



Surface modifications of stainless steel to minimise contamination in mass spectrometers



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ABSTRACT

The effect of electrochemically grown and vapour deposited coatings on the build-up of contamination on stainless steel surfaces in the electrospray ionisation source of a mass spectrometer is investigated, together with their influence on the robustness of the instrument response. Quantification of the contamination build-up on flat samples, using white light interferometry, allowed the identification of the most beneficial treatments. Coating with electrochemically-grown anodic oxide and cathodic oxide films and amorphous carbon films doped with silicon or nitrogen resulted in reduced contamination compared with the uncoated stainless steel surface, and provided improved robustness of the instrument response.

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1. Introduction

Mass spectrometry is a powerful analytical tool with numerous applications, particularly in the fields of environmental chemistry [1], food chemistry [2], and clinical and medical research [3,4]. It is used to identify unknown compounds, to quantify known compounds and to elucidate the structure and chemical properties of molecules. An analyte is introduced into the spectrometer and ionised by an ionisation source. Gas phase ions are subsequently separated according to their mass-to-charge ratio and a mass spectrum of the analyte is produced. Atmospheric pressure ionisation using an electrospray ionisation (ESI) technique, which extracts ions from the solution-phase into the gas-phase free of solvent, is the most widely used method for the production of ions from organic molecules. The efficiency of the extraction is affected by the properties of the sample solution containing the analyte, such as flow rate, liquid surface tension and electrolyte concentration. The ions exist in solution in the test sample with a complex matrix of other compounds. Therefore, spraying an aerosol of the sample solution into the inlet region of the instrument has the potential to contaminate the structural elements of the inlet interface to the detriment of instrument performance.

Sample degradation on contact with surfaces in mass spectrometers has been previously observed and various efforts have been

made to address this problem by a variety of surface treatments [5–11]. However, to the knowledge of the authors, there has been little or no systematic comparison of the build-up of contamination on different surfaces. In previous work [12] the current authors examined the contamination build-up on AISI316L stainless steel test plates that had been strategically positioned within an ESI source. The contamination consisted of both organic and inorganic components, with the morphology and composition depending on the orientation and temperature of the plates. The present study focuses on identifying surface modifications that reduce the build-up of such contamination. Surface modifications that have superior resistance to this type of contamination build-up are first identified and then applied to the sample and extraction cones of a mass spectrometer and their impact on the robustness of the instrument response is investigated.

Three groups of surface modification are studied in this work: (i) electrically conductive ceramic coatings, represented by metal nitrides and metal carbides, deposited by physical vapour deposition (PVD); (ii) electrically conductive amorphous carbon based coatings, represented by doped diamond-like-carbon films, deposited by plasma assisted chemical vapour deposition (PACVD) and (iii) electrochemically generated oxide films formed on the stainless steel substrate, represented by anodically and cathodically modified oxide layers. The coating systems (i) and (ii) are used in tribological applications to suppress adhesive wear and in applications to mitigate corrosion and oxidation. They are electrically conductive, to varying degrees, and because of their anti-stick properties they are used to coat plastic injection and die casting

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moulds, cutting tools, forming tools, medical instruments, and the bearing surfaces of biomedical implants. As such these coating systems have the properties that have the potential to mitigate API-ESI source contamination build-up. The third group (iii) are highly doped (with cation and anion vacancies and cation interstitials) semi-conducting finely porous oxide films, which improve the thermodynamic stability, corrosion resistance and biocompatibility of the surface of stainless steel and, therefore, they too have the potential to prevent the build-up of contamination in the API-ESI source.

In all cases the substrate consisted of AISI316L stainless steel, which is commonly used for instrument components. Blood plasma, which is widely analysed in mass spectrometry and is known to result in significant contamination build-up, was chosen as the exemplar contaminating sample.

2. Experimental

2.1. Sample preparation

Flat test plate samples of dimensions 15×19 mm were cut from AISI316L stainless steel plate (3 mm thick) that had been grit-blasted to a 1200-grade finish. The samples were cleaned by sonication in acetone, then ethanol, and then deionised water. The selected coatings were then applied to the samples. (i) Metal carbide and metal nitride coatings were deposited at Teer Coatings Ltd by closed field unbalanced magnetron sputter ion plating to a thickness of 3–5 μm . In all cases the deposition procedure started with argon ion etching of the sample surface. Argon/reactive gas mixtures, using an industrial closed field unbalanced magnetron sputtering unit with a background vacuum pressure of $<10^{-5}$ mbar and deposition pressure of $2\text{--}4 \times 10^{-3}$ mbar, depending on the reactive gas flow rate, were used to produce the metal carbide and nitride coatings. The substrate temperature, substrate bias voltage and the target-to-substrate distance were prescribed or controlled in order to facilitate the formation of a graded interlayer followed by a monolithic stoichiometric coating. (ii) Plasma-assisted chemical vapour deposition at Diamond Hard Surfaces Ltd was used to deposit 5%Si doped and 20%Si doped tetrahedral amorphous carbon coatings (ta-C:Si5 and ta-C:Si20) and 5%N₂ doped and 25%N₂ doped tetrahedral amorphous carbon coatings (ta-C:N5 and ta-C:N25). In addition, a 5%Cr doped carbon coating consisting of a distinct distribution of nano-crystalline graphite regions within a tetrahedral amorphous carbon matrix (ta-CG:Cr), was similarly deposited, using closed field unbalanced magnetron sputter ion plating at Teer Coatings Ltd. The amorphous carbon films were 3–5 μm thick. The specific coatings selected were selected to represent a range of electrical conductivities, sp^2/sp^3 hybridisation, surface energies and microstructures. The structure of the amorphous carbon coatings examined consisted of a random network of covalently bonded carbon in hybridised tetragonal (sp^3) and trigonal (sp^2) local coordination with less than 1% residual hydrogen. The properties of these films are determined by the ratio of these two hybridisations and doping with nitrogen, silicon and chromium assisted in providing coatings with a range of $sp^3:sp^2$ ratios and thus a range of surface properties [13]. Doping with nitrogen tends to decrease the sp^3 content by generating larger sp^2 clusters. In contrast, doping with silicon generates $\text{C}=\text{C}(\text{Si})\text{C}$ or $\text{C}=\text{CSi}_2$ sites from $\text{C}=\text{CC}_2$, opening up carbon sp^2 rings, preventing sp^2 clustering and increasing the sp^3 content [14–16]. Incorporating chromium atoms at the low concentrations used here ($\sim 5\%$) tends to decrease the sp^3 content, possibly due to the formation of chromium carbide. (iii) Two electrochemically modified oxide layers were produced using pulsed polarisation in sulphuric acid as detailed by Doff et al. [17]. Anodic growth involved the application of a potential in the

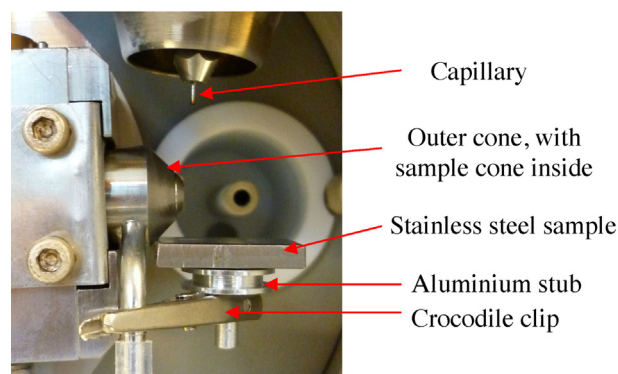


Fig. 1. Photograph of the setup of a flat stainless steel sample placed horizontally in the mass spectrometer.

active region of the potentiodynamic polarisation curve, followed by a potential in the passive region of the curve. In cathodic growth, the dissolution step is achieved by the application of a potential in the transpassive region of the curve.

2.2. Flat plate tests

A Waters Corporation Quattro Micro (a triple quadrupole mass spectrometer incorporating a Z-Spray source) was used to investigate the contamination of flat test plates. The mobile phase of 50:50 acetonitrile (MeCN):deionised water was introduced at a rate of 300 $\mu\text{l}/\text{min}$ from a Waters 515 pump. The blood plasma solution was introduced at a rate of 30 $\mu\text{l}/\text{min}$ from a syringe pump. This method was an accelerated method, based on a standard liquid chromatography-mass spectrometry (LC-MS) setup, and simplified by bypassing the LC system. This enabled the build-up of contamination to be investigated over a much shorter time-scale than would be required with the LC included. All experiments were carried out in ESI+ mode (generating positive ions), with a source temperature of 120 $^{\circ}\text{C}$, a desolvation gas temperature of 450 $^{\circ}\text{C}$ and flow of 800 l/h, a cone voltage of 32 V and a capillary voltage of 3.5 kV.

The uncoated or coated stainless steel samples were placed in the mass spectrometer as shown in Fig. 1, at a distance of 18 mm from the capillary. They were connected to the ion block by a crocodile clip, aluminium stub and conductive carbon tape so that they would be at the same voltage and temperature as the source block. Pooled human blood plasma with lithium heparin anticoagulant was obtained from Innovative Research (US). Before injection into the mass spectrometer, acetonitrile was added to the plasma in a volume ratio of 2:1 to precipitate out proteins, and the resulting supernatant was diluted with water.

2.3. Mass spectrometry

The triple quadrupole detector used in this work has an inlet designed with the capillary carrying the analyte-containing solution positioned orthogonal to the sampling inlet, as shown in Fig. 2. Fine droplets from the edges of the pneumatically generated spray plume enter the sampling inlet, while larger solvent and neutral droplets are directed away [18]. The ions are drawn by the vacuum system and an imposed electric field gradient towards the instrument inlet region consisting of a sample cone and an outer protective cone. Once past this initial inlet section the ions then follow the electric field gradient and pressure gradient towards a skimmer region, which is in the form of an extraction cone, positioned at right-angles to the initial region [19].

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