in Fig. 4. The ratios of intensities of the $C_xH_yO_z^+$ and $C_xH_y^+$ species in Fig. 4(c) and (d) are obviously greater than those in Fig. 4(a) and (b). These ratios provide for two scenarios as a function of exposure to ambient laboratory air after cleaning: (1) the $C_xH_yO_z^+$ components are increasing relative to the $C_xH_y^+$

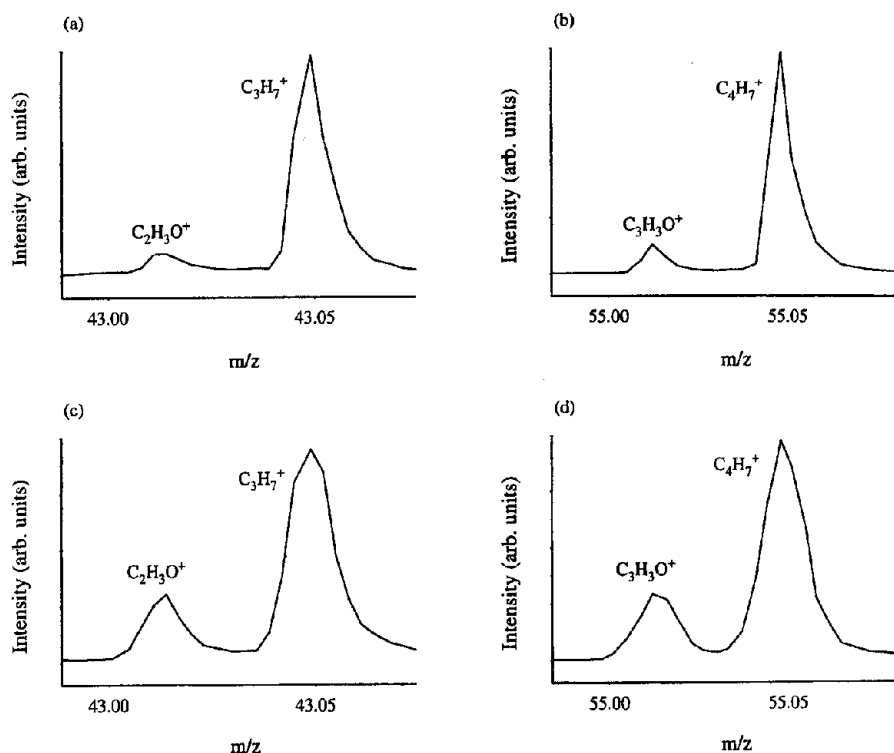


Figure 4. Expanded view for nominal masses 43 and 55. Subplots (a) and (b) are from Fig. 1 and subplots (c) and (d) are from Fig. 2.

components or (2) the $C_xH_y^+$ components are decreasing relative to the $C_xH_yO_z^+$ components. Since contamination from both $C_xH_y^+$ and $C_xH_yO_z^+$ species increases as a function of time, it is suggested here that the contamination from the $C_xH_yO_z^+$ species is increasing relative to the $C_xH_y^+$ species as a function of exposure to ambient laboratory air after cleaning.

The static TOF-SIMS data are supported by recent XPS and TDS data.^{6,7} A decrease in surface contamination after ion sputter-cleaning was observed, which seems obvious since the ion sputter-cleaning process removes material from the surface of the sample. The XPS studies show an increase in signal from carbon and oxygen after cleaning and as a function of time. XPS and TDS could not, however, be used to determine the molecular formulation of the surface contaminants.

It is known that organic molecules in contact with catalytically active transition metals, such as Pt, may be adsorbed onto the metal surface, forming organometallic molecules.¹³ Adding a second metal, such as Ir, can increase the catalytic lifetime of Pt.¹⁴ While forming organometallic bonds, these organic adsorbates may lose some of their constituents, such as H. For example, ethylene (C_2H_4) will lose a hydrogen atom to form ethynyl (C_2H_3), a common constituent of surface and organometallic chemistry.¹⁵ This adsorption process may continue until all the atomic sites are completely saturated, and thus cause the increase in the mass of the prototype kilogram mass standard after the BIPM cleaning procedure and as a function of time.

Considering the above, one can estimate the increase in mass due to the adsorption of hydrocarbon molecules on a prototype kilogram mass. The prototype kilogram mass, a cylinder with a diameter of 39 mm and a height of 39 mm, has a total surface area of 71.68 cm². If we consider one monolayer of adsorbates with surface density of 5×10^{14}

molecules/cm², then 3.58×10^{16} molecules would be adsorbed on the surface. By taking an average hydrocarbon mass, such as $C_4H_7 = 9.158 \times 10^{-17}$ μg/molecule, the total mass of the adsorbed layer would be 3.3 μg, which is approximately the mass change actually observed in the prototype kilogram mass during verification. Although it is difficult to calculate actual surface coverages with SIMS measurements due to possible matrix effects, the observed intensities are certainly consistent with these mass change numbers.

CONCLUSION

The phenomena of mass gain in the prototype kilogram mass, made of Pt-10% Ir alloy, after cleaning and as a function of time has been addressed using TOF-SIMS. It was possible to identify surface contaminants, which appear after cleaning and as a function of time. The contamination is due to oxygenated and non-oxygenated hydrocarbon species from solvents used in cleaning and atmospheric pollutants found in normal laboratory conditions. It has been shown here that the hydrocarbon contaminants increase as a function of storage time under ambient laboratory air.

Acknowledgements

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