

Surface Analysis of Corrosion Inhibitor Films by XPS and ToFSIMS

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Abstract. In recent years developments in the capabilities of techniques such as XPS and static SIMS have led to wider application of these methods for the characterisation of industrial materials. After a brief discussion of recent key developments of these techniques, this paper presents a selection of results from research work at our laboratory in the characterisation of organic film-forming corrosion inhibitors on a range of metal substrates which illustrate the nature of the information available. The inherent advantage of *surface* sensitivity and the advantages of a multi-technique approach for the evaluation of surface molecular structure from complex organic compounds is discussed. The additional benefits for analysis offered by the latest developments in technique are also demonstrated.

Key words: SIMS, XPS, surface analysis, corrosion inhibitor.

The latest instrumental developments of XPS and static SIMS enable wider application of these methods for the characterization of industrial materials. In particular, the ability to determine the molecular structures of organic surfaces has been of key importance in the fields of polymer [1, 2] and adhesion [3] science, as well as in biomaterials and pharmaceuticals research [4].

Other industrial technologies have also benefitted from these technique developments. This paper focuses on their impact in the area of corrosion protection where a metallic surface is covered by an organic film. Modern techniques for surface analysis enable full characterization of film chemistry and structure, providing important information for understanding the mechanisms of environment/film/surface interaction.

In addition to the quantified surface composition data, the routine use of monochromatized X-ray sources in XPS has allowed the chemical state of surfaces to be probed in greater detail. In our laboratory this aspect has been particularly useful for the surface analysis of organic compounds, where accurate measurement of the chemical states of carbon is required to determine functionality. Angle-dependent XPS analysis [5] is also of great value, specifically in the characterization of thin films where segregation/diffusion effects, bonding arrangements and film thickness can be studied.

Using the latest XPS instrumentation, spatially resolved information is also now accessible to reasonably high ($< 5 \mu\text{m}$) spatial resolution [7]. Imaging XPS has the advantage of producing chemical maps which are quantitatively meaningful, and, in general, can produce better quality images than scanning SIMS or Auger from surfaces with no or variable conductivity.

In recent years the full benefits of time-of-flight (ToF) mass spectrometry for static SIMS analysis have begun to be realized [8]. Better sensitivity and an increased mass range at much lower primary beam dose have capitalized on the molecular structure sensitivity of this technique, one of its major strengths alongside the other methods of surface analysis. Furthermore, the introduction of the latest generation of ToFSIMS instruments provides still greater sensitivity and very high mass-resolution sufficient to allow accurate mass measurement of complex molecular secondary ions, thereby substantially improving the accuracy of interpretation and enabling much of the full benefit of conventional mass spectrometry to be realised for surface analysis.

Film-Forming Organic Corrosion Inhibitors

Most corrosion inhibitors are complex mixtures of organic and inorganic compounds designed to adsorb strongly to metal surfaces in order to protect them from environmental attack. Each additive of an inhibitor blend can have a specific role for corrosion protection and the formulation of a blend is assembled for the surface to be protected and the environment in which it needs to act. Therefore, the selection and optimization of the correct inhibitor formulation for the task at hand is an essential stage of plant protection. Similarly, research continues into novel surfactant molecule design for inhibitor formulations. The introduction of more stringent environmental legislation world-wide controlling the use of typical performance chemicals has further stimulated research into the synthesis of new types of inhibitor molecules.

Whilst the composition of different blends can be determined by instrumental analytical chemistry (e.g. GC-MS [9]) and blend performance can be assessed by age-testing using suitable corrosion test rigs, few techniques are available for probing the protected *surface* directly.

In recent years, however, we have shown in this laboratory that, with careful sample preparation, a combination of ToFSIMS and XPS can be used to characterize thin films of organic compounds from commercial grades of surfactants [10], lubricants [11] and inhibitors [12]. As well as being able to provide full chemical analysis of these molecules (and mixtures), this approach has the inherent advantage of *surface* sensitivity, in that only the surface active components of a blend are analysed, since only they reside on the surface. It is thought that it is these components which often control the corrosion protection.

In this paper three types of organic film forming inhibitor are discussed: (i) complex amine-based formulations, for the protection of pipeline steel surfaces used in the oil and gas industry (ii)azole-type molecules, for protection of copper surfaces taken from water recirculators and (iii) results from the ToFSIMS analysis of an imidazoline inhibitor, which also illustrate the capability of high mass resolution analysis.

Experimental

For the amine inhibitor analysis, all XPS experiments were performed using the Fisons (VG) (SSI) M-Probe XPS instrument. Initial experiments at the standard (35°) take-off angle (TOA) were performed using 200 W monochromatized Al $K\alpha$ incident radiation focused into an elliptical spot size of $400 \times 1000 \mu\text{m}$. Survey scan analysis and high resolution analysis of C 1s, O 1s and N 1s regions were recorded. Subsequent angle-dependent experiments were recorded from a separate area of the sample surface and performed at photoelectron take-off angles (TOA) of 90° , 35° and 15° to the sample surface (otherwise using the same analysis conditions). The same experimental parameters were also used, apart from an increase in scan times at low take-off angles in order to compensate for the loss in total signal. All spectra are referenced to the C 1s peak at 285.0 eV binding energy.

Composition tables were derived for each surface by peak-area measurement, followed by the use of Scofield sensitivity factors. High-resolution data were subject to linear background subtraction prior to peak synthesis using the instrument software.

For both the amine and BTA experiments, time-of-flight SIMS spectra were acquired using a VG IX23S instrument based on the Poschenrieder design and equipped with a pulsed liquid metal ion source [13]. A 30 keV Ga^+ primary ion beam was used at an incident angle of 38° to the surface normal. The secondary ions were accelerated to 5 keV for the analysis by applying a sample bias. For each sample, both positive and negative secondary ion spectra were collected using a total primary ion dose that did not exceed 2×10^{11} ions cm^{-2} . Such a dose lies well below the damage threshold of 1×10^{13} ions cm^{-2} for static SIMS [14], such that the analysed surfaces were effectively undamaged as a result of the ToFSIMS studies. A DEC PDP 11 computer system was used for spectral acquisition, storage and processing.

ToFSIMS analysis of oleic imidazoline was carried out using a Phi Perkin Elmer model 7000 ToFSIMS instrument fitted with a high mass resolution reflection mass spectrometer and pulsed caesium ion source. The inhibitor was analysed, cast as a thin film on aluminium foil, using an 8-keV pulsed caesium ion beam and an ion dose well below the static regime, so no charge compensation was required. Both ToFSIMS instruments and the XPS instrument operated with a base pressure of less than 10^{-9} mbar.

Results

Amine Inhibitors on Iron Foil

A typical oil-or gas-field pipeline inhibitor blend could contain a variety of inorganic anions, such as phosphates, chlorides, nitrates, and substituted amines, or other organic surfactants, to assist in the generation of a protective layer. In the ideal case, the blend will rapidly form a thin, permanent and effective barrier layer on the metal surface. The layer will resist liquid and gaseous chemical attack over a wide pH range, be self-healing following abrasion, and blend components will be cheap, readily available and environmentally acceptable. In this work the surface activity of a typical commercial blend of oil-field corrosion inhibitor (or previously unknown composition) has been studied using a simple static immersion test/rinsing procedure for surface preparation [12].

Figure 1 shows the XPS survey scan and Table 1 the corresponding surface composition for a filmed iron coupon. The surface is seen to be largely carbonaceous. It is significant that no iron signal is detected in this spectrum indicating that a thick ($> 3 \text{ nm}$) film is formed. This is not always the case and similar experiments from other inhibitors show much thinner or patchy uptake of inhibitor. Even at low

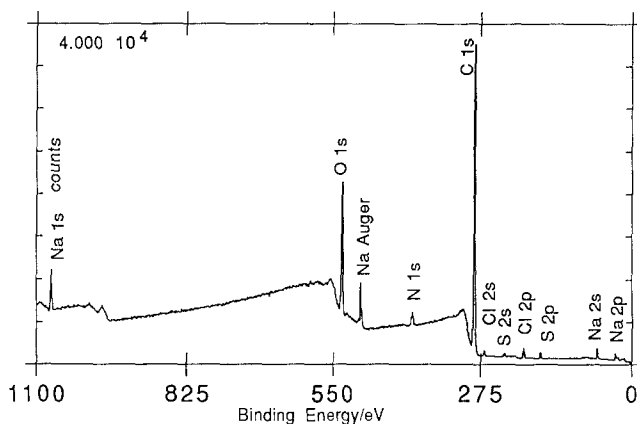


Fig. 1. XPS survey scan for amine inhibitors on iron foil

Table 1. XPS survey scan composition of iron immersed in amine inhibitor

Peak	Composition (atom %)	Approx. binding energy (eV)	Assignment
S 2p	0.4	169	SO ₄ ²⁻
C 12p	0.4	199	Cl ⁻
C 1s	85.5	285	see text
N 1s	1.0	400	see text
O 1s	10.0	534	see text
Fe 2p _{3/2}	0.0	712	-
Na 1s	2.6	1073	Na ⁺

energy resolution, it is possible to identify the most likely chemical states of other anionic and cationic species. High resolution XPS analysis of selected elements identifies carbon bonded to quaternary and tertiary amines as well as hydrocarbon. These nitrogen species were confirmed in the high resolution nitrogen spectrum, where tertiary and quaternary nitrogens are clearly resolved as different peaks (see below and Fig. 3).

ToFSIMS analysis of this coupon provides further information on the adsorbed molecules. Figure 2 shows the positive ion spectrum and molecular ions at 318 and 346 amu corresponding to the quaternary amine structures shown and indicating that there is a mixture of quaternary amines present. The complementary nature of ToFSIMS and XPS information is well illustrated in this case, where XPS identifies and quantifies coverage and the organic functionality/chemical state of solution components and ToFSIMS determines the molecular structure of each component. Although SIMS techniques are not directly quantitative, by monitoring the relative peak heights ToFSIMS can identify the relevant adsorption or surfactant efficiencies for such molecules [10].

Thus in this spectrum, similar molecular ion peak heights imply that the surface concentrations of each chain length of amine are similar. That iron is not detected in the ToFSIMS spectrum indicates post-monolayer thickness (and uniform coverage) of inhibitor. That iron is not detected in the XPS spectrum indicates a film thickness

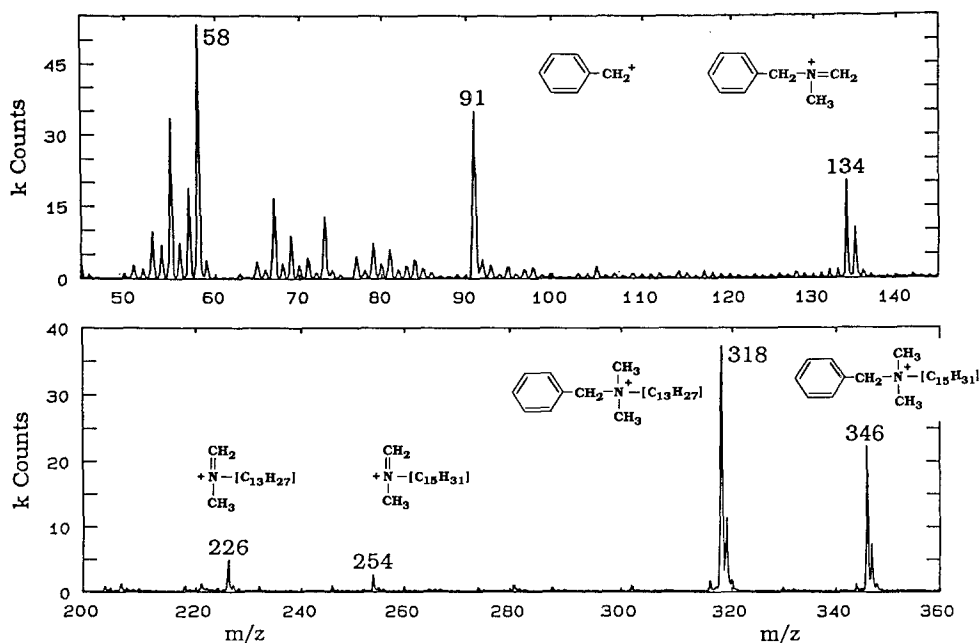


Fig. 2. ToFSIMS spectrum for amine inhibitors on iron foil

greater than 2–3 nm. Thus it can be concluded in this case that precipitation of an iron amine complex of iron containing salt is not a likely mechanism of film formation.

The film composition was probed further for this sample using angle-dependent XPS. Figure 3 shows the high resolution nitrogen spectrum acquired at electron take-off angles of 15, 35 and 90° corresponding to progressively deeper analysis depths. This analysis reveals that, for both inhibitors, the quaternary ammonium and tertiary amine molecules segregate at the iron surface with quaternary species preferentially adsorbed. It is noteworthy that in the survey scan analysis iron was not detected even at the maximum sampling depth (~ 10 nm).

No evidence of chemical bonding between inhibitor and metal is identified in the chemical shifting of iron or nitrogen peaks in XPS or in appearance of iron-amine molecular ions in the ToFSIMS spectra and no evidence of inter-molecular association of inhibitor molecules is found. An ionic adsorption mechanism involving organized association of quaternary ammonium molecules to the iron surface is proposed.

Azole-Type Inhibitors on Copper

As well as analysis of model filmed metal coupons, in this work samples of copper tubing were taken for surface analysis directly from a corrosion-testing loop. The test loop was used for modelling oxygen-free high-conductivity (OFHC) recirculating water cooling systems from power generating turbines. Corrosion testing has shown that a chemically modified benzotriazole (BTA) molecule; C₆-BTA (5-hexyl-1,2,3-benzotriazole) offers greater resilience to corrosion than unsubstituted BTA [15].

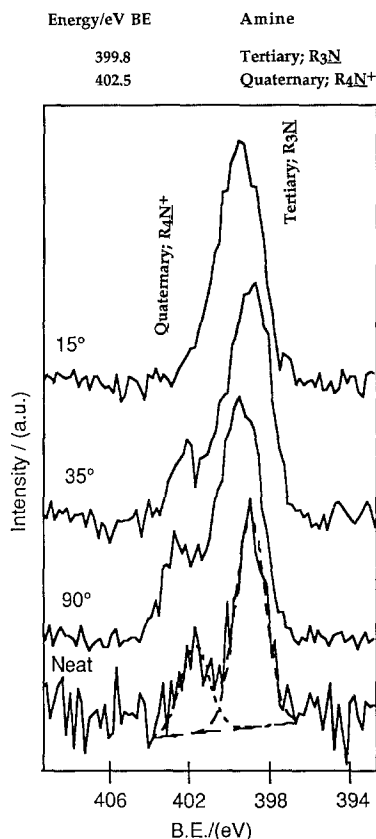


Fig. 3. XPS spectra for amine inhibitors on iron foil at take-off angles of 15, 35 and 90°

XPS and depth-profiling XPS [15] have shown the presence of a thin film of C₆-BTA on the copper surfaces and identified the presence of copper in its first oxidation state at the inhibitor/metal interface. In addition, for a series of increasing filming times, XPS spectra show evidence of incremental film thickness for the organic coating [16].

ToFSIMS analysis of a filmed reference coupon, prepared by simple immersion, confirms some interpretations of the XPS data and shows direct evidence of chemical bonding of inhibitor to copper in the presence of CuC₆-BTA molecular ions (Fig. 4). In addition, networking of C₆-BTA molecules across the copper surface is revealed at higher masses where Cu_n(C₆-BTA)_m quasi-polymeric ions are detected. Secondary ions incorporating copper oxide are also detected.

These characteristics were then examined as a function of filming time for a fixed concentration of inhibitor. Table 2 shows the relative ion intensities for CuC₆-BTA molecular ions as a function of metal exposure time, where it can be seen that longer filming times are characterized by enhanced relative ion yield of higher mass polymer complex fragments.

This finding is in agreement with the XPS analysis of corresponding samples and shows how ToFSIMS can be used to investigate the integrity and growth characteristics of such films. Also, in this work, molecular ion imaging using ToFSIMS has been used to map the distribution of the inhibitor film about the copper surface from corrosion loop samples. Mapping of the CuC₆-BTA molecular ion has been

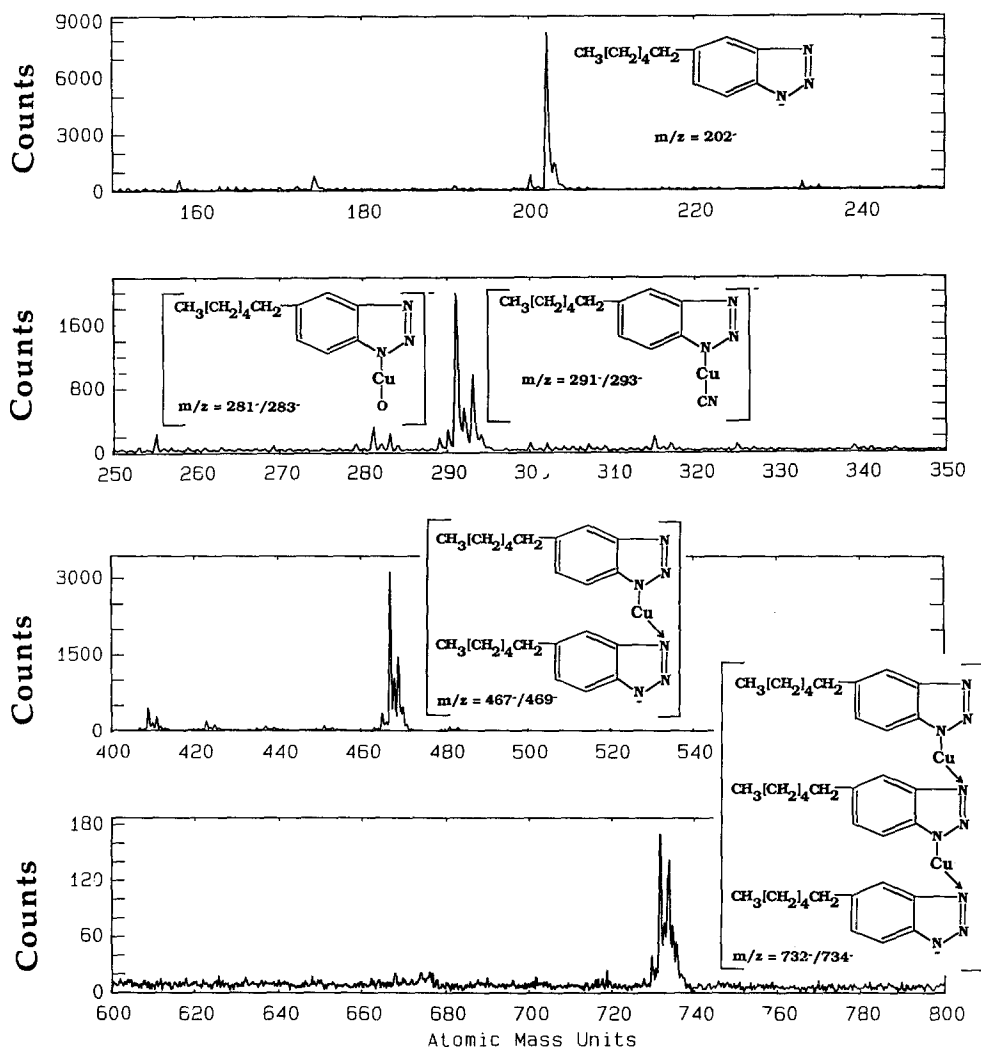


Fig. 4. ToFSIMS spectrum for azole-type inhibitor on copper

achieved under static SIMS conditions. The results show that, in the recirculating loop, inhibitor desorbs from the surface leaving 50–100 μm patches of inhibitor on the surface in certain areas.

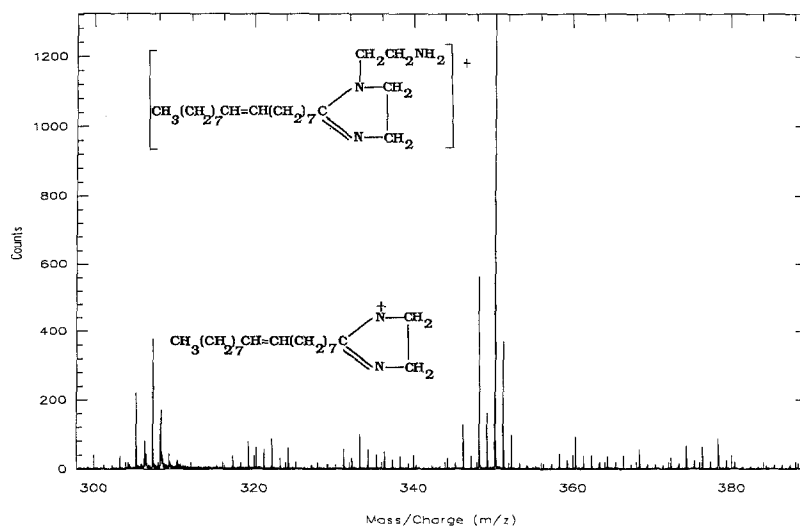
These results show direct evidence of the bonding of inhibitor to copper at the surface of the metal and inter-molecular networking to form an inhibitor film, however it is not possible to determine if the film is a precipitated Cu-salt layer or entirely an inhibitor-surface interaction. The film thicknesses measured in XPS analysis and solution desorption characteristics suggest the latter.

Oleic Imidazoline – High Mass Resolution ToFSIMS

Oleic imidazoline is another commonly used surfactant additive of inhibitor formulations for oilfield applications. Physical parameters such as adsorption efficiency

Table 2. Average relative intensities (peak areas) of secondary ion signals for copper-C₆BTA films

<i>m/z</i>	Ion structure	<i>T</i> = 30 s	<i>T</i> = 1 min	<i>T</i> = 15 mins
202 ⁻	[C ₆ BTA] ⁻	100	100	100
282 ⁻	[(C ₆ BTA) ⁻⁶³ Cu-OH] ⁻	17	20	13
291 ⁻	[(C ₆ BTA)- ⁶³ Cu-CN] ⁻	25	27	30
467 ⁻	[(C ₆ BTA)- ⁶³ Cu-(C ₆ BTA)] ⁻	17	16	40
556 ⁻	[(C ₆ BTA) ₂ ⁶³ Cu ₂ -CN] ⁻	7	7	14
732 ⁻	[(C ₆ BTA) ₃ ⁶³ Cu ₂] ⁻	7	2	19

**Fig. 5.** ToFSIMS spectrum for oleic imidazoline film on aluminium foil

and corrosion rate have recently been investigated for a series of substituted imidazolines [17]. In parallel, however, it is important to probe the surface chemical reaction of such molecules in order more fully to understand the mechanism of inhibitor/surface interaction for input molecular design. This approach has been the basis of much research work in our laboratory [18].

As demonstrated above, ToFSIMS is one of the most useful methods for this type of applied surface analysis. The high mass-resolution and improved sensitivity of the latest generation ToFSIMS instrumentation extends the applicability of ToFSIMS for such studies.

Figure 5 shows part of the positive secondary ion mass spectrum of neat oleic imidazoline cast as a thin film onto aluminium foil. This mass region contains both the molecular ion and an important fragment ion corresponding to the loss of the nitrogen-bonded pendant group. Assignment of the molecular ion (or any other secondary ion) can now be confirmed using accurate mass measurement, to the third decimal place of mass (Fig. 6a), followed by an accurate mass permutation calculation which identifies the empirical formula as C₂₂H₄₄N₃ to a precision of better than 25 ppm.

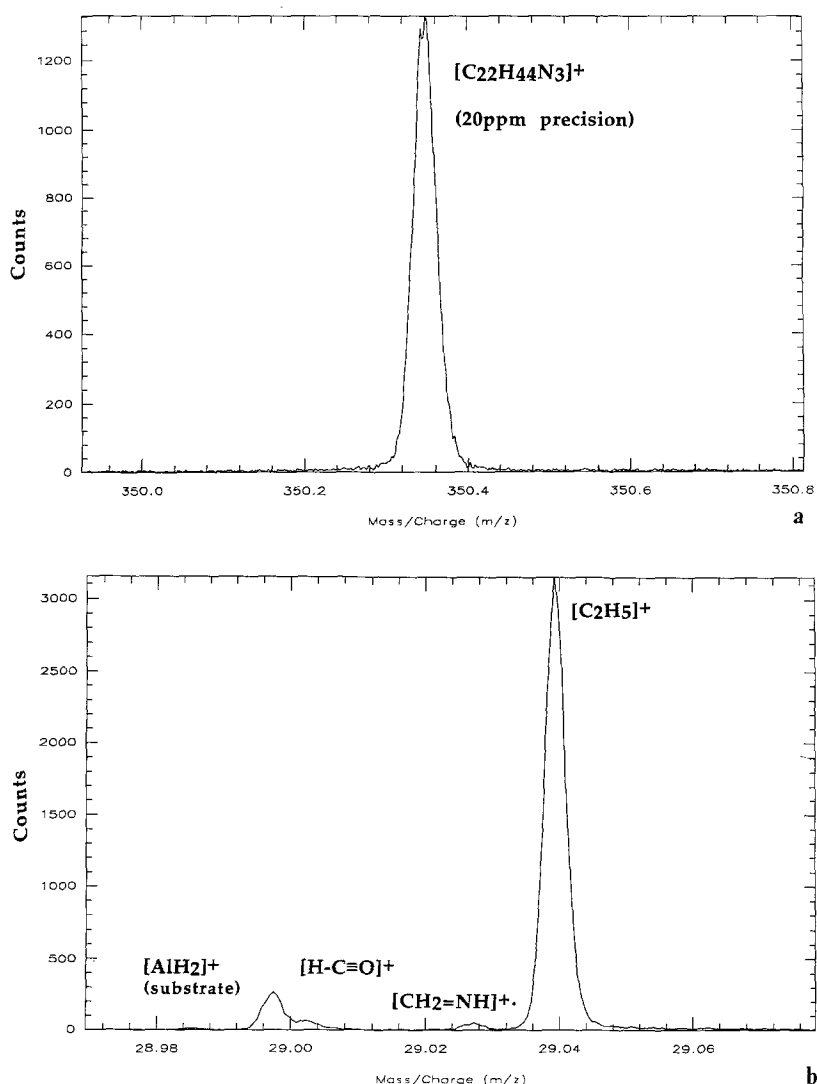


Fig. 6. High-resolution ToFSIMS spectrum for oleic imidazoline film on aluminium foil in **a** high and **b** low mass regions

In addition to this improvement in the resolution of analysis, there is also a substantial gain in sensitivity. This is as a direct consequence of the high mass-resolution, since lower intensity ions which would otherwise be lost in peak overlap with other ions from major surface components are now resolved. This is illustrated in Fig. 6b, where low-mass peaks from the inhibitor molecule are resolved out from an aluminium ion occurring at the same nominal mass and indicating incomplete coverage of the aluminium foil substrate by inhibitor.

Such an enhanced resolution and absolute sensitivity combined with a greater sensitivity at high mass and extended mass range are likely to render this technique especially useful for the characterization of complex natural product derivatives which are currently being considered as more environmentally acceptable corrosion inhibitors.

Conclusions

In reviewing some recent results from a range of inhibitor types, this paper shows how surface analysis techniques can provide important information on the chemical activity and mechanisms of adsorption or organic film-forming corrosion inhibitors. This has been shown for quite different types of inhibitor molecules in industrial formulations as well as for neat compounds and for both the model/coupon samples as well as samples taken directly from recirculating loop apparatus. The compatibility of information content for XPS and ToFSIMS techniques has been described and the benefits of high mass resolution ToFSIMS analysis illustrated.

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