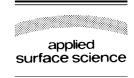


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## Total internal reflection ellipsometry and SPR detection of low molecular weight environmental toxins

A.V. Nabok<sup>a,\*</sup>, A. Tsargorodskaya<sup>a</sup>, A.K. Hassan<sup>a</sup>, N.F. Starodub<sup>b</sup>

<sup>a</sup>Sheffield Hallam University, Materials and Engineering Research Institute, City Campus, Pond Street, Sheffield S11WB, UK <sup>b</sup>Paladin Institute of Biochemistry, National Academy of Sciences of the Ukraine, 9 Leontovicha Street, 01030 Kiev, Ukraine

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### Abstract

The environmental toxins, such as herbicides simazine and atrazine, and T2 mycotoxin were registered with the optical methods of surface plasmon resonance (SPR) and recently developed total internal reflection ellipsometry (TIRE). The immune assay approach was exploited for in situ registration of the above low molecular weight toxins with specific antibodies immobilised onto the gold surface via (poly)allylamine hydrochloride layer using electrostatic self-assembly (ESA) technique. The comparison of two methods of SPR and TIRE shows a higher sensitivity of the latter. © 2004 Elsevier B.V. All rights reserved.

Keywords: Total internal reflection ellipsometry; SPR; Atrazine; Simazine; Mycotoxin; Immune assay

### 1. Introduction

The main goal of this work is to develop an experimental procedure for the registration of environmental toxins, particularly mycotoxin T2, which is regarded as an extremely hazardous compound and, therefore, potential bio-warfare agent [1]. Because of high toxicity of T2, it was first decided to develop an analysis routine using much less toxic analogues, such as commercial herbicides simazine and atrazine.

\* Corresponding author. Tel.: +44 114 2253 512; fax: +44 114 2252 433.

These two compounds are common weed killers, regarded to be lightly to moderately toxic [2]. However, according to recent changes in the European environmental legislation, the concentration of these compounds in drinking water should be kept within ppb range. The registration of both simazine and atrazine has therefore fell into the area of interests of environmental agencies and water industry.

A traditional immune assay approach, which is based upon specific binding of the above toxins to respective antibodies, was chosen for the toxins' registration in conjunction with the optical technique of surface plasmon resonance (SPR). The method of SPR is very common for the immune analysis [3,4], since the

E-mail address: a.nabok@shu.ac.uk (A.V. Nabok).

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specific binding of relatively large immune components (antibodies or antigens) causes noticeable shift of the plasmon resonance. However, this optical technique is struggling with the registration of low molecular weight (in the range of several hundred atomic units) compounds. A recently developed method of total internal reflection ellipsometry (TIRE) [5–8] offers much higher sensitivity, which may be sufficient for the registration of relatively small molecules of simazine, atrazine and T2 mycotoxin having molecular weight of 201.7, 215.7 and 466.6, respectively.

This work represents a successful attempt of the registration of simazine and atrazine using both SPR and TIRE methods. Later, the established measurements' routine has been extended towards the registration of T2 mycotoxin. The results obtained by SPR and TIRE were compared throughout proving a higher sensitivity of the latter.

### 2. Experimental methods

A Kretchmann type [9] SPR experimental setup, made in-house and described earlier in ref. [10], was exploited in the current study. In this method, a ppolarised HeNe laser beam made incident through a semi-cylindrical prism onto the gold coated glass slide attached to the back of the prism. At the angles of incidence higher than the critical angle, the light is totally reflected back into the prism. At a specific angle of incidence the x-component of k-vector of the evanescent field matches the wave vector of the plasmon oscillations at the metal/dielectric interface, the energy will be transferred to the surface plasmons. The observed minimum in the dependence of the measured reflectivity on the angle of incidence is, therefore, called surface plasmon resonance (SPR). The optical parameters, i.e., thickness (d), refractive index (n) and extinction coefficient (k), of the reflecting system, e.g., a gold film with the adsorbed layers on top, can be evaluated by fitting the SPR curve to Fresnel formulae using the least-square technique [11]. The method of SPR is very sensitive to molecular adsorption, however the simultaneous evaluation of n and d of thin transparent (k = 0) films is theoretically impossible [12].

The method of ellipsometry, particularly spectroscopic ellipsometry, is a very sensitive, non-destructive experimental technique of thin film characterisation. The method is based upon the registration of changes in the polarisation of light on reflection from the investigated surface [13]. The obtained two ellipsometric angles of  $\Psi$  and  $\Delta$  represent, respectively, the amplitude ratio and the phase shift of p- and s-components of polarised light, according to the ellipsometry equation [13]:

$$\rho = \frac{R_{\rm p}}{R_{\rm s}} = \tan\left(\Psi\right) \exp\left(\mathrm{i}\Delta\right)$$

where  $R_p$  and  $R_s$  are Fresnel coefficients for 'p' (in the plane of incidence) and 's' (in the plane of the substrate) components of polarised light, respectively. In the spectroscopic ellipsometry, the complete set of parameters d,  $n(\lambda)$  and  $k(\lambda)$  for every layer of the multi-layered reflecting system can be obtained by fitting the experimental spectra  $\Psi(\lambda)$  and  $\Delta(\lambda)$  to a particular model.

In this respect, the spectroscopic ellipsometry is a much more advanced technique as compared to SPR. However, ellipsometry is not as popular as SRP in sensing applications. The main disadvantage of the ellipsometry, apart from the high cost of equipment, is that the laser beam travels through the investigated medium. Changes in the refractive index of the medium, caused by injection of different solutions (gases) into the cell, may interfere with changes in the film optical parameters, which makes this technique unsuitable for in situ measurements.

The recently proposed method of total internal reflection ellipsometry [5–8] (also called plasmon enhanced ellipsometry [5,6]) combines the advantages of the spectroscopic ellipsometry and the Kretchmann type SPR geometry of total internal reflection.

The TIRE experimental setup, shown schematically in Fig. 1, was built on the base of a commercial M2000, J.A. Woollam Co., spectroscopic rotating analyzer instrument, operating in the 370–1000 nm wavelength range. The measurements were performed in-situ in a specially designed 1.5 cm<sup>3</sup> cell attached to the bottom of a 68° trapezoidal glass prism (BK7, n = 1.515) with the gold-coated glass slide attached to it via index matching fluid. The cell has inlet and outlet tubes allowing the injection of different aqueous solutions (n = 1.33) into the cell. The cell was sealed against the sample through a rubber O-ring.

Dedicated WVASE32<sup>®</sup> software (J.A. Woollam) [14] was used for TIRE data fitting. Download English Version:

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