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Chemical state analysis of metal and oxide surface layers using Auger parameters from X-ray photoelectron spectroscopy

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Comparison of the relative kinetic energies of photoelectron and Auger peaks from the same element in XPS, the Auger parameter, provides unique chemical information on the top 10 nm of the surface. The Auger parameter is related directly to the extra atomic relaxation and polarization energies of the element, as presented in a chemical state plot. Previous Auger parameter studies (Wagner 1975; West & Castle 1982) have assumed a homogeneous concentration and chemical state for each element; however, in many surface analysis applications the distributions are not perfectly uniform and conventional Auger parameter analysis is not suitable.

A new method of using the Auger parameter was outlined which can be used to characterize the chemical states of ultra thin films, where bulk Auger parameter values are inaccurate. Two interactions are involved in the relaxation energy of a thin metal film as it develops.

Firstly, non-localized extra atomic screening from ligand neighbours of the substrate can be estimated by an electrostatic model (Moretti 1990). Secondly, the charge transfer from neighbouring metal film atoms during the photoelectron process influences the Auger parameter. As metallic films develop, Auger parameter values will be dominated by the substrate contribution, but gradually the neighbouring film atoms increase their influence until they are dominant in films three or more monolayers thick. A converse model has been used for multilayered oxides on metallic alloy substrates. In this case the core hole screening by conduction band electrons decreases as the oxide overlayer develops and ligand polarization begins to dominate.

The model has been applied to catalyst structures including ruthenium deposited onto alumina substrates (Aas *et al.* 1990), to gain a further understanding of their electronic distribution. Secondly, inhomogeneous oxide layers on brass surfaces, which control the alloys' optical properties, can be analysed in terms of total atom : electron ratios. In both applications where the conventional Auger parameter theory is unsuitable, new information on the surface chemistry has resulted.

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Simple urinary acylcarnitine profiling by gas chromatography mass spectrometry

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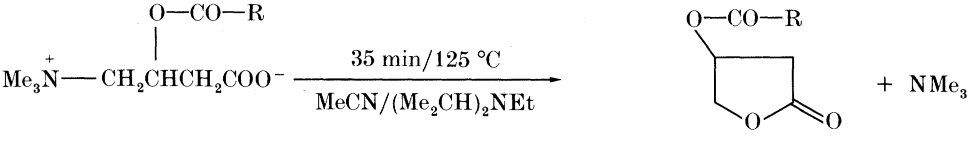
In many cases of sudden infant death, victims have been shown to be deficient in medium-chain acyl-CoA dehydrogenase (MCAD), a key enzyme for β-oxidation of fatty acids. This disease, and several other inborn errors of metabolism leading to organic aciduria, are characterized by concentrations of certain acylcarnitines **1** in urine of the order of 1 μmol ml^{-1}. Normal levels of acylcarnitines are of the order of 1 nmol ml^{-1}. An affordable, routine analytical procedure for traces of urinary acylcarnitines would facilitate diagnosis of acidurias and acidemias. Acylcarnitines are essential to β-oxidation because they carry the fatty acyl units (RCO-) across the mitochondrial membrane. Carnitine detoxifies mitochondria of excesses of acyl groups by carrying them, as acylcarnitines, into urine. Thus profiling of urinary acylcarnitines would also allow the biochemistry of some currently ill-defined diseases, and the metabolic routes of acidic drugs, to be elucidated.

Several methods exist for detecting urinary acylcarnitines but none is ideal for the clinical laboratory (Lowes & Rose 1989). We are developing a simple method based on gas chromatography mass spectrometry (GCMS), following an ion-exchange work-up and a very simple derivatization to volatile lactones **2** (Lowes & Rose 1990):



1 **2**

For example, a standard aqueous mixture of 12 acylcarnitines from R = CH_3 to R = $C_{15}H_{31}$ at the level of 1 nmol ml^{-1} can be easily examined by temperature-programmed GCMS (BP-5 column) following the cyclization shown. All 12 components were resolved, including isomers (e.g. octanoyl, R = $CH_3(CH_2)_6$, and valproyl, R = $(CH_3CH_2CH_2)_2CH$). Diagnostic mass spectra were obtained in electron ionization and ammonia chemical ionization modes.

The detection limits for individual acylcarnitines in the complex matrix of urine are of the order of 1 nmol ml^{-1} but dependent on the chemical background. Many