



Depth profiling using XPS
by Stephen Michael Hunt

A thesis submitted in partial fulfillment Of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

Angle resolved X-ray photoelectron spectroscopy (ARXPS) is now one of the most widely used surface analysis techniques in research because it supplies an abundance of surface, chemical and electronic information. A major limitation of conventional XPS is that sample concentrations are calculated based on the assumption that the elemental concentrations are homogeneous in the outer 100 Å; an assumption that is frequently inaccurate. By exploiting the angular dependence of the XPS sampling depth, it is easy to get a qualitative assessment of surface uniformity. The objective of this work has been to explore the limits to which ARXPS data can be used for quantitative estimation of the depth profile.

Calculating depth/concentration profiles for ARXPS data is a mathematically unstable problem. This means that relatively small errors in the data can propagate into rather large errors in the calculated profiles. It can therefore be inferred that the method used to obtain the approximation greatly influences the error in calculated profiles.

This study has investigated two algorithms that can be used to calculate depth profiles from ARXPS data: Tyler Regularization and Singular Value Decomposition.

The influences of random error and surface roughness have been investigated.

Simulations have been used to quantify how different types of error propagate through the calculations. Optimum parameters for ARXPS experiments and the calculations have been identified. The results have been validated on a series of samples consisting of self-assembled monolayers.

Random error studies suggest that the calculated depth profiles are only semi-quantitative. The accuracy and resolution of the calculated profiles is strongly influenced by the selection of smoothing parameters. Optimum smoothing parameters for different error levels in the measured data have been recommended. Improved accuracy was observed when the number of angles used in the calculations was increased from three to five but no improvement was observed by further increasing the number of angles to 10. Simulations also indicate that surface roughness has a minimal effect except at glancing angles. Based on the calculations, it is recommended that measurements be taken at 10°, 20°, 40°, 50°, and 70°.

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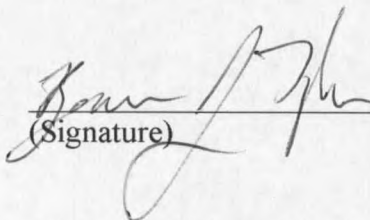
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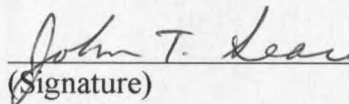
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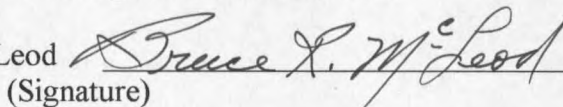
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This work is dedicated to my wife Dana. If not for her untiring love, patience, and support, this work would not be possible.

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ABSTRACT

Angle resolved X-ray photoelectron spectroscopy (ARXPS) is now one of the most widely used surface analysis techniques in research because it supplies an abundance of surface, chemical and electronic information. A major limitation of conventional XPS is that sample concentrations are calculated based on the assumption that the elemental concentrations are homogeneous in the outer 100 Å, an assumption that is frequently inaccurate. By exploiting the angular dependence of the XPS sampling depth, it is easy to get a qualitative assessment of surface uniformity. The objective of this work has been to explore the limits to which ARXPS data can be used for quantitative estimation of the depth profile.

Calculating depth/concentration profiles for ARXPS data is a mathematically unstable problem. This means that relatively small errors in the data can propagate into rather large errors in the calculated profiles. It can therefore be inferred that the method used to obtain the approximation greatly influences the error in calculated profiles.

This study has investigated two algorithms that can be used to calculate depth profiles from ARXPS data: Tyler Regularization and Singular Value Decomposition. The influences of random error and surface roughness have been investigated. Simulations have been used to quantify how different types of error propagate through the calculations. Optimum parameters for ARXPS experiments and the calculations have been identified. The results have been validated on a series of samples consisting of self-assembled monolayers.

Random error studies suggest that the calculated depth profiles are only semi-quantitative. The accuracy and resolution of the calculated profiles is strongly influenced by the selection of smoothing parameters. Optimum smoothing parameters for different error levels in the measured data have been recommended. Improved accuracy was observed when the number of angles used in the calculations was increased from three to five but no improvement was observed by further increasing the number of angles to 10. Simulations also indicate that surface roughness has a minimal effect except at glancing angles. Based on the calculations, it is recommended that measurements be taken at 10°, 20°, 40°, 50°, and 70°.

CHAPTER 1

INTRODUCTION

Conventional X-ray photoelectron spectroscopy (XPS) provides identification of all elements (except H and He) present in outermost 100Å in concentrations greater than 0.1 atomic percent. A major limitation in this technique is that sample concentrations are calculated as a weighed average of concentrations, which implies the elemental concentrations are homogeneous in this region [1]. By exploiting the angular dependence of sampling depth as illustrated in Figure 1, it is possible to get a qualitative assessment of surface uniformity. This is the basis of angle resolved X-ray photoelectron spectroscopy (ARXPS). ARXPS is now one of the most widely used surface analysis techniques in research because it supplies an abundance of surface, chemical and electronic information [2, 3].

Obtaining a quantitative assessment of the depth/concentration profile poses formidable mathematical difficulties. The depth/concentration profile in the upper approximately 100Å has important implications in the study of adhesion, catalysis, composite materials, corrosion, microelectronics, and self-assembling monolayers. In many instances, other surface sensitive techniques cannot be used either because of the destructive nature of the technique or the inability of the technique to provide adequate

depth resolution. Therefore, particular attention has been paid to ARXPS as a tool for obtaining quantitative estimates of concentration profiles in the near surface region.

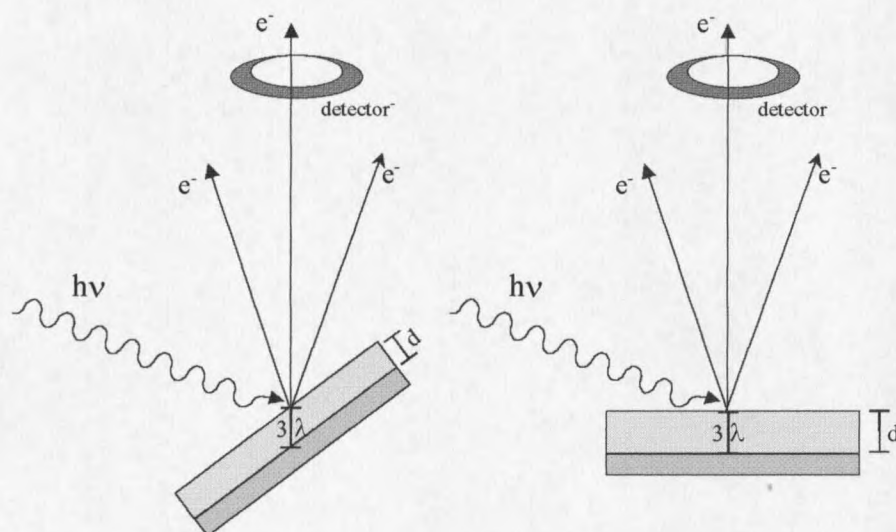


Figure 1. Cartoon Illustrating the Angle Dependence on Sampling Depth

Problems in this Area

Calculating depth/concentration profiles for ARXPS data is a mathematically unstable problem. This can be translated to mean that relatively small errors in the data can propagate into rather large errors in the calculated profiles. Therefore, specialized numerical methods have been developed to approximate the profiles. In general, the method must augment the ARXPS data generated with some prior knowledge of the nature of the solution [4]. This prior knowledge is then used in some manner to restore lost data. However, as one attempts to be more rigorous in the approximation of the

profile, the more the mathematical instability interferes with the solution [5]. It can therefore be inferred that the method used to obtain the approximation greatly influences the error in calculated profiles.

The expression for the intensity of the photoelectron flux as a function of take off angle, from any orbital of an element, has been reduced to a Laplace transform with certain assumptions to produce depth profiles [6-8]. Bussing and Holloway have shown that a unique solution to the inverse Laplace transform is unattainable and suggested that any solution is a selection from a class of equivalent solutions [6-8]. The inverse Laplace transform also takes the form of a class of ill-posed problems commonly referred to as Fredholm Integral of the first kind [5]. Solutions to Fredholm Integrals of the first kind typically employ methods derived from inverse theory. As might be expected, the solution to this expression has been approached with a multitude of methods.

Motivation for Research

The typical x-ray source used in XPS irradiates approximately an $800\mu\text{m} \times 800\mu\text{m}$ spot on the sample surface [3]. As might be expected surface roughness can greatly influence the signal generated by varying the angle between the x-ray source and sample. This affects the effective sampling depth (Figure 1) and introduces systematic error into the data collected. Hence, ARXPS is generally not regarded as useful tool for generating concentration profiles on rough samples.

Secondly, by changing the take-off angle, angle between the source and surface normal, the effective sampling depth is altered (Figure 1). Displayed in Figure 1, this

technique generates a significantly more intense signal from the atoms closest to the surface. The sampling depth is proportional to the mean free path of an escaping electron and the cosine of the angle between the analyzer input axis and sample surface normal. A large angle restricts analysis to the uppermost layers, while small angles ($\approx 0^\circ$ - 10°) can give information from 12-15 atomic layers down.

It is important to understand that by changing the take-off angle you are not viewing different slices of the sample. Therefore, experiments conducted at various take-off angles are only suggestive of a concentration profile. The concern here is how this affects the resolution of deeper features in the approximated concentration profile.

Obviously, surface roughness and signal intensity is a result of the sample and technique used in analysis; not the method used to approximate the profile. However, the method used to calculate the profiles and their associated parameters greatly influences how these problems filter through to the approximated concentration profile.

Research Objectives

- To understand uniform error propagation when calculating concentration depth profiles from angle resolved x-ray photoelectron spectra using the following algorithms: Tyler Regularization and Singular Value Decomposition. Particularly as it related to accuracy of the overlayer thickness, overlayer composition, gradient of the interface, and substrate composition.
- To determine the effect of surface roughness on measured signal intensities and calculated profiles.
- To determine optimal experimental and algorithmic parameters for the Tyler Regularization Algorithm and Singular Value Decomposition Algorithm.

- Verify findings by collecting XPS data on self-assembling monolayers (SAMs).

CHAPTER 2

BACKGROUND

Conventional X-ray Photoelectron Spectroscopy

Conventional X-ray Photoelectron Spectroscopy is an information-rich technique (Table 1). However, it is important to understand that the level of sophistication used in interpretation of the data determines the detail of the chemistry, organization and morphology that can then be analyzed. This versatility makes it the most widely used surface characterization technique in research [2].

Theory and Principle

A fundamental understanding of the photoelectric effect and the photoemission process is indispensable to the understanding of XPS. When a surface is irradiated by a photon one of three things can happen: 1) the photon can pass through, 2) the photon can interact with an atomic orbital electron yielding partial energy loss, or 3) the photon can interact with an atomic orbital electron with total energy loss. It is this third process, displayed in Figure 2, that is primary to XPS. When a given photon impinges upon an atom, electrons will be ejected (photoemission) given that the frequency of excitation is

greater than some threshold level distinctive to each element. This ejected electron will then possess some kinetic energy, KE , which can then be measured.

Table 1. Information Derived from an XPS experiment from Ratner and Castner [1]

In the outermost 10nm of a surface, XPS can provide

- Identification of all elements (except H and He) present at concentrations >0.1 atomic percent
 - Semi-quantitative determination of the approximate elemental surface composition (error $< \pm 10\%$)
 - Information about the molecular environment (oxidation state, bonding atoms, etc.)
 - Information about aromatic or unsaturated structures from shakeup ($\pi^* \rightarrow \pi$) transitions
 - Identification of organic groups using derivatization reactions
 - Non-destructive elemental depth profiles 10nm into the sample and surface heterogeneity assessment using (1) angular dependant XPS studies and (2) photoelectrons with differing escape depths
 - Destructive elemental depth profiles several hundred nanometers into the sample using ion etching (for inorganics)
 - Lateral variations in surface composition (spatial resolution of 8-150 μ m, depending upon the instrument)
 - 'Fingerprinting' of materials using valence band spectra and identification of bonding orbitals
 - Studies on hydrated (frozen) surfaces
-

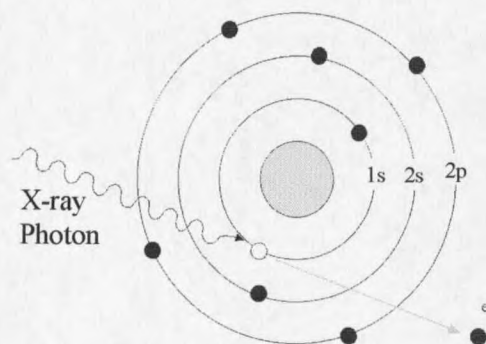


Figure 2. Cartoon of an atom undergoing photoemission

The binding energy can then be calculated according to the following equation:

$$E_B = h\nu - KE \quad (1)$$

where E_B is the binding energy of the electron and $h\nu$ is the energy of the X-ray source.

With $h\nu$ being a known quantity and the ability to accurately measure KE it is possible to calculate the binding energy, which is directly related to the type of atom and the molecular environment from which the electron came.

Quantitation of Conventional XPS Data

To quantify data from an XPS spectrum the intensity of the inelastically scattered electrons (total number of electrons emitted that have lost no energy) are calculated by integrating the area underneath the peak representing each specific element. The common equation used to describe the photoelectron intensity as a function of elemental concentration is given by:

$$F_{i,j}^*(\theta) = \frac{A \cdot \sigma_{i,j} \cdot \Psi}{\sin \phi} \cdot \int_0^\infty \eta_j(x) \cdot e^{\frac{-x}{\lambda_{i,j} \cdot \cos \theta}} dx \quad (2)$$

where F_{ij}^* is the absolute signal intensity of peak i of the j^{th} element in the sample; A is a constant that includes X-ray flux, area of the sample being irradiated, and the detector efficiency; σ_{ij} is the photoionization cross-section, Ψ is the transmission function of the detector; ϕ is the angle between the X-ray and the surface; θ is the angle between the surface normal and the photoelectron electron trajectory; $n_j(x)$ is the concentration of element j at a depth x ; and λ is the electron attenuation length (i.e., the distance an electron can travel before being elastically scattered). Commonly, the normalized signal intensity is used and can be calculated by correcting for differences in the photoionization cross-section, transmission function, sampling depth and changes in X-ray incidence.

$$F_{i,j}(\theta) = F_{i,j}^*(\theta) \cdot \left(\frac{\sigma_{i,j} \cdot \Psi \cdot \lambda_{i,j}}{\sin \phi} \right)^{-1} = \frac{A}{\lambda_{i,j}} \cdot \int_0^{\infty} \eta_j(x) \cdot e^{\frac{-x}{\lambda_{i,j} \cos \theta}} dx \quad (3)$$

It is common in XPS to define a new variable in order to reduce the number of unknowns in Equation 3. This is accomplished by defining the relative composition, $n_{i,j}(x)$ as

$$n_{i,j}(x) = A \cdot \eta_j \quad (4)$$

The relative composition reduces Equation 3 to an equation with one unknown as follows:

$$F(\theta) = \int_0^{\infty} n_{i,j}(x) \cdot e^{\frac{-x}{\lambda_{i,j} \cos \theta}} dx \quad (5)$$

For conventional XPS, Equation 5 is further simplified by assuming all elemental concentrations are homogeneous throughout the XPS sampling depth. This allows Equation 3 to be integrated to obtain:

$$F_{i,j}(\theta) = n_{i,j} \cdot \cos(\theta) \quad (6)$$

Calculation of the atomic percentages is then:

$$\eta_j = 100 \left(\frac{\eta_{i,j}}{\sum_{k=1}^m \eta_{i,k}} \right) \quad (7)$$

It is important to note that if the concentration is not homogeneous in the sampling depth Equation 4 is not valid and Equation 3 must be used in conjunction with a smoothing technique as discussed in the next section. Homogeneity is typically determined qualitatively by performing experiments at different take-off angles, θ , which effectively changes the sampling depth as displayed in Figure 1.

Angle Resolved X-ray Photoelectron Spectroscopy

Obtaining a quantitative concentration profile when the sampling depth is not homogeneous is not mathematically straightforward. Equation 3 is a Laplace transform of the depth profile of the concentration profile, $n_j(x)$. Bussing and Holloway have shown that inverse transforming finite sets of data does not produce unique solutions, rather any solution is a selection from a class of equivalent solutions ranging from smooth to highly oscillatory [6-8].

The Laplace transform in Equation 5 is in the form of one general class of ill-posed problems commonly referred to as a Fredholm integral of the first kind[9]. These equations take the following form:

$$F(\theta) = \int_0^{\infty} n(x) \cdot K(x, \theta) \cdot dx \quad (8)$$

where $F(\theta)$ is the known "right-hand side" and $n(x)$ the unknown function to be solved.

The function of two variables is commonly referred to as the Kernel and is generally derived from theory. For calculating concentration profiles $K(x, \theta) = \exp(-x/\lambda \cos(\theta))$.

Equation 8 is analogous to the matrix equation:

$$K \cdot n = F \quad (9)$$

It should be apparent that this is an "ill posed" problem, in that we are attempting to reconstruct a whole function from a finite number of discrete points. Applying the Kernel to a function is generally regarded as a smoothing operation, so the solution, which requires inverting the operator, will be extremely sensitive to small changes or errors in the input. That is to say, oscillations in the solution, $n(x)$, are observed when simply minimizing the sum of squared errors as follows:

$$\phi(n) = \left\| \int_0^{\infty} n(x) \cdot K(x, \theta) dx - F(\theta) \right\|^2 \quad (10)$$

Most algorithms have utilized iterative approaches that forward transforms a hypothetical $n_{i,j}(x)$ and optimizes the calculated intensities, $F(\theta)$, subject to some constraints. This optimization typically stabilizes the solution when calculated according to Equation 10. A common constraint is to restrict the atomic percentages to be physically realistic (i.e. 0%-100%). However, additional constraints tend to considerably limit the form of the resulting concentration profiles. Methods that employ inverse

theory have been used successfully, two of which will be discussed below; the Singular Value Decomposition algorithm and the Tyler Regularization algorithm.

The Tyler Algorithm

Tikhonov proposed in the early 1960's that Equation 10 might be replaced with a similar equation as follows [5, 10]:

$$\varphi(n) = \left\| \int_0^\infty n(x) \cdot K(x, \theta) dx - F(\theta) \right\|^2 + \alpha \cdot g(n) \quad (11)$$

where α is a positive numerical operator or smoothing parameter. Tikhonov set $g(n) = \|n(x)\|^2$ where Tyler sets $g(n) = \|n(x)K(x, \theta)\|^2$ which is equivalent to $\|n(x)\|^2$ under certain conditions. Using the relationship that increasing α pulls the solution away from minimizing the first term in Equation 11 in favor of minimizing $\alpha\|n(x)\|^2$.

This method attempts to minimize two positive functionals. The first measures the agreement of the model to the data. When done alone, the agreement between the model and the data becomes very good, however, the solution becomes unstable, oscillatory, or just unrealistic. This defines the first term alone as a highly degenerate minimization problem. The second term in Equation 11 is typically referred to as a stabilizing functional or regularizing operator. The regularizing operator measures the "smoothness" in the desired solution. Therefore minimizing the regularizing operator alone gives a stable or likely solution that may have no correlation to the measured data.

Equation 11 is a Fredholm integral equation of the second kind and has stable, unique minimums for values of α greater than zero. It can be readily observed that

Equation 10 is simply a limiting case of Equation 11 and as α approaches zero the solution to Equation 11 approaches that of Equation 10. Choosing an appropriate value for α that is large enough to stabilize the problem without "smoothing out" any of the real features is then of principal concern for obtaining a realistic solution.

A method of applying non-negativity constraints to Fredholm Integrals of the first kind was developed by Butler, Reeds, and Dawson in the early 1980's [11]. Britten, Travis, and Brown demonstrated that by constraining the solution, $n(x)$, to be physically realistic (i.e., non-negative) the solution could be further stabilized and greatly improved the agreement between postulated and calculated distributions [12]. Tyler later presented a modified version of the Butler, Reeds and Dawson algorithm for solution to Fredholm Integral Equations of the first kind as they apply to the approximation of concentration profiles [5]. It is this approach, presented by Tyler, which will be used in this work.

It has been shown that for a particular smoothing parameter, α , the solution, $n(x)$, can be solved for by minimizing Equation 11. Equation 11 has been shown to have a unique minimum, which is readily found by setting the gradient equal to zero as follows [11]:

$$\nabla \phi = K(x, \theta) \left[\int_0^\infty n(x) \cdot K(x, \theta) dx - F(\theta) \right] + \alpha K = 0 \quad (12)$$

If the solution, $n(x)$, can be expressed as a linear of functions such that:

$$n(x) = \max \left[0, \sum_i^n c_i \cdot e^{\frac{-x}{SF \cos \theta}} \right], \quad \text{where } SF = 1.5 \cdot \max(\lambda) \quad (13)$$

$$n(x) = \max \left[0, \sum_i^n c_i x^i \right], \quad \text{or} \quad (14)$$

$$n(x) = \max \left[0, \sum_i^n c_i \cdot \cos(\omega \cdot x) \right] \quad \text{where} \quad \omega = \frac{\pi}{180 \cdot 2^i}, \text{ or} \quad (15)$$

$$n(x) = \max \left[0, \sum_i^n c_i \sum_{m=0}^M \frac{(2i-2m)!}{2^i m! (i-m)! (i-2m)!} x^{i-2m} \right] \quad (16)$$

where $M = i/2$, or $(n-1)/2$ whichever is an integer

where,

$$K(x, \theta) = e^{\frac{-x}{\lambda \cos \theta}} \quad (17)$$

If we then define a new variable M such that:

$$M_{i,j} = \int_D K(x, \theta_i) \cdot K(x, \theta_j) dx \quad (18)$$

$D =$ all intervals on which $n(x) > 0$

Equation 11 can then be rewritten as follows:

$$(M + \alpha I)c = F \quad (19)$$

The Tyler algorithm applies a non-negativity constraint iteratively. M is initially calculated over the interval of 0 to ∞ to generate an estimate of c . The estimate of the solution, $n(x)$, is then calculated according to Equation 13. M is then recalculated only over the intervals for which the approximating function is non-negative. The process is repeated until:

$$\frac{\|(M + \alpha I)c - F\|}{\|F\|} \leq 10^{-6} \quad (20)$$

Singular Value Decomposition

The second method used in this work to approximate concentration profiles from ARXPS data uses Singular Value Decomposition (SVD) to solve the inverse problem. This can be regarded as a general linear least squares problem as in Equation 10 or a limiting case of the Tyler Algorithm. For all practical purposes, we will consider it a limiting case of the Tyler algorithm with α equal to zero, and solve by the method outlined in the previous section.

As mentioned above, Equation 19 with α equal to zero is an unstable problem. The matrix M is typically very close to singular in which case a zero pivot element may be encountered resulting in no solution. Alternatively, a very small pivot may be encountered, which leads to fit parameters with very large magnitudes that are balanced to cancel out almost precisely when the function is evaluated. SVD overcomes this problem by allowing the user to remove possible singularities and inverting M in Equation 15. This enables calculation of the vector c as follows:

$$c = V \cdot [diag(1/w_j)] \cdot (U^T \cdot F) \quad (21)$$

where,

$$M = \begin{pmatrix} U \end{pmatrix} \cdot \begin{pmatrix} w_1 & & & \\ & w_2 & & \\ & & \ddots & \\ & & & w_j \end{pmatrix} \cdot \begin{pmatrix} V^T \end{pmatrix} \quad (22)$$

In Equation 21 and 22 U is an $i \times j$ matrix whose columns are orthonormal, W is an $j \times j$ matrix with positive or zero elements (the singular values), and V is a $j \times j$ orthogonal matrix. The decomposition in Equation 22 can always be done regardless of how close to

singular the M matrix is. If F lies within the range of M the singular set of equations has an solution (in fact it has more than one solution since any vector in the null space can be added to c in any linear combination) when calculated by Equation 21. If F does not lie within the range of M the singular set of equations has no solution. However, Equation 21 will construct the closest solution in a least squares sense.

The SVD algorithm overcomes the singularity or near singularity problem as follows: if any singular value w_j is zero, its reciprocal in Equation 21 is set to zero as opposed to infinity. Similarly, if any singular value w_j is near zero, it is also set to zero. This corresponds to adding to the fitted parameters c a zero multiple, as opposed to some random large multiple, of any linear combination of basis functions that are degenerate in the fit [4]. Editing additional singular values (not close to zero) can also identify additional linear combinations of variables that do not greatly affect the minimization of Equation 11. However, this is beyond the scope of this work.

This algorithm, implemented similar to the Tyler algorithm above, has three notable differences: α is set equal to zero, the matrix inversion is done using singular value decomposition, and the adjustable parameter is the number of singular values used. By adjusting the number of singular values, w_j 's, used it effectively smoothes or dampens the approximated solution, $n(x)$ (e.g. the more singular values used the more unstable the solution).

Atomic Force Microscopy

Binnig, Quate and Gerber first introduced atomic force microscopy in 1986 as a new instrument for examining the surfaces of thin insulated crystals [13]. It operates under the same principles as the record player or reading Braille just on a smaller scale.

The Atomic Force Microscope (AFM) probes the surface of a sample with a sharp tip, approximately $240\mu\text{m}$ long, $2.5\mu\text{m}$ thick, and often less than $20\mu\text{m}$ in diameter [3]. The tip is located at the free end of a cantilever as shown in Figure 3. Forces between the surface and tip cause the cantilever to deflect; this deflection is then measured using a laser photodiode detector. The detector electronics then produce a map of the surface topography. The measured signal is then used to control movements of the piezoelectric crystal on which the cantilever is mounted, via a feed back loop (Figure 3).

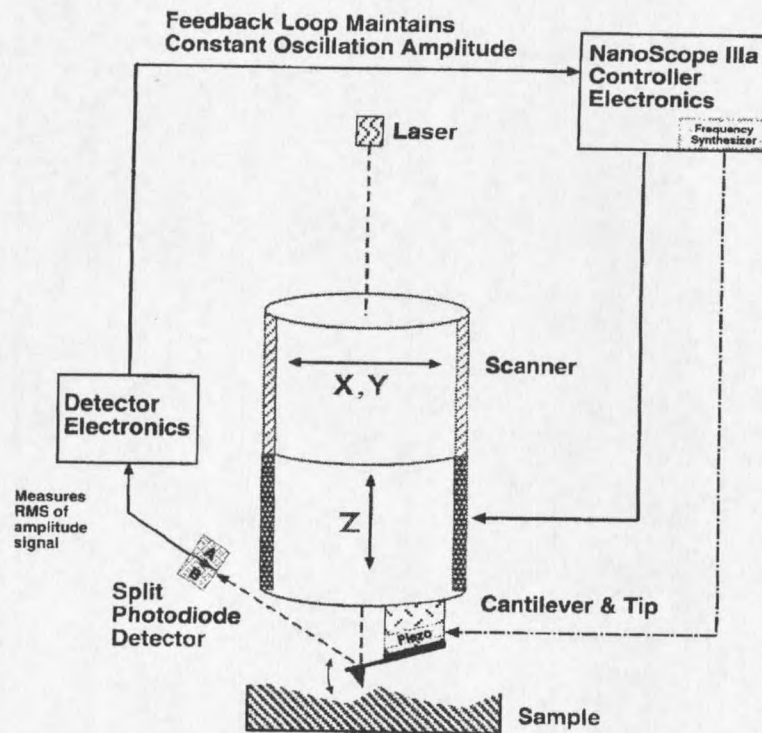


Figure 3. Schematic of Tapping™ Mode AFM [14]

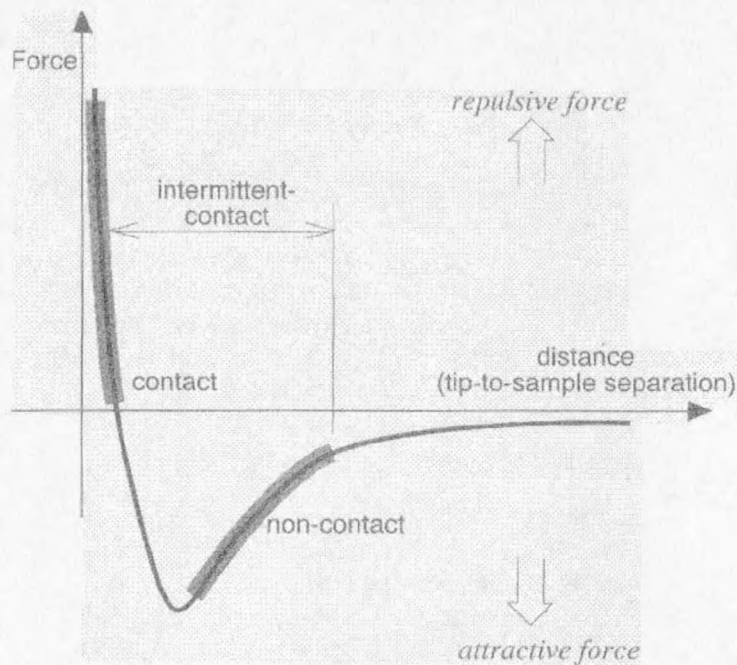


Figure 4. Relationship Between van der Waals Force and Tip to Surface Distance [15]

There are three primary modes in which the AFM is capable of operating: Contact Mode, Non-contact Mode, and TappingTM Mode. The advantages and disadvantages of each are summarized in Table 2. The AFM has two principal modes of interaction between the tip and sample: attractive and repulsive. Figure 4 demonstrates this dependence of van der Waals force on tip to sample distance and the corresponding tip interaction associated with each type of experiment.

Contact Mode AFM operates under the principle that as the cantilever pushes the tip to the sample, the cantilever flexes as opposed to forcing the tip atoms closer to the sample atoms. This can be seen in the slope of the curve in Figure 4 in the contact regime. Rather than decreasing interatomic distances, the surface is likely to deform instead [15]. Only in contact mode is the AFM able to achieve atomic resolution [14]. Other forces on cantilever which can contribute in contact mode are lateral forces, capillary forces and the force exerted by the cantilever itself [15].

Table 2. Advantages and Disadvantages of Contact Mode AFM, Tapping mode AFM, and Non-contact Mode AFM [14].

Contact Mode AFM

Advantages:

- High scan speeds (throughput)
- Contact mode AFM is the only AFM technique that can obtain “atomic resolution” images.
- Rough samples with extreme changes in vertical topography can sometimes be scanned more easily in contact mode.

Disadvantages:

- Lateral (shear) forces can distort features in the image.
- The forces normal to the tip-sample interaction can be high in air due to capillary forces from the absorbed fluid layer in the sample surface.
- The combination of lateral forces and high normal forces can result in reduced spatial resolution and may damage soft samples (i.e., biological samples, polymers, and silicon) due to scraping between the tip and sample.

Non-contact Mode AFM

Advantage:

- No force exerted on the sample surface.

Disadvantages:

- Lower lateral resolution, limited by the tip-sample separation
- Slower scan speed than Tapping Mode and Contact Mode to avoid contacting the absorbed fluid layer, which results in the tip getting stuck.
- Non-contact usually only works on extremely hydrophobic samples, where the absorbed fluid layer is at a minimum. If the fluid layer is too thick, the tip becomes trapped in the absorbed fluid layer causing unstable feedback and scraping of the sample.

Tapping Mode AFM

Advantages:

- Higher lateral resolution on most samples (1nm to 5nm).
- Lower forces and less damage to soft samples imaged in air.
- Lateral forces are virtually eliminated, so there is no scraping.

Disadvantages:

- Slightly slower scan speed than contact mode AFM.

Due to these disadvantages, applications for non-contact mode AFM imaging have been limited.

Non-contact mode AFM is, generally speaking, more suited for analyzing soft or elastic samples. In non-contact mode, the cantilever is vibrated near its resonant frequency (about 100-400kHz) with an amplitude on the order of a 10-100Å [15]. However, because the total force between the tip and sample is very low in this regime as seen in Figure 4, difficulties are often encountered when collecting an image.

The third mode typically available in atomic force microscopy is Tapping™ mode or intermittent-contact mode. This mode operates under the same principle as non-contact AFM except the tip is brought close enough to the sample that it just barely touches the surface. Again the system detects deviations in amplitude of the cantilever when vibrating near its resonant frequency. Tapping™ mode AFM nearly eliminates the lateral forces seen in contact mode and has been found to be more effective for imaging larger areas that have larger variance in surface features than non-contact mode [15].

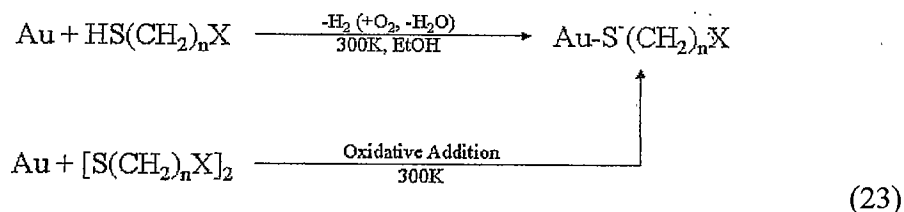
Self-Assembling Monolayers

Self-assembled monolayers (SAMs) have attracted much attention as a model system for the study of thin-film organic materials. The interest in the properties of these thin-film organic materials is due to the wide range of applications now being discovered: supramolecular assembly, wetting, tribology, biological interfaces, electrochemistry, corrosion inhibition, etc.

Particular attention, however, has been paid to SAMs consisting of n-alkane thiols adsorbed on gold. This system has been proven to be thermally stable, well ordered, and can easily be made using ω -substituted thiols to modify surface properties. The

overlayers are formed in a simple, near equilibrium procedure. They also exhibit strong adsorbate-substrate bonding and, for $n > 5$, the chain-terminating group has no knowledge of the underlying gold substrate. Gold is used as the substrate because it is reasonably inert and allows for manipulation in air with lessened concern for contamination. Few functional groups besides thiols (or disulfides which dissociate upon adsorption) bind strongly to gold.

Samples are generally prepared using a mica wafers primed with an adhesion layer of $\sim 40 \text{ \AA}$ of titanium. The gold ($> 2000 \text{ \AA}$) is then deposited by e-beam evaporation onto the wafers. Samples are then immersed in ethanol solutions of the adsorbate ($\sim 10^{-1} \text{ M}$) contained in glass jars (no precautions are generally used to exclude air). The reaction is believed to proceed as follows:



Previous studies have established that this procedure produces polycrystalline gold films exhibiting a strong (111) texture and grains $> 1000 \text{ \AA}$ in size [16]. These dense monolayers assemble rather quickly, however well ordered systems can take days to form. It is the understanding of the author that the less ordered the system the more susceptible the samples are to oxidation in air.

CHAPTER 3

EXPERIMENTAL

Computer Simulated Data

Because this is an ill-posed problem, conventional methods for determining error propagation cannot be utilized. It is the purpose of this work to place an upper bound on how the error in the initial data propagates through the calculations. Although the algorithms are being evaluated on computer simulated data with known amounts of error, this is still an ill-posed problem and does not make the solution any more stable.

Flat Surface

The computer generated data was simulated by integrating Equation 5 for a number of profiles, $n(x)$. The data consisted of four components in two layers as displayed in Figure 5. Each layer consisted of a 1:5 mixture of two hypothetical elements with inelastic mean free paths, λ , of $30\text{\AA}$. Uniformly distributed error of 1%, 2%, and 5% was also introduced to the data. Depth profiles were then calculated using each algorithm from data sets consisting of three take-off angles (10° , 40° , & 80°), five take-off angles (10° , 20° , 40° , 60° , & 80°) and ten take-off angles (10° , 20° , 30° , 40° , 50° , 60° , 65° , 70° , 75° , & 80°).

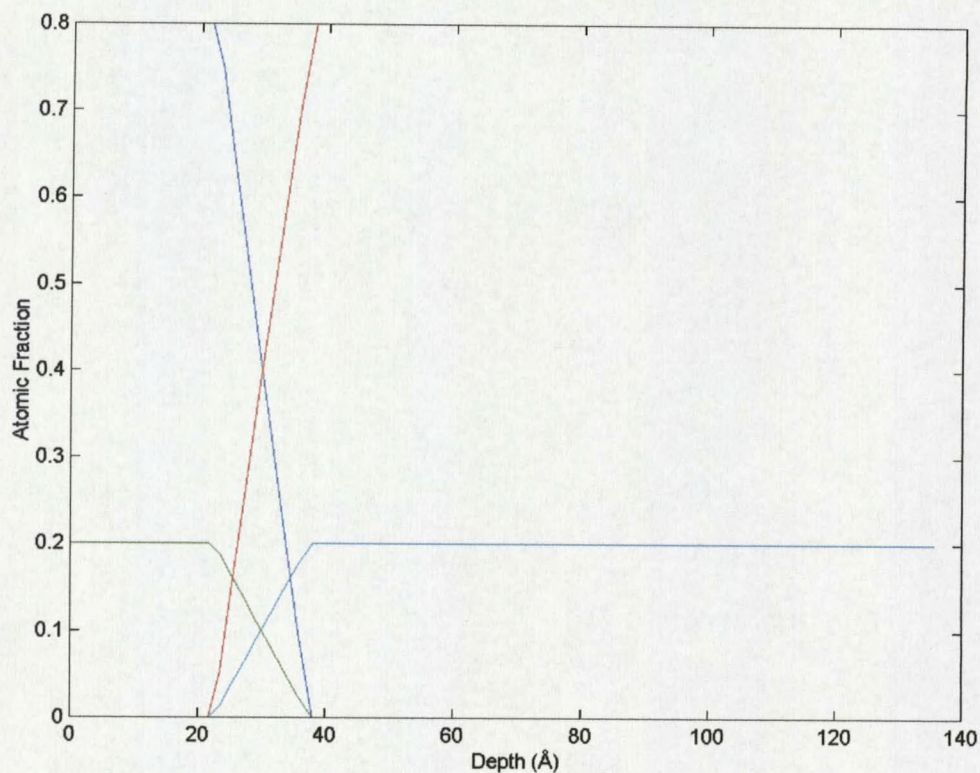


Figure 5. Example of Profile Used to Generate Computer Simulated Data

In order to determine the effect of depth of an interface on accuracy, resolution and stability data was simulated at four different depths: $\lambda/4$, $\lambda/2$, λ , and 2λ . At each depth the gradient of the interface was changed to help determine how large changes in the shape in the interface must be to resolve them from other gradients. The different slopes and gradients used are shown in Figures 6-10:

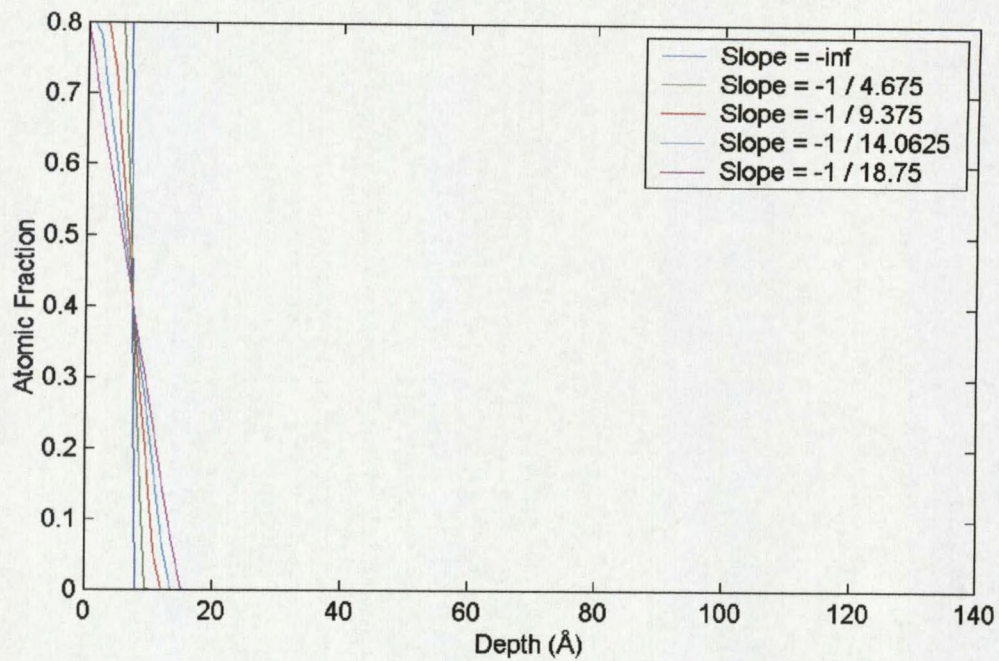


Figure 6. Simulated Data with a $\lambda/4$ Overlay

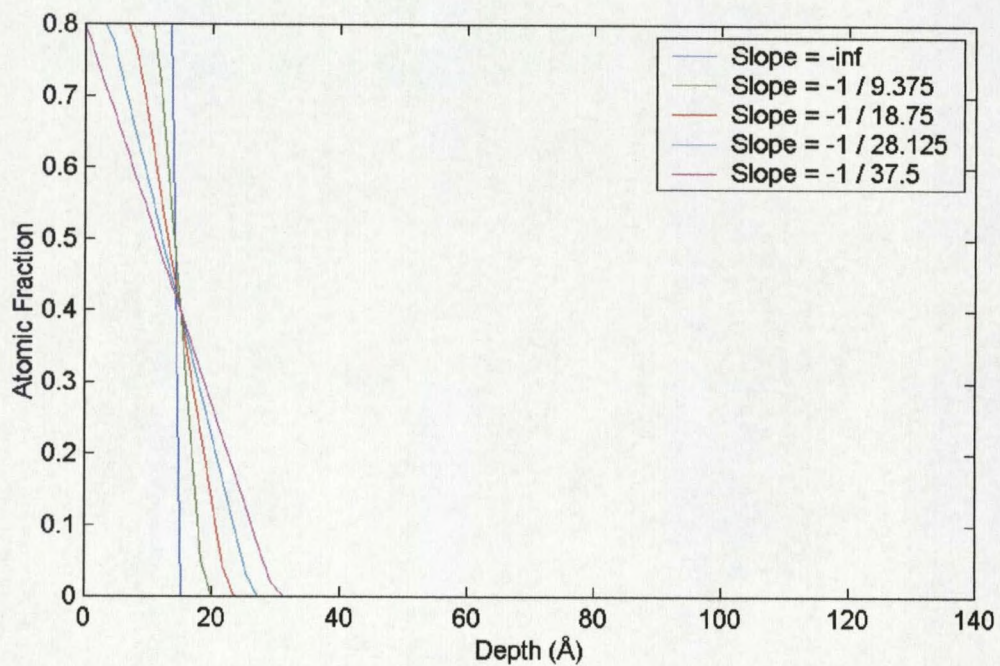


Figure 7. Simulated Data with a $\lambda/2$ Overlay

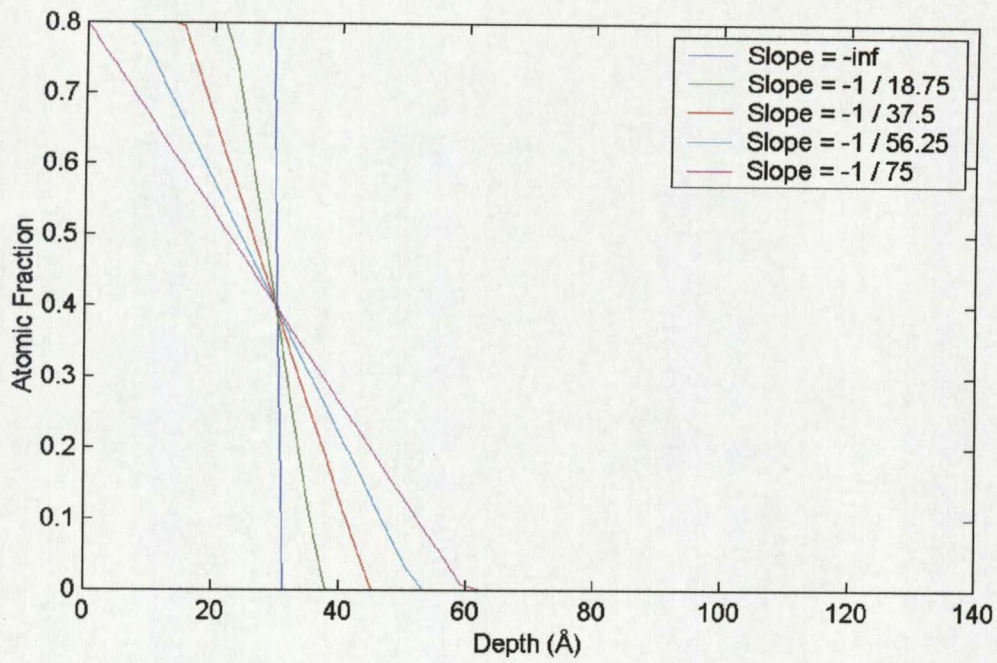


Figure 8. Simulated Data with a 1λ Overlayer

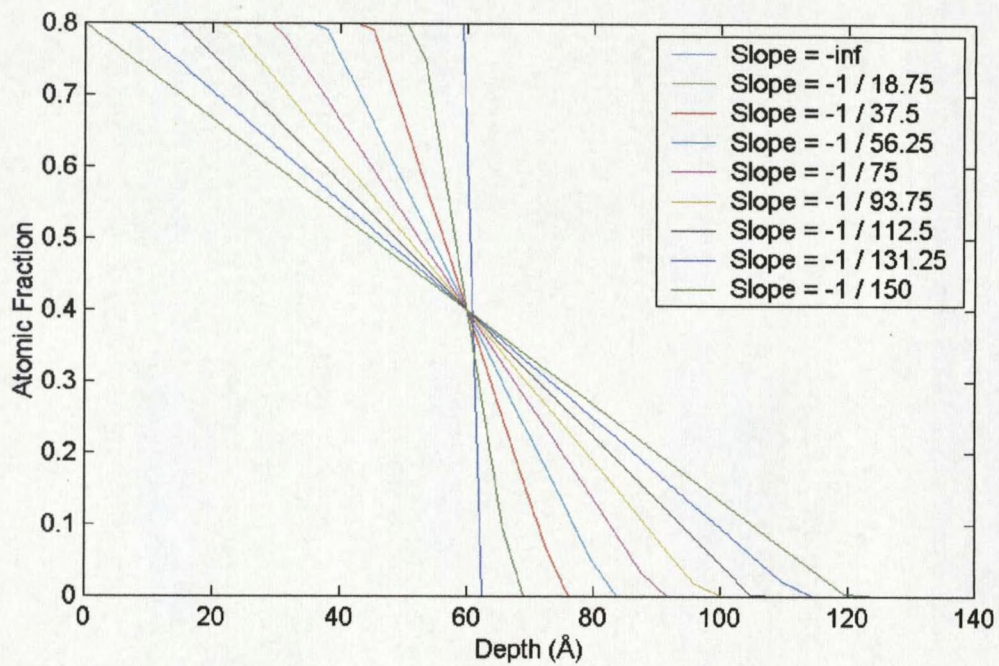


Figure 9. Simulated Data with a 2λ Overlayer

Simulated Rough Surface

Data was also simulated for three-dimensional wavelike surfaces of varying amplitude. This was accomplished by generating a mesh surface according to the following equation:

$$H = A \cos(x) \cos(y) \Big|_{x=0 \dots 2\pi, y=0 \dots 2\pi} \quad (24)$$

where H is the height of the surface and A is an adjustable parameter that varies the amplitude to period ratio. The x and y gradients were calculated and the appropriate adjustments were made to the take-off angle to impose a 1λ overlayer on the surface.

This was done as follows:

$$\phi = \alpha \tan\left(\frac{\partial H}{\partial x}\right), \quad \beta = \alpha \tan\left(\frac{\partial H}{\partial y}\right) \quad (25 \text{ \& } 26)$$

$$\theta_{actual} = \frac{1}{\sqrt{1 + \tan^2(\theta + \phi)} \sqrt{1 + \tan^2(\beta)}} \quad (27)$$

where θ_{actual} is the actual angle between the surface normal. The corresponding intensities, $F(\theta_{actual})$, were then calculated for each point on the 150×150 wavelike grid. The average intensity for each take-off angle was then calculated for use in both the Tyler Regularization and SVD methods. Again, three data sets using three, five and ten measurements as described above were used to test the algorithms.

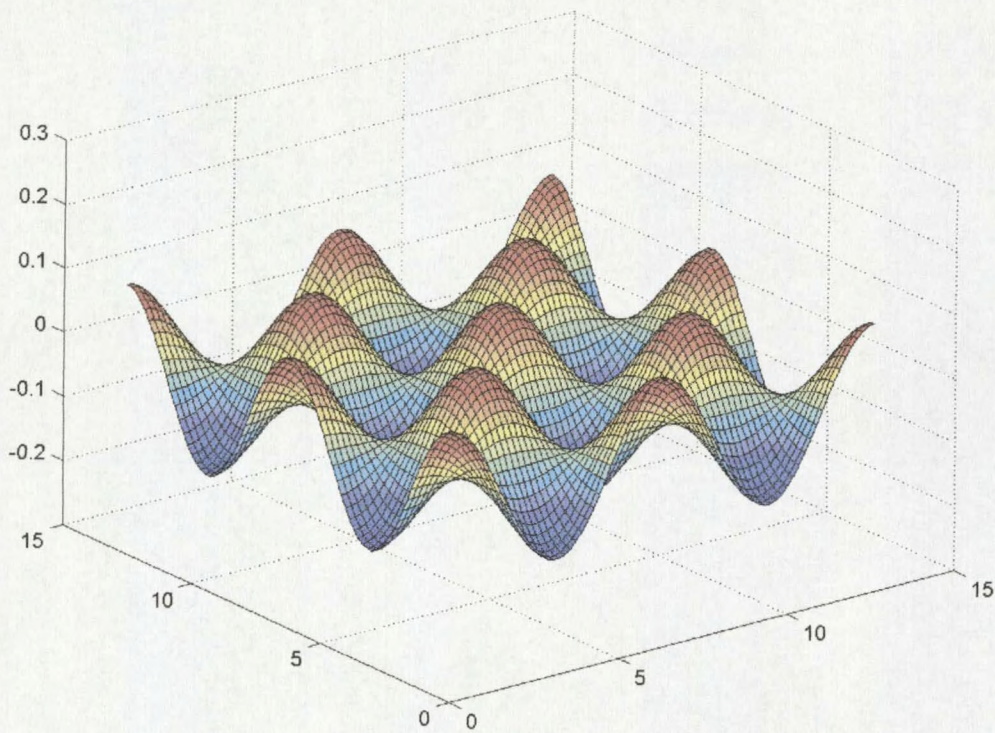


Figure 10. Example of the Wavelike Surface

Fourteen values for A in Equation 24 were chosen (0.02, 0.04...0.28). The A values were chosen to correspond to the same magnitude of the samples on which data was collected experimentally. Roughness is defined as the ratio of the actual surface area to the area of the projected surface. This was calculated for the simulated data as follows:

$$\frac{SA}{PSA} = (2\pi)^{-2} \iint \sqrt{(-A \sin(x) \cos(y))^2 + (-A \cos(x) \sin(y))^2 + (-1)^2} dy dx \quad (28)$$

Profile Approximation

Profiles for all the simulated data were approximated using both the Tyler Regularization and SVD algorithms. For the Tyler Regularization algorithm the profiles were approximated using 20 different smoothing parameters, α , corresponding to Equation 29.

$$\alpha = 1.8^{1-n} \quad n=1,2,\dots,20 \quad (29)$$

The SVD algorithm approximated the profiles using between one and one less than the number of take-off angles used. Data were simulated using both the exponential (Equation 13) and the power (Equation 14) approximation functions. The data for each were stored on compact disk for further analysis. Cosine (Equation 15) and Legendre polynomial (Equation 16) approximating functions were also attempted. These functions produced highly unstable solutions, and therefore, no further analysis was attempted.

Experimentally Collected Data

Duplicate samples of three chain length alkanethiols (C8, C12, and C16) were prepared at the University of Washington and sent Montana State University for analysis. The samples were prepared by vapor deposition of $> 200\text{\AA}$ of gold onto a clean mica wafer that had been primed with an adhesion layer of $\sim 40\text{\AA}$ of titanium. The samples were then immersed in 20mM ethanol solutions of the C8, C12, or C16 thiol adsorbate contained in glass jars and shipped to Montana State University. Upon receiving of the samples (~ 3 days after submersion) they were rinsed with an ethanol solution, placed in separate containers, labeled, and stored under a constant N_2 purge.

XPS Spectra were collected using a Physical Electronics Instrument Model 5600 spectrometer at ten take-off angles (10° , 20° , 30° , 40° , 50° , 60° , 65° , 70° , 75° , & 80°). Spectra were obtained from two spots on each sample. The SAMs were mounted on a sample holder using both double-sided adhesive tape and copper arms attached to the sample holder. They were then placed into a vacuum chamber at a pressure of $\sim 10^{-8}$ mmHg. An $800\mu\text{m}$ -diameter area was irradiated using a monochromatized 0.2mm aluminum $K\alpha$ X-ray source at 300 watts. The pass energies used for all elements during data acquisition were 117.40eV. The XPS spectra were integrated using MultiPak[®] Version 2.2 distributed by Physical Electronics to produce the signal intensities. The intensities were normalized under the assumptions of equal inelastic mean free paths and constant density to remove any instrument variation. The resulting scaled intensities were then used in both the Tyler Regularization and SVD algorithms.

The profiles for the data were approximated using subsets of three angles, five angles and the full data set. The optimal adjustable parameter (α and number of singular values) for each overlayer thickness and interface gradient were determined by these simulated data experiments.

The topography of each sample was determined using a Digital Instruments Dimension 3100 Series Scanning Probe Microscope in tapping mode AFM. The AFM analyses were performed using a $1\mu\text{m}^2$, $100\mu\text{m}^2$, and $2500\mu\text{m}^2$ scan area at a scan rate of $\sim 1\text{Hz}$. The surface area of each scan was determined using 3100 Series software. The ratio of the surface area to the area of the projected surface was then calculated.

CHAPTER 4

OPTIMUM SMOOTHING AND ASSOCIATED STABILITY

As previously mentioned the algorithms will be evaluated using three criteria: stability, accuracy, and resolution. The first step in the analysis of the simulated data is to determine the optimum smoothing parameter (α) or number of singular values used for each combination of depth and gradient. This enables comparison of the best data sets (according to the selection criteria) for each depth and gradient. The selection criterion is the mean squared error of the profile.

$$\varepsilon = \left\| \text{True Profile} - \text{Calculated Profile} \right\| \quad (30)$$

Three primary gradients (infinite, $-1/18.75$, and $-1/37.5$) will be discussed extensively. This will enable a closer comparison of the different interface depths. Although the discussion will focus primarily on these three gradients, any trends discussed apply to all gradients unless otherwise noted.

Tyler Regularization

Exponential Approximating Function

Table 3 summarizes the optimum smoothing parameters for the Regularization Algorithm using the Kernel function as the approximating function. (Tables and Figures are located at the end of the chapter.) General trends can be observed from this data. The most predominant trend in the data set is the value of the optimum smoothing parameter increases with increasing data set error. Also, the optimum value of the smoothing parameter tends to decrease with increasing depth of the interface, and increase slightly as the gradient deviates from infinity. The relationship between the number of measurements and optimum smoothing value displays negligible difference between those with five measurements and those with ten measurements. However, when only three measurements are used, the optimum smoothing parameter is smaller than the optimum for cases using more measurements. The above generalizations are not, however, without exception.

The associated stability data for the optimized α values are located in Table 4. The stability of the algorithm at the optimal smoothing parameter decreases as the percent error in the data decreases. This counterintuitive result arises because a smaller smoothing parameter is used when smaller error is introduced into the data. Thus, by increasing the smoothing parameter convergence would be improved. This was confirmed by re-computing the percentage converged for all error levels (0%, 1%, 2%,

and 5%) using the largest optimum smoothing parameter from each depth and gradient as illustrated in Figures 11 and 12.

Another interesting trait of the Tyler Regularization Method is that a plot of error (as defined by Equation 30) against the smoothing parameter (α) shows that there is a very broad minimum. This suggests that the depth profile is not sensitive to small variations in the smoothing parameter. This trend is shown for the case using five measurements in Figures 13-17 and is seen in the cases with three and ten measurements.

For typical real XPS data, the actual profile is not known and the best smoothing must be found using other criteria. The method typically used by Tyler is displayed in Equation 31.

$$\varepsilon = \|NF_{\text{Calculated}} - NF_{\text{Input}}\| \quad (31)$$

Where NF_{Input} is the normalized ARXPS signal intensities, and $NF_{\text{Calculated}}$ is the normalized intensity data calculated using Equation 5 with the approximated profile as $n(x)$. Each element is normalized with respect to its highest signal intensity over all take-off angles.

The optimum smoothing parameters and corresponding stability data can be found in Tables 5 and 6. Similarly, the same type of broad minimum previously mentioned can be seen for all depths and gradients. An interesting feature observed when comparing the smoothing parameters from both methods is that the smoothing parameter selected using Equation 31 is smaller than that found when using Equation 30 at shallow interfaces and larger than that found using Equation 30 when observing deeper features. It appears that the two methods will predict the same smoothing parameter when features are between

15Å and 30Å. Another interesting feature is that the gradient does not seem to affect the selection of the smoothing parameter. These trends are displayed in Figures 16 and 17, where the line is the smoothing parameter selected using Equation 30 and the attached circular marker is that selected by predictive optimum (Equation 31).

It is expected that the predictive criterion (Equation 31) is more sensitive to the upper 30Å of the approximated profile. This will be explored in the next chapter

Power Approximating Function

The data for the optimum smoothing value and corresponding stability for use of the Regularization algorithm with the power approximating function (Equation 14) data

$$n(x) = \max \left[0, \sum_i^n c_i x^i \right] \quad (14)$$

is shown in Table 7 and 8. The most obvious aspect of this data set is its instability. This is most likely a result of the magnitude ratio between the largest and smallest terms ($c \cdot x^n$: $c \cdot x$) in Equation 14. This will cause the matrix **M** in Equation 18 to approach singularity and thus the solution to be highly oscillatory. Even in the cases where the ratio is at its smallest (3 measurements) the stability data is not favorable. Therefore, it can be concluded that Equation 14 is not a viable alternative to Equation 13 in the Tyler Regularization Algorithm.

Singular Value Decomposition

Exponential Approximating Function

Tables 9 and 10 summarize the optimum number of singular values and the associated stability data for the SVD Algorithm as selected by Equation 30 using the kernel as the approximating function. It should be reiterated that the stability data in Table 10 reflects the stability of the method with the smoothing and not the actual method. From the data it is inferred that the optimum number of singular values used in calculation goes through a maximum as the depth of the interface increases. The gradient has no considerable effect on the number of singular values when the interface is near the surface. As the features become deeper in the sample ($>30\text{\AA}$) the optimum number of singular values decreases as the interface becomes more abrupt. The relationship between the number of measurements and number of singular values used does not provide any noticeable trends other than the number used with ten measurements is almost equal to that when five measurements are used. This possibly indicates that ten measurements may provide little additional information to five measurements.

A noteworthy concern, however, is that when this algorithm uses too few singular values (one and possibly two) the model does not represent the actual data. Similar to Tyler Regularization, a plot of the mean squared error (Equation 30) against the optimum number of singular values again displays a broad minimum which may indicate the true optimum may be any value in the range of integers shown in Figure 18. This is alarming

when observing (Table 9) the cases that used 5 and 10 measurements with the optimum numbers typically between 2-3 singular values when error is present.

When the predictive criteria (Equation 31) of selecting the optimum number of singular values is used there appears to be little discrepancy from the mean squared error in the approximated profile (Equation 30) for interfaces near the surface (Figure 19). However at deeper interfaces, there is a notable discrepancy at low error levels and gradual interfaces (Figure 30). This discrepancy reveals that the predicted optimum tends to be less than the actual optimum. Again, the optimum number of singular values may be any one of a series of integers due the relatively flat minimum when plotted against the predicted error.

Power Approximating Function

Tables 13 and 14 summarize the optimum number of singular values and their associated stability data. It appears from these results that the solution, when stable, is very unlikely to provide any reasonable approximation of the data. This is seen in two ways: first in the stability data as the number of unstable cases, and secondly in Table 13 by the number of cases selecting one singular value as the optimum.

The case of one singular value, while it does converge, provides no dependable information. Two common profiles observed when too few singular values are selected are to approximate the surface as a single layer or to provide an approximated profile where the layers become cyclical and the depth of the original interface becomes shifted. Figures 21 and 22 provide examples of each the typical profiles when no error is present.

The first example is more common when one singular value is used, while the second example is more common when two singular values are used.

Summary of Smoothing

While the power approximating yielded unstable results, the exponential approximating function appeared very durable when used with the Tyler algorithm. The broad minimum seen when plotting the mean squared error verses the smoothing parameter, α , indicates the mean squared error is not sensitive to small changes in the smoothing parameter. In addition, the level of optimal smoothing was directly related to the error present in the original data. At higher error levels, more something was required to minimize the mean squared error. The predictive criterion appeared to steadily under smooth at overlays thinner than $\sim 30\text{\AA}$ and oversmooth as the overlayer becomes thicker.

The Singular Value Decomposition algorithm gave similar results. Again, the power approximating function was highly unstable and determined not to be a practical alternative to the exponential approximating function. The error in the original data did not a significant effect on the mean squared error when using the exponential approximating function. The optimal number of singular values was consistently either 2 or 3 when more than five measurements were used. The predictive criterion typically selected the same number of singular values.

Table 3. Optimum Smoothing Parameter for Regularization Algorithm using Exponential Function (Equation 13)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	1.41E-05	1.41E-05	1.48E-04	1.41E-05
0.00	3	1%	1.48E-04	4.80E-04	1.41E-05	1.41E-05
0.00	3	2%	2.67E-04	1.56E-03	1.41E-05	1.41E-05
0.00	3	5%	5.29E-02	5.04E-03	1.41E-05	4.57E-05
0.00	5	0%	1.41E-05	1.41E-05	1.41E-05	1.48E-04
0.00	5	1%	2.67E-04	4.57E-05	2.80E-03	4.80E-04
0.00	5	2%	8.64E-04	2.80E-03	5.04E-03	8.64E-04
0.00	5	5%	2.94E-02	1.63E-02	1.63E-02	1.56E-03
0.00	10	0%	1.41E-05	1.41E-05	1.41E-05	1.41E-05
0.00	10	1%	4.80E-04	8.23E-05	8.64E-04	8.64E-04
0.00	10	2%	1.56E-03	4.80E-04	5.04E-03	1.56E-03
0.00	10	5%	5.29E-02	2.94E-02	1.63E-02	4.80E-04
-18.75	3	0%	1.41E-05	1.41E-05	1.41E-05	1.41E-05
-18.75	3	1%	1.56E-03	8.64E-04	1.41E-05	1.41E-05
-18.75	3	2%	9.07E-03	2.80E-03	1.56E-03	2.54E-05
-18.75	3	5%	9.53E-02	1.63E-02	2.80E-03	8.23E-05
-18.75	5	0%	2.80E-03	8.64E-04	1.41E-05	1.48E-04
-18.75	5	1%	5.04E-03	2.80E-03	5.04E-03	4.80E-04
-18.75	5	2%	1.63E-02	9.07E-03	9.07E-03	1.56E-03
-18.75	5	5%	9.53E-02	2.94E-02	1.63E-02	2.80E-03
-18.75	10	0%	1.41E-05	4.57E-05	1.41E-05	1.41E-05
-18.75	10	1%	9.07E-03	5.04E-03	1.56E-03	8.64E-04
-18.75	10	2%	2.94E-02	1.63E-02	9.07E-03	1.56E-03
-18.75	10	5%	1.71E-01	9.53E-02	2.94E-02	1.56E-03
-37.50	3	0%	N/A	5.04E-03	2.80E-03	1.41E-05
-37.50	3	1%	N/A	9.07E-03	5.04E-03	1.41E-05
-37.50	3	2%	N/A	9.07E-03	5.04E-03	1.41E-05
-37.50	3	5%	N/A	1.63E-02	5.04E-03	1.41E-05
-37.50	5	0%	N/A	1.56E-03	1.41E-05	2.54E-05
-37.50	5	1%	N/A	5.04E-03	5.04E-03	1.56E-03
-37.50	5	2%	N/A	2.94E-02	1.63E-02	2.80E-03
-37.50	5	5%	N/A	5.29E-02	5.29E-02	5.04E-03
-37.50	10	0%	N/A	4.80E-04	8.23E-05	1.41E-05
-37.50	10	1%	N/A	9.07E-03	5.04E-03	1.56E-03
-37.50	10	2%	N/A	2.94E-02	1.63E-02	2.80E-03
-37.50	10	5%	N/A	9.53E-02	5.29E-02	9.07E-03

Table 4. Percent Converged for Regularization Algorithm using Exponential Function (Equation 13)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	100.00%	100.00%	100.00%	100.00%
0.00	3	1%	99.60%	98.70%	99.80%	100.00%
0.00	3	2%	99.60%	99.60%	94.80%	99.80%
0.00	3	5%	100.00%	99.50%	82.60%	92.50%
0.00	5	0%	100.00%	100.00%	100.00%	100.00%
0.00	5	1%	84.50%	81.80%	99.90%	98.30%
0.00	5	2%	92.00%	98.20%	99.90%	94.20%
0.00	5	5%	99.60%	99.60%	99.60%	77.10%
0.00	10	0%	100.00%	100.00%	100.00%	100.00%
0.00	10	1%	84.70%	69.90%	97.70%	99.60%
0.00	10	2%	93.70%	87.10%	99.90%	98.30%
0.00	10	5%	99.80%	99.90%	99.60%	50.00%
-18.75	3	0%	100.00%	100.00%	100.00%	100.00%
-18.75	3	1%	100.00%	99.90%	99.90%	100.00%
-18.75	3	2%	100.00%	100.00%	98.00%	99.80%
-18.75	3	5%	100.00%	100.00%	88.90%	92.50%
-18.75	5	0%	100.00%	100.00%	100.00%	100.00%
-18.75	5	1%	99.30%	98.30%	100.00%	99.10%
-18.75	5	2%	99.70%	99.60%	99.90%	99.10%
-18.75	5	5%	99.90%	99.90%	99.80%	89.50%
-18.75	10	0%	100.00%	100.00%	100.00%	100.00%
-18.75	10	1%	99.30%	98.90%	98.50%	99.50%
-18.75	10	2%	100.00%	99.80%	99.70%	98.20%
-18.75	10	5%	100.00%	100.00%	100.00%	78.40%
-37.5	3	0%	N/A	100.00%	100.00%	100.00%
-37.5	3	1%	N/A	100.00%	100.00%	100.00%
-37.5	3	2%	N/A	100.00%	99.90%	99.80%
-37.5	3	5%	N/A	100.00%	96.10%	93.00%
-37.5	5	0%	N/A	100.00%	100.00%	100.00%
-37.5	5	1%	N/A	99.60%	100.00%	100.00%
-37.5	5	2%	N/A	99.90%	100.00%	100.00%
-37.5	5	5%	N/A	100.00%	100.00%	97.70%
-37.5	10	0%	N/A	100.00%	100.00%	100.00%
-37.5	10	1%	N/A	99.80%	99.80%	99.90%
-37.5	10	2%	N/A	100.00%	100.00%	99.70%
-37.5	10	5%	N/A	100.00%	100.00%	99.10%

Table 5. Optimum Smoothing Parameter as Predicted by Equation 31 for Regularization Algorithm using Exponential Function (Equation 13)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	1.41E-05	1.41E-05	2.94E-02	8.64E-04
0.00	3	1%	4.57E-05	4.80E-04	1.63E-02	4.80E-04
0.00	3	2%	8.23E-05	8.64E-04	1.63E-02	1.71E-01
0.00	3	5%	2.67E-04	5.04E-03	5.29E-02	3.09E-01
0.00	5	0%	1.41E-05	8.64E-04	1.41E-05	4.80E-04
0.00	5	1%	2.54E-05	4.80E-04	5.29E-02	2.80E-03
0.00	5	2%	2.67E-04	1.56E-03	5.29E-02	9.07E-03
0.00	5	5%	1.56E-03	5.04E-03	5.29E-02	3.09E-01
0.00	10	0%	2.54E-05	1.41E-05	1.41E-05	8.64E-04
0.00	10	1%	4.57E-05	8.64E-04	2.80E-03	2.80E-03
0.00	10	2%	2.67E-04	2.80E-03	2.94E-02	9.07E-03
0.00	10	5%	8.64E-04	1.63E-02	5.29E-02	5.29E-02
-18.75	3	0%	1.00E+00	1.41E-05	1.41E-05	8.64E-04
-18.75	3	1%	2.54E-05	2.67E-04	2.94E-02	4.80E-04
-18.75	3	2%	1.48E-04	8.64E-04	1.63E-02	1.71E-01
-18.75	3	5%	4.80E-04	2.80E-03	5.29E-02	3.09E-01
-18.75	5	0%	1.00E+00	4.57E-05	1.41E-05	4.80E-04
-18.75	5	1%	2.54E-05	4.57E-05	5.29E-02	2.80E-03
-18.75	5	2%	8.23E-05	1.56E-03	5.29E-02	9.07E-03
-18.75	5	5%	1.56E-03	5.04E-03	5.29E-02	3.09E-01
-18.75	10	0%	4.57E-05	2.54E-05	1.41E-05	8.64E-04
-18.75	10	1%	2.54E-05	1.48E-04	2.80E-03	2.80E-03
-18.75	10	2%	2.67E-04	2.80E-03	2.94E-02	9.07E-03
-18.75	10	5%	8.64E-04	9.07E-03	5.29E-02	5.29E-02
-37.50	3	0%	N/A	1.41E-05	1.56E-03	8.64E-04
-37.50	3	1%	N/A	1.48E-04	2.80E-03	4.80E-04
-37.50	3	2%	N/A	8.64E-04	1.63E-02	1.71E-01
-37.50	3	5%	N/A	2.80E-03	5.29E-02	3.09E-01
-37.50	5	0%	N/A	9.07E-03	1.56E-03	8.64E-04
-37.50	5	1%	N/A	2.54E-05	2.80E-03	2.80E-03
-37.50	5	2%	N/A	8.64E-04	2.80E-03	9.07E-03
-37.50	5	5%	N/A	5.04E-03	5.29E-02	9.53E-02
-37.50	10	0%	N/A	4.57E-05	1.48E-04	8.64E-04
-37.50	10	1%	N/A	1.48E-04	9.07E-03	2.80E-03
-37.50	10	2%	N/A	2.67E-04	1.63E-02	9.07E-03
-37.50	10	5%	N/A	5.04E-03	5.29E-02	5.29E-02

Table 6. Optimum Smoothing Parameter as Predicted by Equation 31 for Regularization Algorithm using Exponential Function (Equation 13)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	100.00%	100.00%	100.00%	100.00%
0.00	3	1%	93.60%	98.70%	100.00%	100.00%
0.00	3	2%	94.70%	97.80%	100.00%	100.00%
0.00	3	5%	95.50%	99.50%	100.00%	100.00%
0.00	5	0%	100.00%	100.00%	100.00%	100.00%
0.00	5	1%	44.90%	94.40%	100.00%	100.00%
0.00	5	2%	79.00%	96.40%	100.00%	100.00%
0.00	5	5%	86.10%	95.60%	99.90%	100.00%
0.00	10	0%	100.00%	100.00%	100.00%	100.00%
0.00	10	1%	52.20%	95.50%	99.20%	99.90%
0.00	10	2%	69.50%	97.40%	100.00%	100.00%
0.00	10	5%	71.00%	99.10%	100.00%	100.00%
-18.75	3	0%	100.00%	100.00%	100.00%	100.00%
-18.75	3	1%	99.50%	99.50%	100.00%	100.00%
-18.75	3	2%	99.00%	99.30%	100.00%	100.00%
-18.75	3	5%	97.60%	98.90%	100.00%	100.00%
-18.75	5	0%	100.00%	100.00%	100.00%	100.00%
-18.75	5	1%	57.80%	89.10%	100.00%	100.00%
-18.75	5	2%	63.10%	98.00%	100.00%	100.00%
-18.75	5	5%	87.40%	97.00%	100.00%	100.00%
-18.75	10	0%	100.00%	100.00%	100.00%	100.00%
-18.75	10	1%	50.30%	80.80%	99.30%	99.90%
-18.75	10	2%	77.50%	98.70%	100.00%	100.00%
-18.75	10	5%	77.20%	98.00%	100.00%	100.00%
-37.5	3	0%	N/A	100.00%	100.00%	100.00%
-37.5	3	1%	N/A	100.00%	100.00%	100.00%
-37.5	3	2%	N/A	99.50%	100.00%	100.00%
-37.5	3	5%	N/A	99.20%	100.00%	100.00%
-37.5	5	0%	N/A	100.00%	100.00%	100.00%
-37.5	5	1%	N/A	87.20%	100.00%	100.00%
-37.5	5	2%	N/A	99.00%	100.00%	100.00%
-37.5	5	5%	N/A	98.10%	100.00%	100.00%
-37.5	10	0%	N/A	100.00%	100.00%	100.00%
-37.5	10	1%	N/A	84.80%	99.90%	100.00%
-37.5	10	2%	N/A	85.50%	100.00%	100.00%
-37.5	10	5%	N/A	97.40%	100.00%	100.00%

Table 7. Optimum Smoothing Parameter for Regularization Algorithm using Power Function (Equation 14)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	Unstable	1.71E-01	1.71E-01	3.09E-01
0.00	3	1%	3.09E-01	3.09E-01	9.53E-02	5.56E-01
0.00	3	2%	1.71E-01	5.56E-01	1.41E-05	1.41E-05
0.00	3	5%	3.09E-01	1.00E+00	5.56E-01	2.67E-04
0.00	5	0%	1.41E-05	4.80E-04	8.23E-05	8.64E-04
0.00	5	1%	Unstable	Unstable	Unstable	Unstable
0.00	5	2%	Unstable	Unstable	Unstable	Unstable
0.00	5	5%	Unstable	Unstable	Unstable	Unstable
-18.75	3	0%	Unstable	5.04E-03	5.29E-02	3.09E-01
-18.75	3	1%	9.53E-02	9.53E-02	5.29E-02	3.09E-01
-18.75	3	2%	1.71E-01	1.71E-01	5.29E-02	5.56E-01
-18.75	3	5%	5.56E-01	5.56E-01	5.56E-01	5.56E-01
-18.75	5	0%	1.41E-05	1.41E-05	8.23E-05	8.64E-04
-18.75	5	1%	Unstable	Unstable	Unstable	Unstable
-18.75	5	2%	Unstable	Unstable	Unstable	Unstable
-18.75	5	5%	Unstable	Unstable	Unstable	Unstable
-37.50	3	0%	N/A	2.80E-03	1.41E-05	1.71E-01
-37.50	3	1%	N/A	9.53E-02	1.41E-05	1.71E-01
-37.50	3	2%	N/A	1.71E-01	2.94E-02	1.71E-01
-37.50	3	5%	N/A	5.56E-01	5.56E-01	5.56E-01
-37.50	5	0%	N/A	2.94E-02	2.54E-05	8.64E-04
-37.50	5	1%	N/A	Unstable	Unstable	5.56E-01
-37.50	5	2%	N/A	Unstable	Unstable	Unstable
-37.50	5	5%	N/A	Unstable	Unstable	Unstable

Table 8. Percent Converged for Regularization Algorithm using Power Function (Equation 14)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
Infinite	3	0%	Unstable	100.00%	100.00%	100.00%
Infinite	3	1%	20.90%	85.10%	97.90%	50.00%
Infinite	3	2%	37.80%	84.80%	86.50%	97.60%
Infinite	3	5%	43.50%	73.90%	85.00%	87.30%
Infinite	5	0%	100.00%	100.00%	100.00%	100.00%
Infinite	5	1%	Unstable	Unstable	Unstable	Unstable
Infinite	5	2%	Unstable	Unstable	Unstable	Unstable
Infinite	5	5%	Unstable	Unstable	Unstable	Unstable
-18.75	3	0%	Unstable	100.00%	100.00%	100.00%
-18.75	3	1%	44.20%	62.70%	96.90%	100.00%
-18.75	3	2%	48.00%	49.20%	90.10%	90.30%
-18.75	3	5%	60.50%	57.70%	87.40%	54.90%
-18.75	5	0%	100.00%	100.00%	100.00%	100.00%
-18.75	5	1%	Unstable	Unstable	Unstable	Unstable
-18.75	5	2%	Unstable	Unstable	Unstable	Unstable
-18.75	5	5%	Unstable	Unstable	Unstable	Unstable
-37.5	3	0%	N/A	100.00%	100.00%	100.00%
-37.5	3	1%	N/A	58.40%	92.70%	100.00%
-37.5	3	2%	N/A	60.10%	90.20%	99.20%
-37.5	3	5%	N/A	71.30%	86.60%	87.20%
-37.5	5	0%	N/A	100.00%	100.00%	100.00%
-37.5	5	1%	N/A	Unstable	Unstable	45.10%
-37.5	5	2%	N/A	Unstable	Unstable	Unstable
-37.5	5	5%	N/A	Unstable	Unstable	Unstable

Table 9. Optimum Number of Singular Values for Singular Value Decomposition using Exponential Function (Equation 13)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	2	2	2	2
0.00	3	1%	2	2	2	2
0.00	3	2%	2	2	2	2
0.00	3	5%	2	2	2	2
0.00	5	0%	3	4	4	2
0.00	5	1%	2	3	3	2
0.00	5	2%	2	3	3	2
0.00	5	5%	2	2	3	2
0.00	10	0%	4	4	5	5
0.00	10	1%	2	3	3	2
0.00	10	2%	2	3	3	2
0.00	10	5%	2	3	3	2
-18.75	3	0%	2	2	2	2
-18.75	3	1%	2	2	2	2
-18.75	3	2%	2	2	2	2
-18.75	3	5%	2	2	2	2
-18.75	5	0%	4	3	4	2
-18.75	5	1%	3	3	3	2
-18.75	5	2%	3	3	3	2
-18.75	5	5%	2	2	3	2
-18.75	10	0%	5	5	5	5
-18.75	10	1%	3	3	3	2
-18.75	10	2%	3	3	3	2
-18.75	10	5%	2	2	3	2
-37.50	3	0%	N/A	2	2	2
-37.50	3	1%	N/A	2	2	2
-37.50	3	2%	N/A	2	2	2
-37.50	3	5%	N/A	2	2	2
-37.50	5	0%	N/A	4	4	2
-37.50	5	1%	N/A	3	3	2
-37.50	5	2%	N/A	3	3	2
-37.50	5	5%	N/A	3	3	2
-37.50	10	0%	N/A	4	6	5
-37.50	10	1%	N/A	3	3	2
-37.50	10	2%	N/A	3	3	2
-37.50	10	5%	N/A	2	3	2

Table 10. Percent Converged for Singular Value Decomposition using Exponential Function (Equation 13)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	100.00%	100.00%	100.00%	100.00%
0.00	3	1%	100.00%	100.00%	100.00%	100.00%
0.00	3	2%	100.00%	100.00%	100.00%	100.00%
0.00	3	5%	99.60%	100.00%	100.00%	100.00%
0.00	5	0%	100.00%	100.00%	100.00%	100.00%
0.00	5	1%	100.00%	72.60%	99.20%	100.00%
0.00	5	2%	100.00%	69.80%	91.90%	100.00%
0.00	5	5%	100.00%	100.00%	51.50%	100.00%
0.00	10	0%	100.00%	100.00%	100.00%	100.00%
0.00	10	1%	100.00%	99.90%	99.90%	100.00%
0.00	10	2%	100.00%	97.80%	99.10%	100.00%
0.00	10	5%	100.00%	68.00%	79.40%	100.00%
-18.75	3	0%	100.00%	100.00%	100.00%	100.00%
-18.75	3	1%	100.00%	100.00%	100.00%	100.00%
-18.75	3	2%	100.00%	100.00%	100.00%	100.00%
-18.75	3	5%	100.00%	100.00%	100.00%	100.00%
-18.75	5	0%	100.00%	100.00%	100.00%	100.00%
-18.75	5	1%	84.40%	99.20%	99.70%	100.00%
-18.75	5	2%	55.80%	87.60%	95.30%	100.00%
-18.75	5	5%	100.00%	100.00%	55.50%	100.00%
-18.75	10	0%	100.00%	100.00%	100.00%	100.00%
-18.75	10	1%	95.00%	100.00%	100.00%	100.00%
-18.75	10	2%	81.30%	99.80%	99.20%	100.00%
-18.75	10	5%	100.00%	100.00%	84.00%	100.00%
-37.5	3	0%	N/A	100.00%	100.00%	100.00%
-37.5	3	1%	N/A	100.00%	100.00%	100.00%
-37.5	3	2%	N/A	100.00%	100.00%	100.00%
-37.5	3	5%	N/A	100.00%	100.00%	100.00%
-37.5	5	0%	N/A	100.00%	100.00%	100.00%
-37.5	5	1%	N/A	100.00%	99.80%	100.00%
-37.5	5	2%	N/A	99.10%	97.30%	100.00%
-37.5	5	5%	N/A	63.50%	63.10%	100.00%
-37.5	10	0%	N/A	100.00%	100.00%	100.00%
-37.5	10	1%	N/A	100.00%	100.00%	100.00%
-37.5	10	2%	N/A	100.00%	99.80%	100.00%
-37.5	10	5%	N/A	100.00%	93.70%	100.00%

Table 11. Optimum Smoothing Parameter as Predicted by Equation 31 for SVD Algorithm using Exponential Function (Equation 13)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	2	2	2	2
0.00	3	1%	2	2	2	2
0.00	3	2%	2	2	2	2
0.00	3	5%	2	2	2	2
0.00	5	0%	3	3	4	2
0.00	5	1%	3	3	3	2
0.00	5	2%	2	3	3	2
0.00	5	5%	2	2	2	2
0.00	10	0%	3	3	4	2
0.00	10	1%	3	3	2	2
0.00	10	2%	3	3	2	2
0.00	10	5%	2	3	2	2
-18.75	3	0%	2	2	2	2
-18.75	3	1%	2	2	2	2
-18.75	3	2%	2	2	2	2
-18.75	3	5%	2	2	2	2
-18.75	5	0%	3	3	4	2
-18.75	5	1%	3	3	3	2
-18.75	5	2%	3	3	3	2
-18.75	5	5%	1	2	2	2
-18.75	10	0%	3	3	4	2
-18.75	10	1%	3	3	2	2
-18.75	10	2%	3	3	2	2
-18.75	10	5%	1	3	2	2
-37.50	3	0%	N/A	2	2	2
-37.50	3	1%	N/A	2	2	2
-37.50	3	2%	N/A	2	2	2
-37.50	3	5%	N/A	2	2	2
-37.50	5	0%	N/A	3	4	2
-37.50	5	1%	N/A	3	3	2
-37.50	5	2%	N/A	3	3	2
-37.50	5	5%	N/A	3	2	2
-37.50	10	0%	N/A	3	4	2
-37.50	10	1%	N/A	3	4	2
-37.50	10	2%	N/A	3	2	2
-37.50	10	5%	N/A	3	2	2

Table 12. Predicted (Equation 31) Percent Converged using the Optimum Number of Singular Values with the Exponential Approximating Function (Equation 13)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	100.00%	100.00%	100.00%	100.00%
0.00	3	1%	100.00%	100.00%	100.00%	100.00%
0.00	3	2%	100.00%	100.00%	100.00%	100.00%
0.00	3	5%	99.60%	100.00%	100.00%	100.00%
0.00	5	0%	100.00%	100.00%	100.00%	100.00%
0.00	5	1%	50.20%	72.60%	99.20%	100.00%
0.00	5	2%	100.00%	69.80%	91.90%	100.00%
0.00	5	5%	100.00%	100.00%	100.00%	100.00%
0.00	10	0%	100.00%	100.00%	100.00%	100.00%
0.00	10	1%	83.80%	99.90%	100.00%	100.00%
0.00	10	2%	53.80%	97.80%	100.00%	100.00%
0.00	10	5%	100.00%	68.00%	100.00%	100.00%
-18.75	3	0%	100.00%	100.00%	100.00%	100.00%
-18.75	3	1%	100.00%	100.00%	100.00%	100.00%
-18.75	3	2%	100.00%	100.00%	100.00%	100.00%
-18.75	3	5%	100.00%	100.00%	100.00%	100.00%
-18.75	5	0%	100.00%	100.00%	100.00%	100.00%
-18.75	5	1%	84.40%	99.20%	99.70%	100.00%
-18.75	5	2%	55.80%	87.60%	95.30%	100.00%
-18.75	5	5%	100.00%	100.00%	100.00%	100.00%
-18.75	10	0%	100.00%	100.00%	100.00%	100.00%
-18.75	10	1%	95.00%	100.00%	100.00%	100.00%
-18.75	10	2%	81.30%	99.80%	100.00%	100.00%
-18.75	10	5%	100.00%	75.80%	100.00%	100.00%
-37.5	3	0%	N/A	100.00%	100.00%	100.00%
-37.5	3	1%	N/A	100.00%	100.00%	100.00%
-37.5	3	2%	N/A	100.00%	100.00%	100.00%
-37.5	3	5%	N/A	100.00%	100.00%	100.00%
-37.5	5	0%	N/A	100.00%	100.00%	100.00%
-37.5	5	1%	N/A	100.00%	99.80%	100.00%
-37.5	5	2%	N/A	99.10%	97.30%	100.00%
-37.5	5	5%	N/A	63.50%	100.00%	100.00%
-37.5	10	0%	N/A	100.00%	100.00%	100.00%
-37.5	10	1%	N/A	100.00%	61.20%	100.00%
-37.5	10	2%	N/A	100.00%	100.00%	100.00%
-37.5	10	5%	N/A	89.00%	100.00%	100.00%

Table 13. Optimum Number of Singular Values for Singular Value Decomposition using Power Function (Equation 13)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	1	2	2	2
0.00	3	1%	2	2	2	2
0.00	3	2%	2	2	2	2
0.00	3	5%	2	2	2	2
0.00	5	0%	1	1	1	2
0.00	5	1%	1	1	1	2
0.00	5	2%	1	1	1	2
0.00	5	5%	1	1	1	2
-18.75	3	0%	1	2	2	2
-18.75	3	1%	2	2	2	2
-18.75	3	2%	2	2	2	2
-18.75	3	5%	2	2	2	2
-18.75	5	0%	1	1	1	2
-18.75	5	1%	1	1	1	2
-18.75	5	2%	1	1	1	2
-18.75	5	5%	1	1	1	2
-37.50	3	0%	N/A	2	2	2
-37.50	3	1%	N/A	2	2	2
-37.50	3	2%	N/A	2	2	2
-37.50	3	5%	N/A	2	2	2
-37.50	5	0%	N/A	1	1	2
-37.50	5	1%	N/A	1	1	2
-37.50	5	2%	N/A	1	1	2
-37.50	5	5%	N/A	1	1	2

Table 14. Percent Converged for Singular Value Decomposition using Power Function (Equation 13)

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
Infinite	3	0%	100.00%	100.00%	100.00%	100.00%
Infinite	3	1%	13.80%	100.00%	100.00%	100.00%
Infinite	3	2%	41.50%	100.00%	100.00%	100.00%
Infinite	3	5%	61.00%	97.20%	100.00%	99.90%
Infinite	5	0%	100.00%	100.00%	100.00%	100.00%
Infinite	5	1%	100.00%	100.00%	100.00%	100.00%
Infinite	5	2%	100.00%	100.00%	100.00%	100.00%
Infinite	5	5%	100.00%	100.00%	100.00%	100.00%
-18.75	3	0%	100.00%	100.00%	100.00%	100.00%
-18.75	3	1%	2.20%	100.00%	100.00%	100.00%
-18.75	3	2%	21.80%	100.00%	100.00%	100.00%
-18.75	3	5%	52.50%	95.30%	100.00%	99.90%
-18.75	5	0%	100.00%	100.00%	100.00%	100.00%
-18.75	5	1%	100.00%	100.00%	100.00%	100.00%
-18.75	5	2%	100.00%	100.00%	100.00%	100.00%
-18.75	5	5%	100.00%	100.00%	100.00%	100.00%
-37.5	3	0%	N/A	100.00%	100.00%	100.00%
-37.5	3	1%	N/A	100.00%	100.00%	100.00%
-37.5	3	2%	N/A	97.20%	100.00%	100.00%
-37.5	3	5%	N/A	87.10%	100.00%	99.90%
-37.5	5	0%	N/A	100.00%	100.00%	100.00%
-37.5	5	1%	N/A	100.00%	100.00%	100.00%
-37.5	5	2%	N/A	100.00%	100.00%	100.00%
-37.5	5	5%	N/A	100.00%	100.00%	100.00%

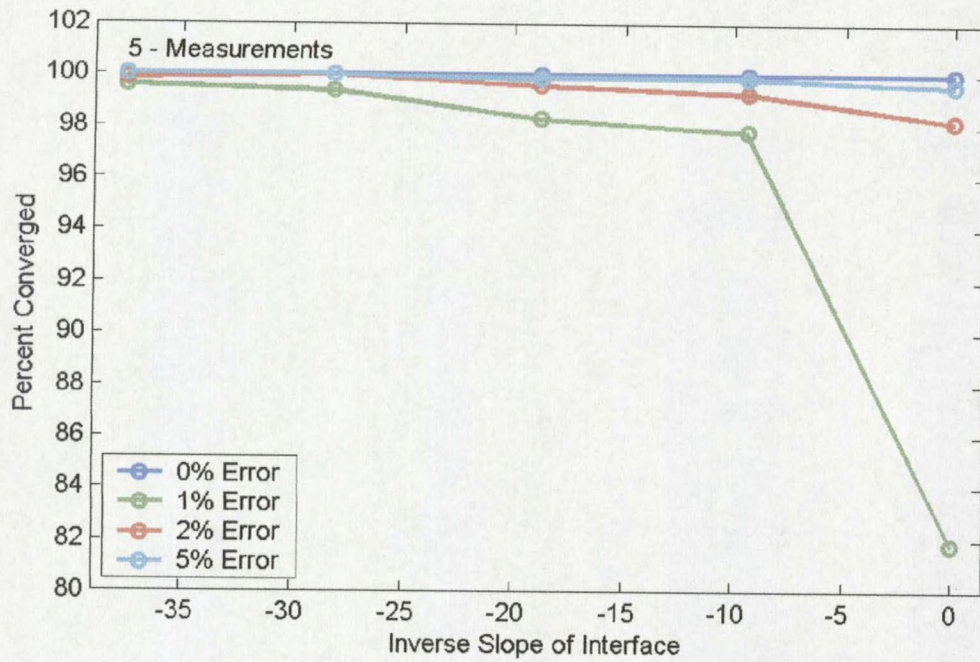


Figure 11. Stability Data for Mean Depth Interface of 15Å using Optimum Smoothing

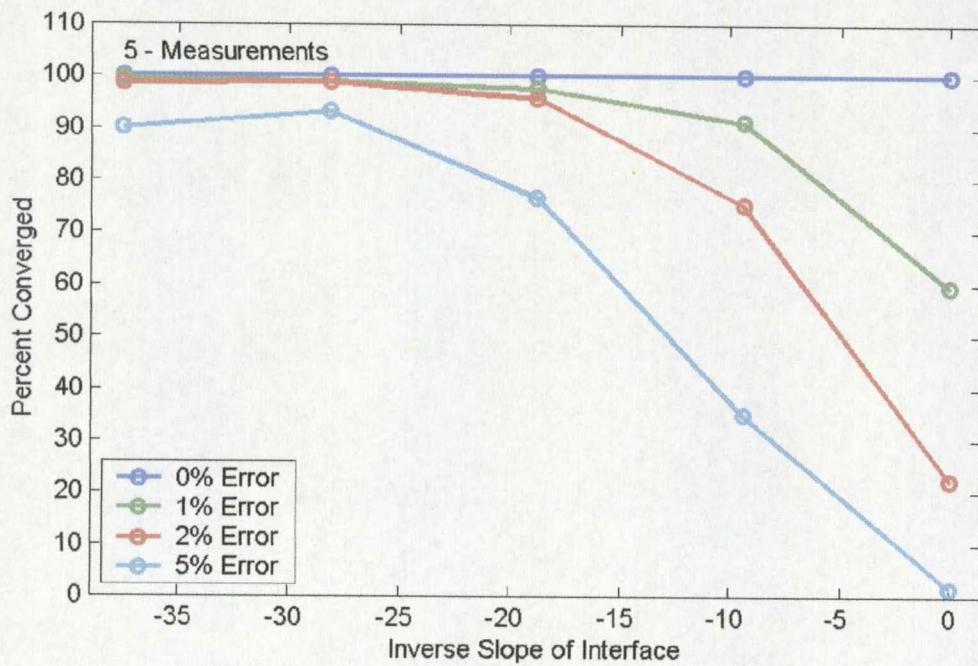


Figure 12. Stability Data for Mean Depth Interface of 15Å using Smallest Smoothing Parameter from all Error Levels at Each Gradient

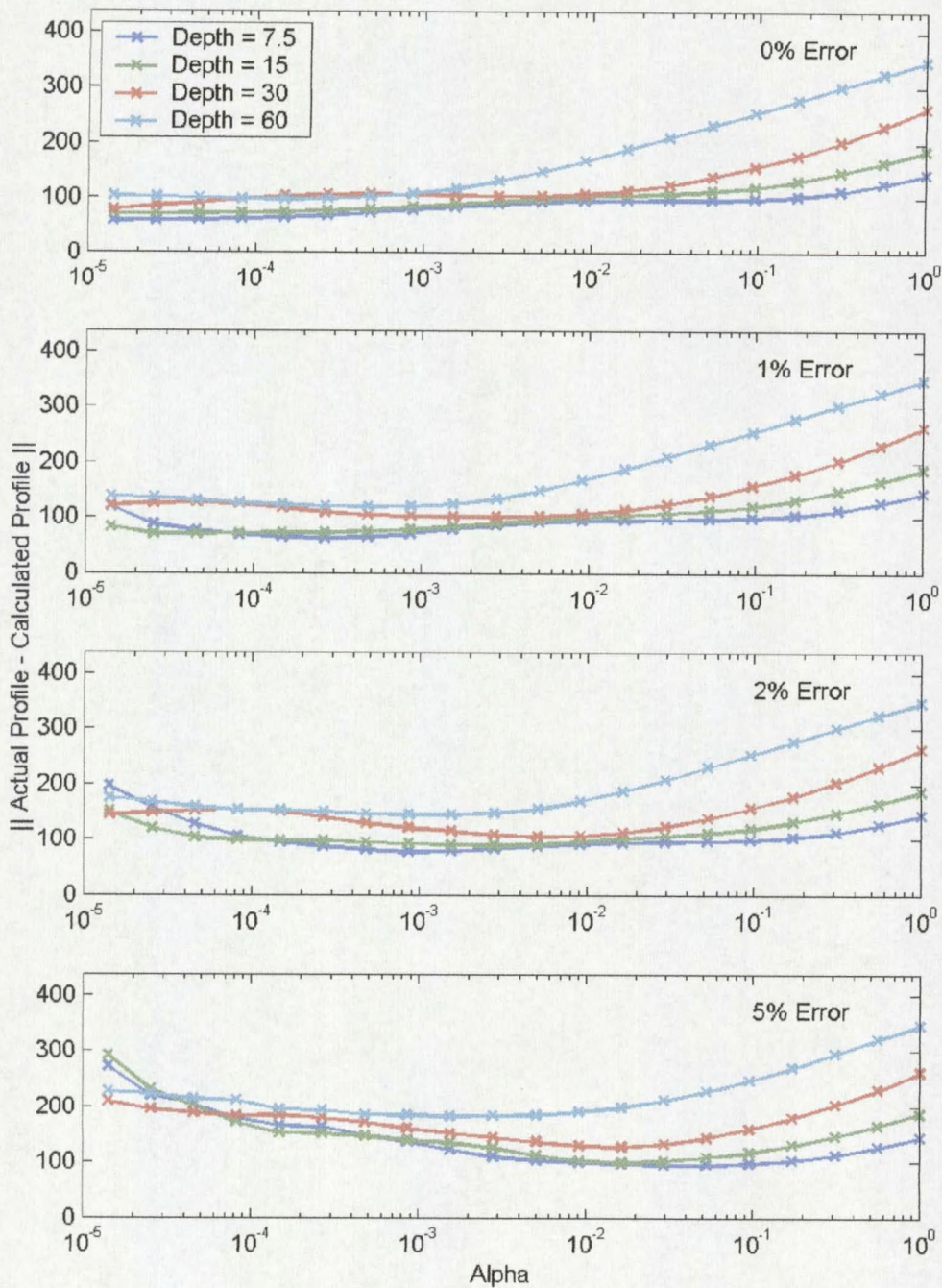


Figure 13. Mean Squared Error versus Smoothing Parameter (α) for case of the inverse gradient equal to zero

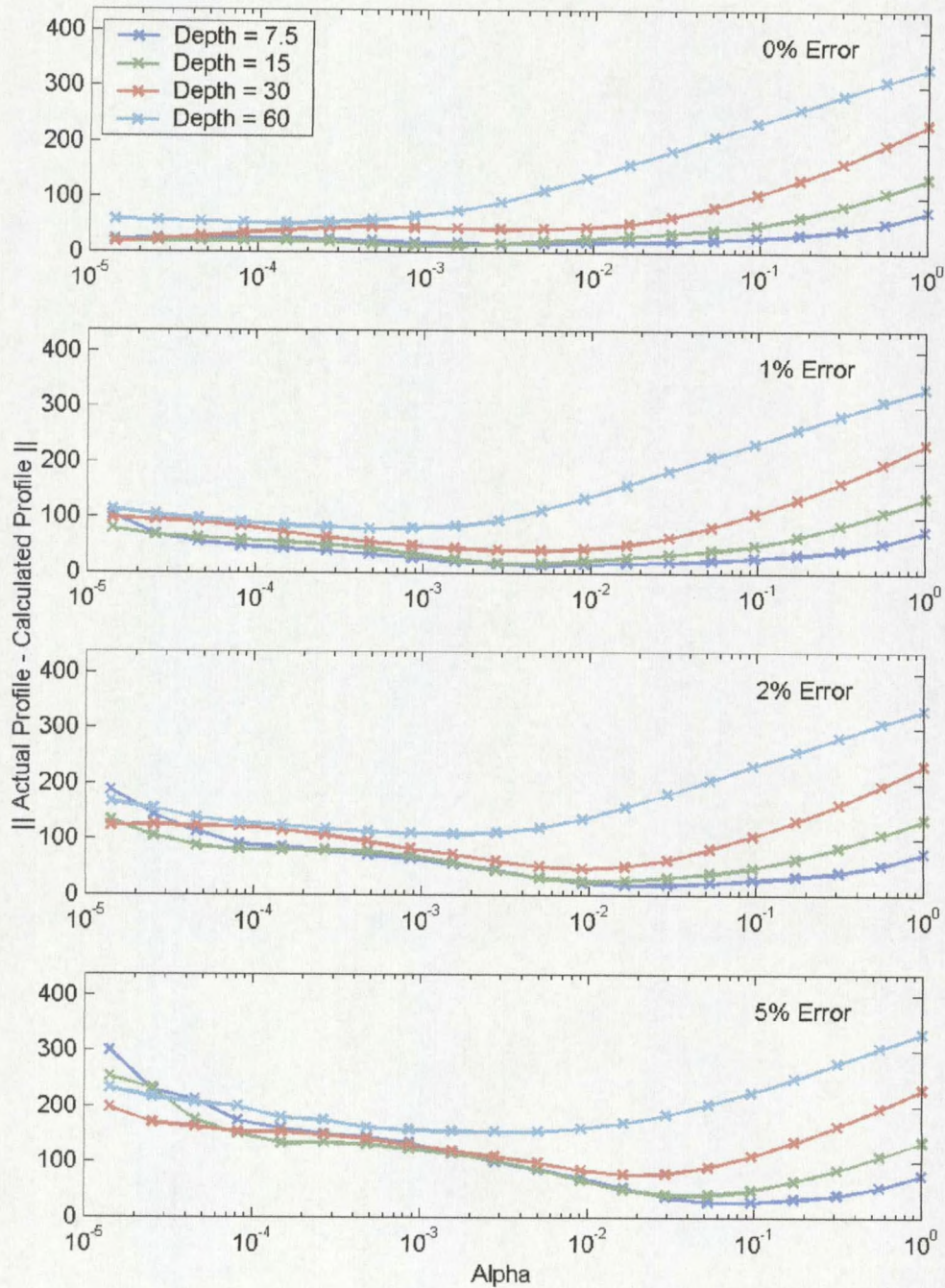


Figure 14. Mean Squared Error versus Smoothing Parameter (α) for case of the inverse gradient equal to -18.75

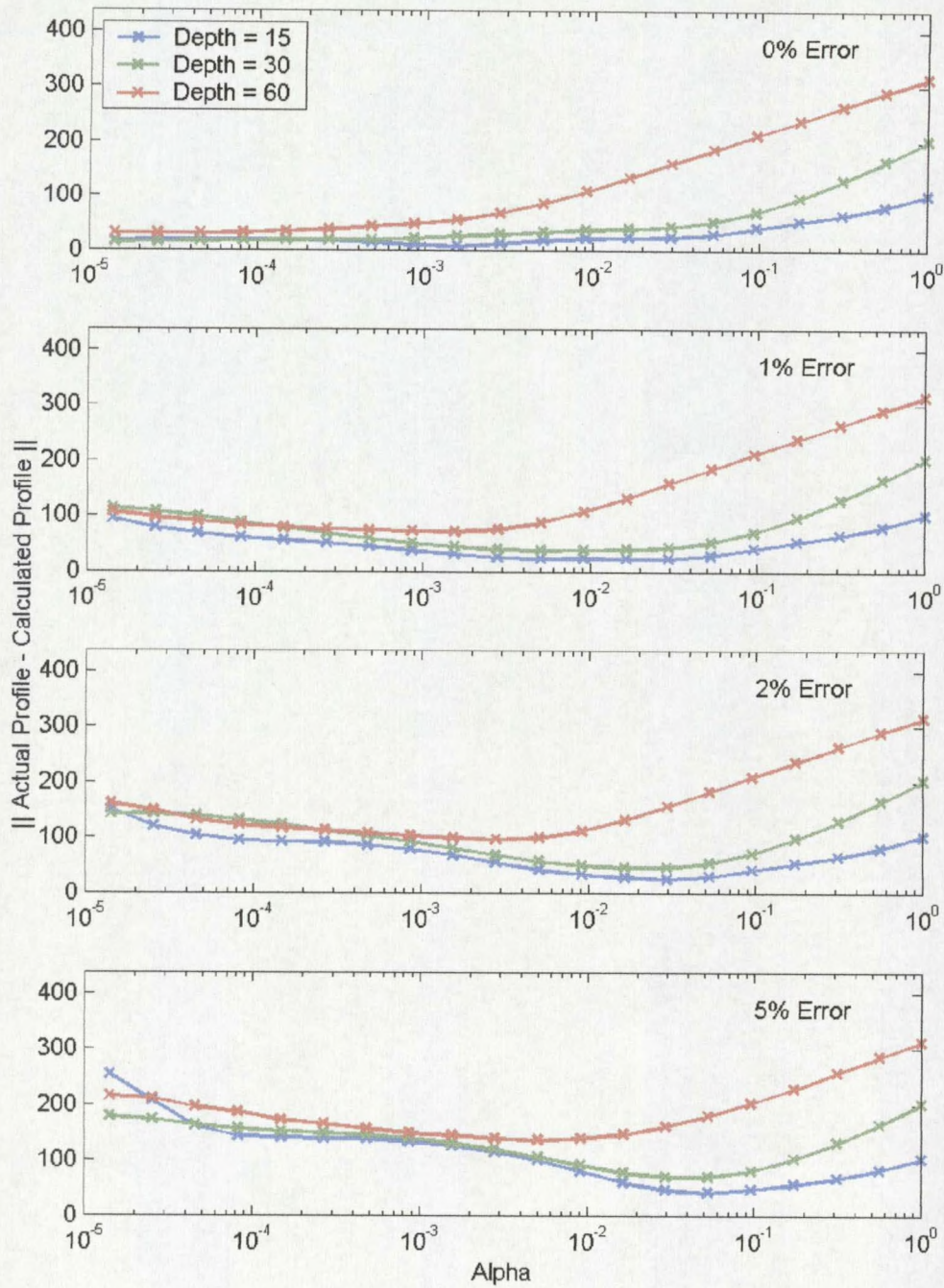


Figure 15. Mean Squared Error versus Smoothing Parameter (α) for case of the inverse gradient equal to -37.5

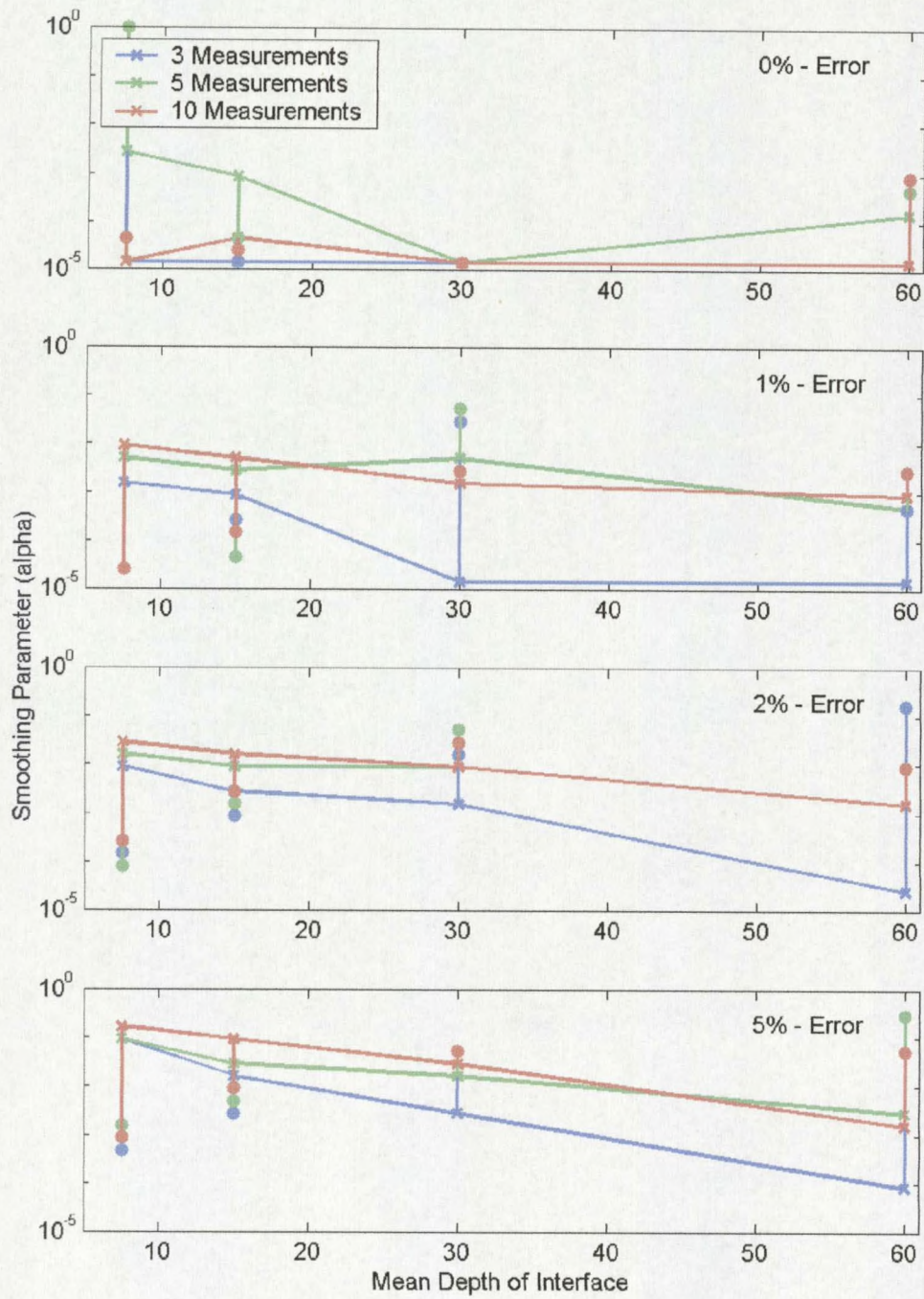


Figure 16. Comparison of Smoothing Parameters as a Function of Depth with an Inverse Gradient of -18.75 (X = Actual Best & O = Predicted Best)

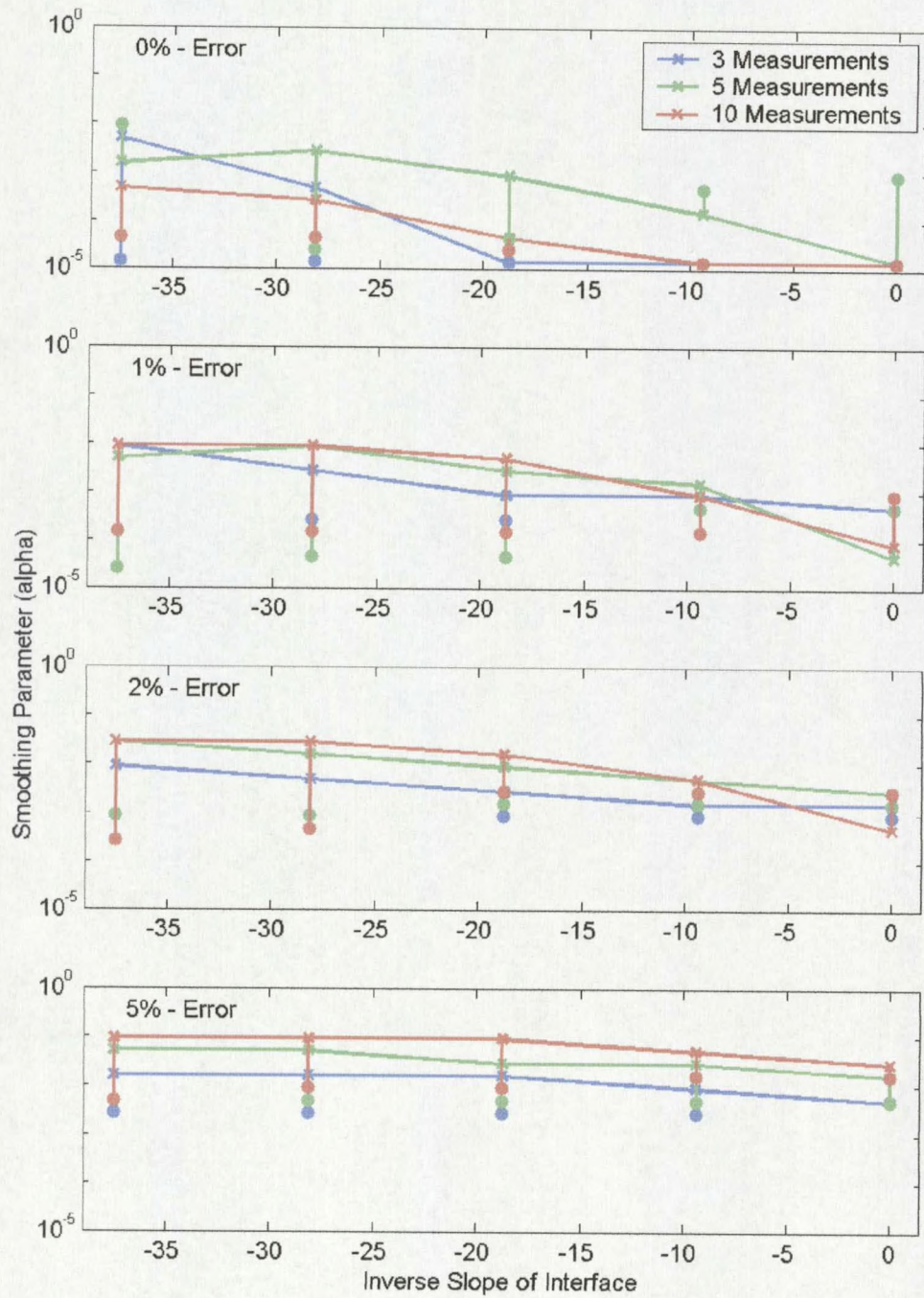


Figure 17. Comparison of Smoothing Parameters as a Function of Inverse Slope at a Depth of 15 Å (X = Actual Best & O = Predicted Best)

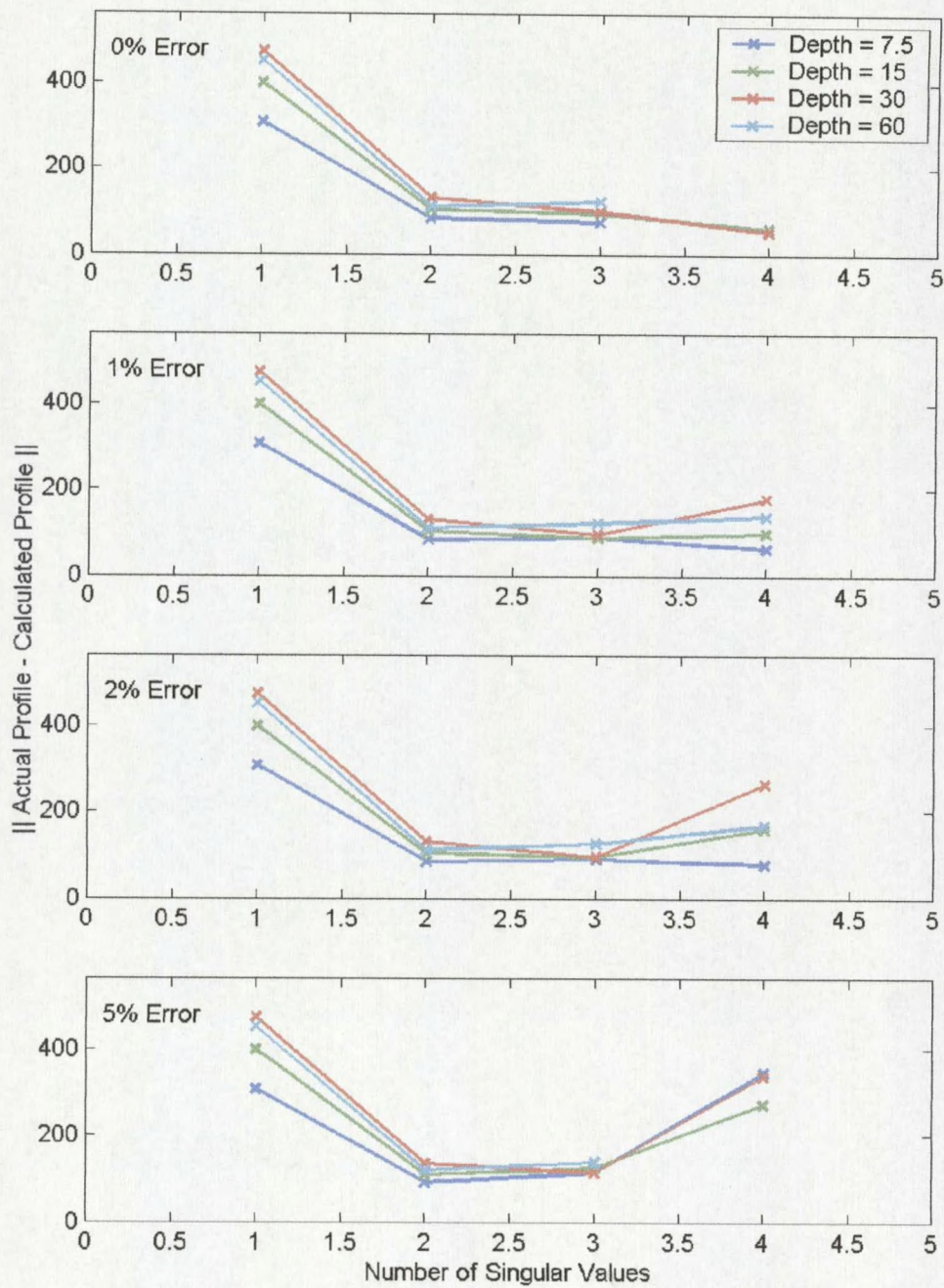


Figure 18. Mean Squared Error Verses number of Singular Values using 5 Measurements with inverse slope of zero.

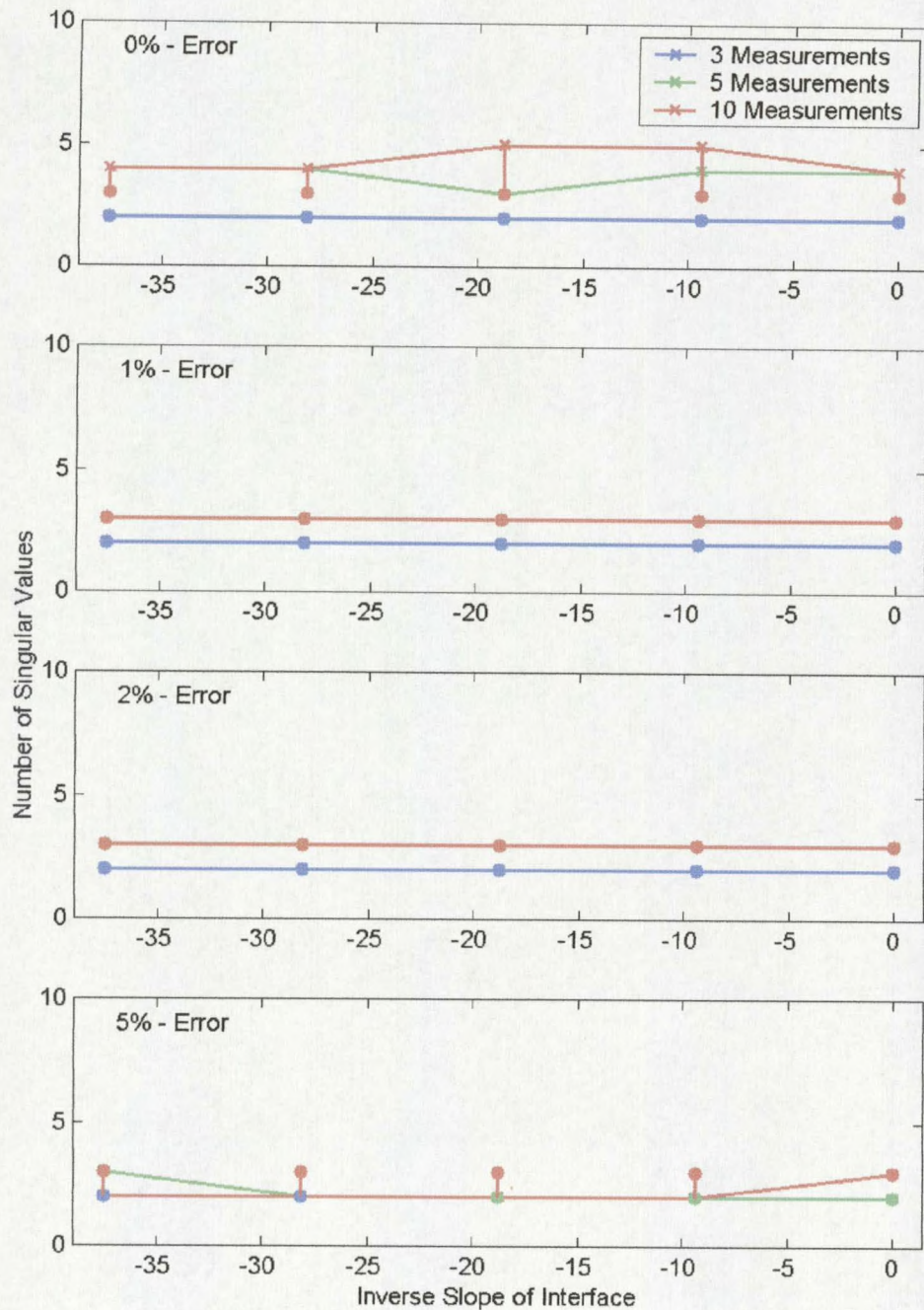


Figure 19. Comparison of Singular Values as a Function of Inverse Slope at a Depth of 15Å (X = Actual Best & O = Predicted Best)

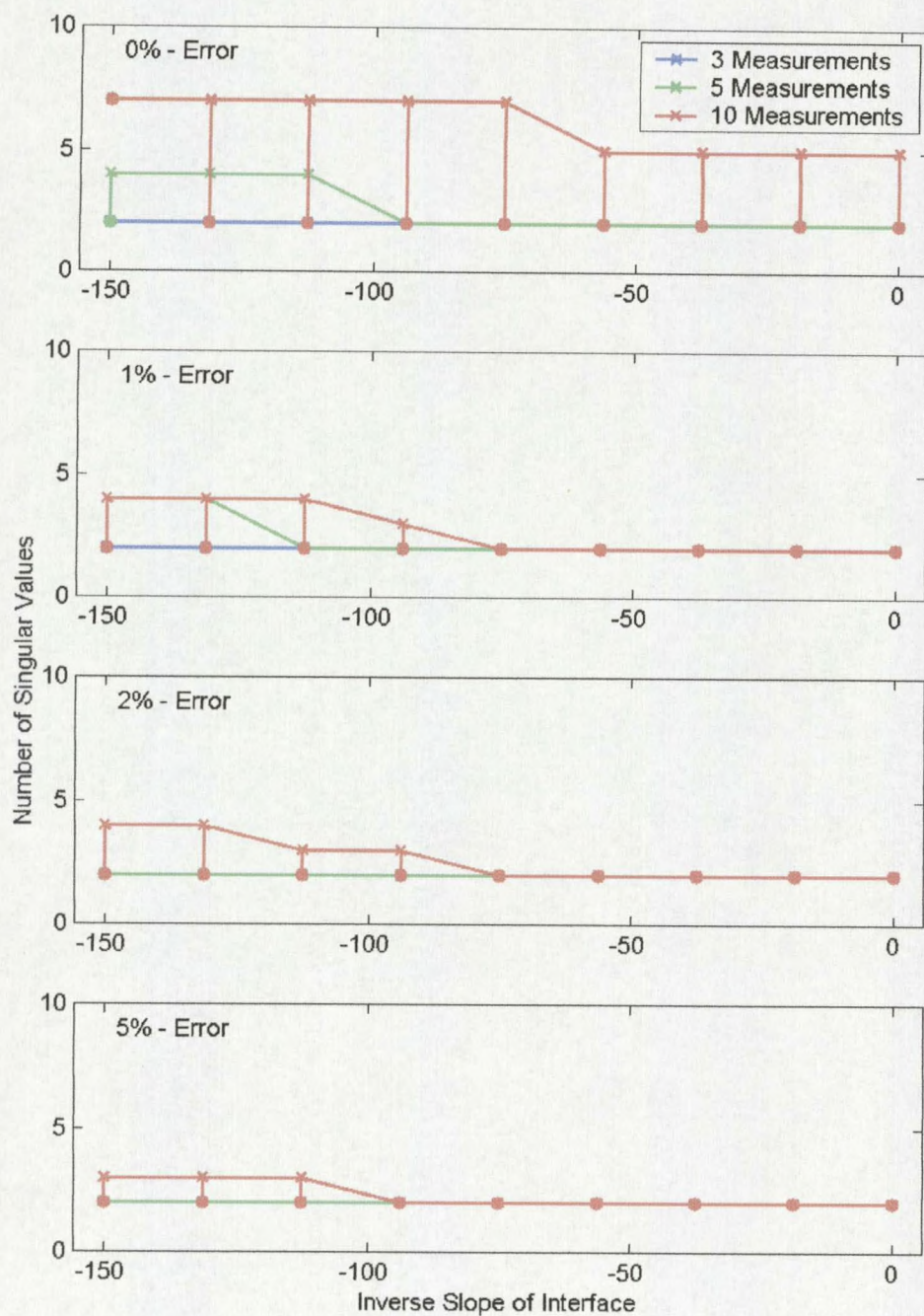


Figure 20. Comparison of Singular Values as a Function of Inverse Slope at a Depth of $60\text{\AA}$ (X = Actual Best & O = Predicted Best)

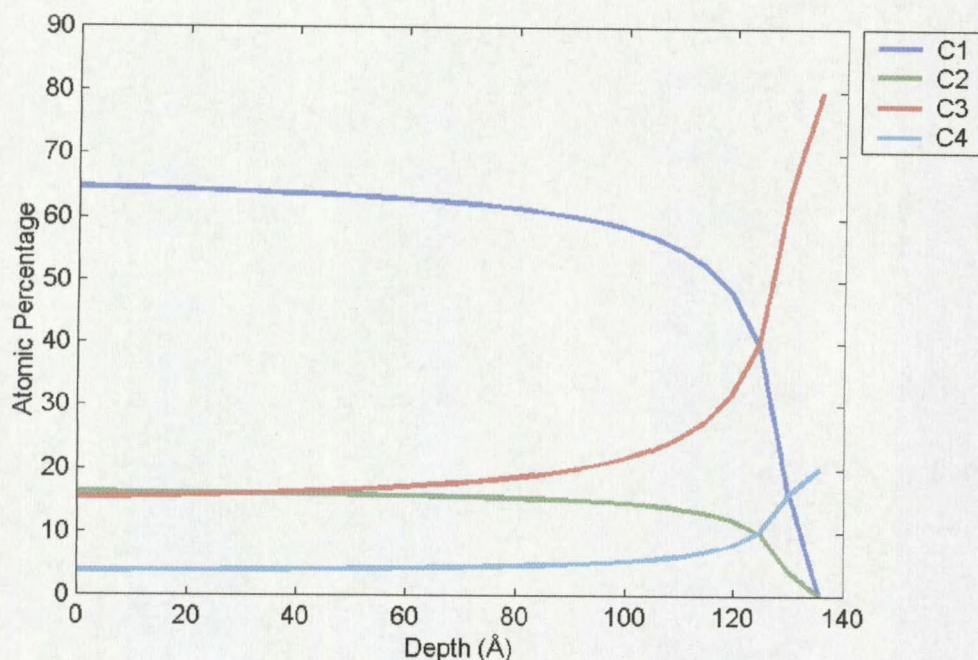


Figure 21. Approximated Profile using SVD Algorithm with Power Approximating Function where Depth of Interface = 30Å , and Inverse Gradient = 0

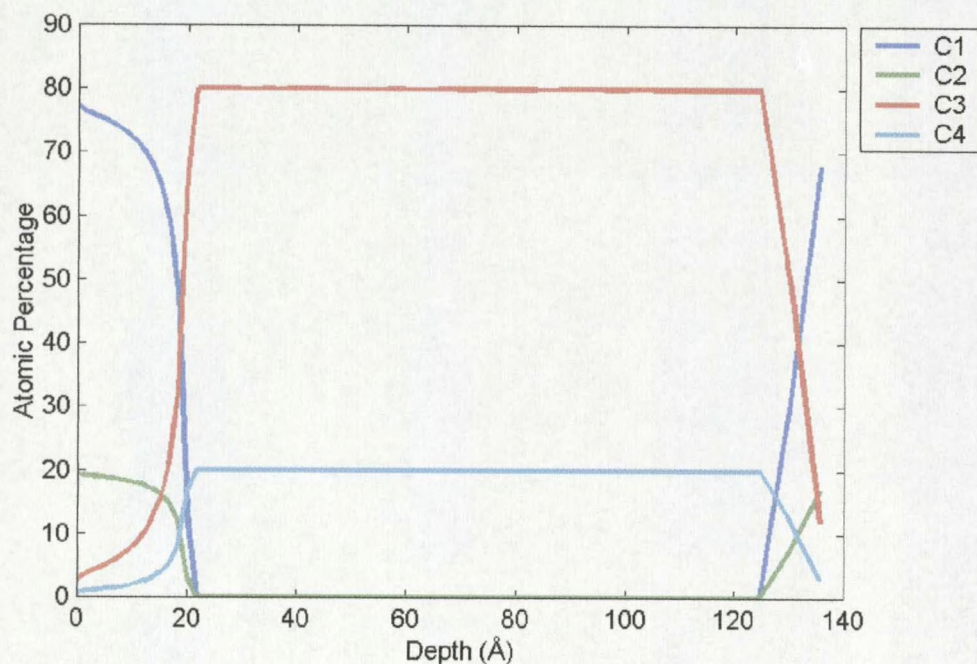


Figure 22. Approximated Profile using SVD Algorithm with Power Approximating Function where Depth of Interface = 30Å , and Inverse Gradient = 60

CHAPTER 5

ACCURACY & RESOLUTION OF TYLER REGULARIZATION

The next issue is the evaluation of the Tyler Algorithm for accuracy and resolution. This will be approached using four criteria for accuracy: mean squared error (Equation 30), deviation from the mean position of the interface, error from the actual concentration at different depths (0, 3.21, 6.78, 16.68, 29.27, 45.29, 66.67, 91.60 Å), and a qualitative evaluation of the approximated profile. This should provide for a comprehensive investigation of how accuracy is affected as the overlayer depth changes, the gradient of the interface changes, and how random error affects the approximated profile. The latter three criteria will indicate if the predictive method is more sensitive near the surface. The algorithm's ability to determine the sharpness of the interface (resolution) will be evaluated by comparing the inverse gradient to include the case where the gradient is infinite. The inverse gradient will be evaluated in three regions: the upper region (75-50% of the maximum concentration), lower region (50-25% of the maximum concentration), and overall (75-25% of the maximum concentration). As in the previous chapter, examples will be primarily drawn from the three key gradients (infinite, $-1/18.75$, and $-1/37.5$), however, any trends discussed will apply to all gradients.

Mean Squared Error (Equation 30)

The mean squared error of the approximated profile according to Equation 30 is first used for the discussion of accuracy because every point in the profile is weighted equally. This enables the profile to be evaluated as a whole and is the reason it was used in the previous chapter to select the optimum smoothing parameter.

Table 15 summarizes the mean squared error according for the Tyler Regularization algorithm. The mean squared error tends to increase as the overlayer thickness increases and tends to decrease as the inverse slope of the interface deviates from zero. This is expected because the Tyler Regularization algorithm attempts to minimize two positive functionals. As the smoothing parameter increases the solution becomes more stable but is less correlated to the measured data. Other trends observed are that mean squared error tends to decrease as the number of measurements is increased. However, little information is gained by exceeding five measurements. Also as previously stated in Chapter 4, the more random error introduced into the data set before calculation of the depth profile the more error (mean squared error) is observed in that profile.

This measure of error alone in no way provides a comprehensive analysis as to the accuracy of the Tyler regularization algorithm. As noted earlier, the mean squared error weights every point along the approximated profile equally and it is well understood that the XPS apparatus is more sensitive to the atoms near the surface. Therefore, if an experimenter is only interested in the upper 30Å of the sample, one might be willing to sacrifice accuracy deeper in the sample for better accuracy near the surface.

Although the mean squared error is used as the selection criteria for the true optimum (Equation 30), this method of selecting the smoothing parameter is unavailable with real data sets. Therefore, comparison between the true optimum and the predicted optimum can still provide a considerable amount of information. Table 16 summarizes the mean squared error data for those cases where the optimum smoothing was selected using the predictive method. Again, error tends to increase with overlayer thickness and as the inverse slope approaches zero. However, the relationship between mean squared error and slope is less pronounced, in some cases is very flat, and appears to undergo a minimum. Another observation is that increasing the number of measurements does not necessarily decrease the error in the calculated profile. Examples of these trends can be seen in Figure 23.

No correlation could be determined involving the percent difference between the predicted error or mean squared error and the overlayer thickness. However, closer to the surface ($< 30\text{\AA}$) the percent difference significantly decreases as the inverse gradient approaches zero. An example of this is shown in Figure 24. Deeper in the sample, any relationship between the gradient and the percent deviation in the predicted error from the mean squared error cannot be distinguished.

Percent Deviation from True Mean of the Depth of Interface

True Optimum Cases

The second criterion used in the discussion of accuracy is the percent deviation from the mean position of the interface. This criterion evaluates the algorithm's ability to

determine the overlayer thickness. For gradual interfaces, the value used is the depth where the concentration is midway between the concentrations in the overlayer and the substrate.

The corresponding data used in the analysis can be found in Table 17. The most notable feature in this data is the magnitude of the percent standard deviations in Table 18. All data was plotted as a function of depth and inverse gradient of the interface. Any bias in estimation of the position of the interface is small relative to the standard deviations.

Observed trends with the relative standard deviation were that it typically increased with depth of the interface and error introduced in the data (Figure 25). These relationships are possibly a direct influence of the selected smoothing parameter. There does not appear to be any correlation between the gradient of the interface and the relative standard deviation. An interesting feature of this data is that the relative standard deviations typically decreased as more measurements were taken, but it appears little benefit is gained from taking any more than five. Changing the angles at which the measurements were taken may either improve or possibly worsen depending on the take-off angles used.

Predicted Optimum Cases

The same analysis that was performed on the true optimum cases was also performed on the predicted optimum cases. This data is found in Tables 19 and 20. Again any bias in the estimation of the overlayer thickness as it relates to the mean depth

of the interface, and gradient of the interface are again obscured by large variance in the data.

The predominant trend in this data set is that the relative standard deviation goes through a minimum around 30Å (Figure 26). Again, this can be attributed to the selected smoothing parameter. It was previously mentioned that the predicted smoothing parameter is smaller in magnitude than the true optimum at depths shallower than approximately 30Å and larger than the true optimum with thicker overlayers as displayed in Figures 16. A correlation between the relative standard deviation and the gradient of the interface or the number of measurements was not observed.

Error from Actual Value

The last criteria used in the discussion of accuracy will be the error from the actual atomic fractions at different depths in the sample (0, 3.21, 6.78, 16.68, 29.27, 45.29, 66.67, 91.60 Å). Because of the sheer size of this data set, the tabulated data will not be included in the text. Rather, selected plots that illustrate key points and trends will be provided. The full data set can be found in Appendix A.

This criterion is included to address two commonly observed features in the approximated profiles. The first feature is some instability at the surface that dissipates quickly ($< \sim 5\text{\AA}$) with depth. This feature is clearly illustrated in Figure 27. The second feature of concern is that deeper in the sample the approximated profile begins to tail (Figure 27) and therefore provides questionable results. However, it should be noted that

the tailing is most pronounced at depths $>3\lambda$ which contribute little to the XPS signal. This may reflect the intensity of the XPS signal in this region.

True Optimum Cases

The deviation from the true atomic percentage was plotted against both overlayer thickness and the inverse gradient of the interface. It becomes increasingly obvious that the error associated with any given depth is directly related to how near that point is to the interface. Typically, the closer the point being analyzed is to the interface the more error present. Figures 28 and 29 display how this affects evaluation of features at both the surface and deep in the sample.

An alternative way to evaluate the approximated profiles is to qualitatively evaluate the different regions in the calculated profiles and determine what factors affect the various regions in the profile. When the profiles are evaluated in this manner, it becomes obvious that the surface instability and the tailing of the profile with depth are both a result of increasing error. The dependence of these features on the error is demonstrated in Figures 30 and 31. These features are observed at all overlayer thickness' and interface gradients to varying degrees with no apparent correlation.

Predicted Optimum Cases

The same analysis performed on the true optimum cases was performed on the predicted optimum cases. Again, the error is inflated at points near the interface, which suppress the appearance of any trends. An interesting feature that is exposed when looking at the predicted optimum is that the predicated optimum tends to demonstrate

more severe surface instability and tailing than the true optimum for thin overlayers ($<30\text{\AA}$). Just the opposite trend is observed when the overlayer is thicker, which indicates that under-smoothing may be even more directly related to surface instability and tailing than the error involved in the measurements. This is illustrated in Figures 32-35. The relationship between the smoothing parameter for both data sets and overlayer thickness can be found in Chapter 4 and is illustrated in Figure 16.

Resolution

The next logical step in the evaluation of the Tyler Regularization algorithm is the analysis of the algorithm's resolution. Here resolution is defined as the ability to distinguish between interface gradients. Resolution is essential for analysis where the actual interface is of concern or if the interface is very near the surface. Because of the algorithm's tendency to tail when under-smoothed, the analysis is divided into three parts: the upper region (75-50% of the maximum value before the interface), the bottom region (50-25% of the maximum value before the interface), and the total interface region (75-25% of the maximum value before the interface). Because of the volume of data used in the analysis, tables will not be included in this section. The data can be found in Appendix A.

True Optimum

Initial inspection of the data indicates that evaluation of the gradient in either the lower region or as a whole does not provide any useable information. Both regions tend to underestimate the inverse gradient (i.e., they tend to broaden the interfacial region) and

have very large standard deviations. These large standard deviations hide any trends that may be present in the data.

The slope of the interface in the upper region does provide some interpretable information. However, due to large variance in the data set at thick interfaces less obvious trends are concealed. This suggests that the bias in the estimate of the gradient at the interface is small relative to the standard deviation. The data for the inverse gradient and the corresponding standard deviations in the upper region is given in Tables 21 and 22.

Initial comparison of the data with that in the previous chapter indicates that the resolution at the interface is not significantly correlated with the smoothing parameter. The standard deviation, however, tends to increase with larger smoothing parameters and/or error levels. The approximated gradient also tends to predict a somewhat smoother gradient as the interface becomes deeper. This appears to be more a function of signal intensity than of the selected smoothing parameter. Probably the most obvious trend in the data is how the magnitude of the standard deviation increases with depth of the interface. These large standard deviations at deep interfaces indicate that prediction of the sharpness of the interface varies greatly even when all other parameters are held constant and therefore the gradient may frequently be incorrectly determined.

The deviation from the true gradient at different interface depths tends to overestimate the inverse gradient (smoother interface) at more gradual interfaces and underestimate the inverse gradient (sharper interface) at sharper interfaces. However, there does not appear to be any relationship that will allow prediction of when the

gradient will be over or underestimated. Again little improvement is observed when using 10 measurements rather than 5, as illustrated in Figure 36.

Predicted Optimum

Using the predictive criteria for selecting the optimum displays similar trends as those in the previous section with two notable exceptions. The most notable exception is that the very large standard deviations overshadow any bias toward estimating the gradient. (This can be seen in Tables 23 and 24.) Therefore, any observed trends other than those with the standard deviations will not be discussed. The other exception is that, at thinner overlayers, using three measurements appears to produce less variance in the approximation while just the opposite appears to be true at thicker overlayers. This is illustrated in Figure 37.

Optimum Values

In evaluating the Tyler algorithm with the simulated data sets it becomes evident that the optimum smoothing is almost solely dependent on the error present in the data. It has also been determined that little additional information is obtained by collecting spectra at more than five take-off angles. Rather, the profile is better enhanced by reducing the error in the data by achieving a better peak to noise ratio. Table 25 provides a summary table for the optimum values at the various error levels. It is believed that although the mean and median are also present in the table, the mode is the optimum value because high leverage points have little impact on its selection.

Table 15. Mean Squared Error for Tyler Regularization Algorithm According Using Data Equation 30 as the Selection Criteria

Inverse Slope of Interface (x100)	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	80.9	92.8	101.1	121.4
0.00	3	1%	81.6	92.1	97.4	119.2
0.00	3	2%	81.3	92.0	102.0	120.5
0.00	3	5%	98.5	107.5	139.5	149.2
0.00	5	0%	59.2	71.6	79.2	98.5
0.00	5	1%	62.5	70.4	102.0	120.1
0.00	5	2%	79.0	90.0	105.8	145.4
0.00	5	5%	95.3	100.0	127.6	183.7
0.00	10	0%	59.5	69.6	70.2	91.5
0.00	10	1%	60.7	56.9	94.8	106.1
0.00	10	2%	70.6	78.1	99.4	125.8
0.00	10	5%	95.1	99.9	116.3	155.5
-18.75	3	0%	21.6	16.1	40.1	89.8
-18.75	3	1%	20.6	23.9	38.8	87.3
-18.75	3	2%	23.3	30.0	52.7	87.7
-18.75	3	5%	43.9	61.8	97.8	119.9
-18.75	5	0%	16.1	12.7	19.4	53.3
-18.75	5	1%	14.9	18.3	41.4	79.9
-18.75	5	2%	18.6	24.9	47.9	110.2
-18.75	5	5%	28.3	40.6	77.2	154.4
-18.75	10	0%	4.3	7.1	12.1	41.2
-18.75	10	1%	15.6	17.5	34.3	62.9
-18.75	10	2%	17.0	23.0	42.5	87.4
-18.75	10	5%	23.9	35.4	65.1	129.1
-37.5	3	0%	N/A	26.0	32.7	79.0
-37.5	3	1%	N/A	25.6	36.4	76.5
-37.5	3	2%	N/A	31.7	49.0	75.3
-37.5	3	5%	N/A	65.0	86.0	100.9
-37.5	5	0%	N/A	8.9	15.2	32.0
-37.5	5	1%	N/A	24.3	38.9	72.9
-37.5	5	2%	N/A	25.8	46.5	97.7
-37.5	5	5%	N/A	42.4	70.5	137.4
-37.5	10	0%	N/A	9.6	9.4	16.5
-37.5	10	1%	N/A	14.6	26.9	58.4
-37.5	10	2%	N/A	23.0	42.6	79.6
-37.5	10	5%	N/A	38.2	64.0	119.3

Table 16. Mean Squared Error for Tyler Regularization Algorithm According Using Data Equation 31 as the Selection Criteria

Inverse Slope of Interface (x100)	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	80.9	92.8	161.5	136.3
0.00	3	1%	87.9	92.1	141.4	127.9
0.00	3	2%	91.2	92.2	141.2	298.9
0.00	3	5%	111.2	107.5	188.0	319.0
0.00	5	0%	59.2	85.5	79.2	103.0
0.00	5	1%	88.3	75.6	139.4	134.1
0.00	5	2%	88.4	91.1	139.1	169.6
0.00	5	5%	123.5	113.4	143.7	295.3
0.00	10	0%	60.4	69.6	70.2	101.2
0.00	10	1%	74.1	73.8	97.4	115.4
0.00	10	2%	83.8	86.8	109.4	145.9
0.00	10	5%	116.9	100.5	122.6	203.9
-18.75	3	0%	94.4	16.1	40.1	99.5
-18.75	3	1%	54.4	32.2	110.1	91.6
-18.75	3	2%	52.1	40.1	86.1	281.9
-18.75	3	5%	80.0	73.2	145.9	303.6
-18.75	5	0%	75.7	21.7	19.4	59.0
-18.75	5	1%	70.2	63.5	82.8	94.9
-18.75	5	2%	91.6	59.2	82.6	136.6
-18.75	5	5%	117.0	87.5	90.9	277.4
-18.75	10	0%	5.2	8.2	12.1	56.6
-18.75	10	1%	79.7	51.8	34.5	71.5
-18.75	10	2%	78.8	42.1	48.0	107.9
-18.75	10	5%	111.7	72.7	67.2	176.1
-37.5	3	0%	N/A	34.9	35.4	83.0
-37.5	3	1%	N/A	50.5	36.7	78.1
-37.5	3	2%	N/A	57.6	57.1	263.1
-37.5	3	5%	N/A	83.1	114.8	285.7
-37.5	5	0%	N/A	23.6	27.3	49.5
-37.5	5	1%	N/A	79.8	41.4	76.5
-37.5	5	2%	N/A	80.0	69.4	112.3
-37.5	5	5%	N/A	101.1	70.5	203.0
-37.5	10	0%	N/A	18.0	10.5	42.1
-37.5	10	1%	N/A	50.3	29.5	58.8
-37.5	10	2%	N/A	77.3	42.6	86.2
-37.5	10	5%	N/A	92.6	64.0	152.4

Table 17. Percent Deviation from True Mean Depth of the Interface for the True Optimum Cases using the Tyler Regularization Algorithm

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	4.54%	2.60%	1.55%	2.25%
0.00	3	1%	-0.63%	-0.35%	-0.98%	2.46%
0.00	3	2%	-0.59%	-0.28%	-5.45%	1.91%
0.00	3	5%	-5.58%	-1.37%	-5.81%	-1.27%
0.00	5	0%	-0.13%	0.02%	-0.94%	0.93%
0.00	5	1%	-1.81%	-5.46%	-0.82%	-1.89%
0.00	5	2%	0.74%	-1.86%	-1.95%	-1.79%
0.00	5	5%	0.27%	-2.38%	-5.32%	-10.72%
0.00	10	0%	-0.66%	0.39%	0.16%	0.61%
0.00	10	1%	-2.31%	-5.28%	-1.73%	-1.49%
0.00	10	2%	-1.97%	-5.17%	-1.10%	-2.64%
0.00	10	5%	-1.88%	-0.64%	-3.51%	-10.27%
-18.75	3	0%	8.56%	4.76%	0.47%	1.32%
-18.75	3	1%	1.68%	-0.38%	-2.15%	1.55%
-18.75	3	2%	-5.01%	-2.52%	-4.66%	1.07%
-18.75	3	5%	-21.98%	-8.53%	-4.06%	-2.11%
-18.75	5	0%	-8.00%	-3.76%	-3.37%	0.01%
-18.75	5	1%	-4.66%	-1.62%	-2.59%	-2.70%
-18.75	5	2%	-4.35%	-1.87%	-3.87%	0.47%
-18.75	5	5%	-13.01%	-6.55%	-6.65%	-7.13%
-18.75	10	0%	-2.67%	-1.95%	-1.83%	0.23%
-18.75	10	1%	-8.69%	-2.21%	-1.76%	-2.36%
-18.75	10	2%	-5.91%	-1.66%	-2.71%	-3.37%
-18.75	10	5%	-10.26%	-6.64%	-5.37%	-8.08%
-37.5	3	0%	N/A	-2.80%	-4.68%	-1.53%
-37.5	3	1%	N/A	-7.87%	-6.77%	-1.08%
-37.5	3	2%	N/A	-8.89%	-8.07%	-1.17%
-37.5	3	5%	N/A	-14.83%	-9.13%	-4.36%
-37.5	5	0%	N/A	-2.09%	-2.43%	-0.43%
-37.5	5	1%	N/A	-1.66%	-6.70%	-4.56%
-37.5	5	2%	N/A	-7.93%	-9.18%	-2.19%
-37.5	5	5%	N/A	-14.30%	-13.52%	0.13%
-37.5	10	0%	N/A	-4.90%	-2.12%	0.40%
-37.5	10	1%	N/A	-1.88%	-4.31%	-4.46%
-37.5	10	2%	N/A	-4.88%	-7.65%	-4.53%
-37.5	10	5%	N/A	-13.38%	-11.14%	2.27%

Table 18. Percent Standard Deviation from True Mean Depth of the Interface for the True Optimum Data using the Tyler Regularization Algorithm

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	0.00%	0.00%	0.00%	0.00%
0.00	3	1%	7.93%	9.53%	10.37%	4.01%
0.00	3	2%	10.85%	9.28%	21.61%	12.52%
0.00	3	5%	6.59%	14.85%	37.81%	40.82%
0.00	5	0%	0.00%	0.00%	0.00%	0.00%
0.00	5	1%	8.46%	13.37%	3.63%	13.46%
0.00	5	2%	11.16%	7.29%	5.79%	29.96%
0.00	5	5%	46.38%	7.83%	10.55%	40.68%
0.00	10	0%	0.00%	0.00%	0.00%	0.00%
0.00	10	1%	5.29%	16.34%	4.51%	5.54%
0.00	10	2%	49.02%	23.27%	4.77%	14.25%
0.00	10	5%	6.40%	5.81%	8.26%	35.31%
-18.75	3	0%	0.00%	0.00%	0.00%	0.00%
-18.75	3	1%	10.79%	7.21%	9.74%	4.07%
-18.75	3	2%	11.82%	8.91%	12.68%	12.47%
-18.75	3	5%	5.33%	13.50%	34.81%	40.90%
-18.75	5	0%	0.00%	0.00%	0.00%	0.00%
-18.75	5	1%	8.79%	3.38%	2.76%	13.36%
-18.75	5	2%	8.37%	4.31%	4.41%	27.56%
-18.75	5	5%	7.65%	7.99%	10.36%	40.27%
-18.75	10	0%	0.00%	0.00%	0.00%	0.00%
-18.75	10	1%	5.98%	2.41%	3.92%	5.55%
-18.75	10	2%	5.94%	3.03%	4.09%	14.28%
-18.75	10	5%	4.70%	4.81%	6.42%	33.13%
-37.5	3	0%	N/A	0.00%	0.00%	0.00%
-37.5	3	1%	N/A	7.00%	3.05%	4.23%
-37.5	3	2%	N/A	11.70%	7.09%	12.44%
-37.5	3	5%	N/A	19.09%	31.03%	41.84%
-37.5	5	0%	N/A	0.00%	0.00%	0.00%
-37.5	5	1%	N/A	3.63%	3.26%	6.25%
-37.5	5	2%	N/A	5.46%	3.16%	22.28%
-37.5	5	5%	N/A	10.42%	5.53%	41.68%
-37.5	10	0%	N/A	0.00%	0.00%	0.00%
-37.5	10	1%	N/A	3.28%	3.80%	4.33%
-37.5	10	2%	N/A	4.38%	3.92%	13.01%
-37.5	10	5%	N/A	7.40%	5.18%	36.88%

Table 19. Percent Deviation from True Mean Depth of the Interface for the Predicted Optimum Cases using the Tyler Regularization Algorithm

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	4.54%	2.60%	-9.27%	-1.45%
0.00	3	1%	-4.42%	-0.35%	-6.57%	0.33%
0.00	3	2%	-5.19%	-2.06%	-7.07%	76.43%
0.00	3	5%	-3.88%	-1.37%	-10.79%	54.93%
0.00	5	0%	-0.13%	-0.79%	-0.94%	0.67%
0.00	5	1%	-2.88%	-2.82%	-8.05%	-2.65%
0.00	5	2%	-2.58%	-3.32%	-8.20%	-3.91%
0.00	5	5%	11.77%	-5.57%	-8.66%	65.26%
0.00	10	0%	-0.57%	0.39%	0.16%	0.56%
0.00	10	1%	0.40%	-2.67%	0.00%	-1.89%
0.00	10	2%	3.00%	-3.09%	-2.31%	-3.35%
0.00	10	5%	9.39%	-1.67%	-5.01%	11.26%
-18.75	3	0%	-56.30%	4.76%	0.47%	-2.08%
-18.75	3	1%	-3.10%	-2.78%	-10.51%	-0.46%
-18.75	3	2%	-1.80%	-4.72%	-8.23%	75.92%
-18.75	3	5%	0.66%	-6.33%	-12.53%	55.44%
-18.75	5	0%	-44.62%	-7.26%	-3.37%	-0.26%
-18.75	5	1%	2.61%	-5.79%	-9.29%	-3.32%
-18.75	5	2%	-5.07%	-5.50%	-9.42%	-4.43%
-18.75	5	5%	8.65%	-8.46%	-9.88%	64.60%
-18.75	10	0%	-2.54%	-1.61%	-1.83%	-0.43%
-18.75	10	1%	19.66%	-6.11%	-1.41%	-2.63%
-18.75	10	2%	0.18%	-4.44%	-4.07%	-3.92%
-18.75	10	5%	10.40%	-5.45%	-6.60%	10.71%
-37.5	3	0%	N/A	4.69%	-3.97%	-4.19%
-37.5	3	1%	N/A	-1.13%	-5.64%	-2.77%
-37.5	3	2%	N/A	-4.90%	-11.60%	74.38%
-37.5	3	5%	N/A	-10.34%	-17.87%	55.95%
-37.5	5	0%	N/A	-1.99%	-4.42%	-3.00%
-37.5	5	1%	N/A	3.11%	-5.99%	-5.31%
-37.5	5	2%	N/A	-7.26%	-7.13%	-6.05%
-37.5	5	5%	N/A	-9.44%	-13.52%	30.43%
-37.5	10	0%	N/A	-5.46%	-1.73%	-2.73%
-37.5	10	1%	N/A	0.99%	-5.62%	-4.80%
-37.5	10	2%	N/A	3.71%	-7.65%	-5.72%
-37.5	10	5%	N/A	-1.90%	-11.14%	9.10%

Table 20. Percent Standard Deviation from True Mean Depth of the Interface for the Predicted Best Data using the Tyler Regularization Algorithm

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	0.00%	0.00%	0.00%	0.00%
0.00	3	1%	12.04%	9.53%	1.70%	4.28%
0.00	3	2%	14.53%	11.60%	3.88%	29.05%
0.00	3	5%	22.48%	14.85%	27.02%	65.82%
0.00	5	0%	0.00%	0.00%	0.00%	0.00%
0.00	5	1%	22.20%	7.01%	0.93%	5.51%
0.00	5	2%	15.60%	9.50%	1.92%	13.77%
0.00	5	5%	101.49%	12.72%	6.04%	43.17%
0.00	10	0%	0.00%	0.00%	0.00%	0.00%
0.00	10	1%	74.48%	3.97%	2.85%	3.36%
0.00	10	2%	101.63%	6.31%	2.29%	11.30%
0.00	10	5%	143.76%	7.59%	4.93%	39.97%
-18.75	3	0%	0.00%	0.00%	0.00%	0.00%
-18.75	3	1%	13.41%	10.94%	1.05%	4.32%
-18.75	3	2%	15.95%	11.75%	3.69%	29.33%
-18.75	3	5%	25.54%	17.75%	25.27%	65.15%
-18.75	5	0%	0.00%	0.00%	0.00%	0.00%
-18.75	5	1%	63.35%	24.97%	0.85%	5.50%
-18.75	5	2%	28.52%	8.98%	1.84%	14.02%
-18.75	5	5%	85.73%	13.25%	5.89%	43.46%
-18.75	10	0%	0.00%	0.00%	0.00%	0.00%
-18.75	10	1%	135.44%	7.73%	3.26%	3.35%
-18.75	10	2%	67.56%	6.79%	2.33%	11.35%
-18.75	10	5%	142.76%	10.89%	4.94%	40.00%
-37.5	3	0%	N/A	0.00%	0.00%	0.00%
-37.5	3	1%	N/A	10.20%	4.07%	4.44%
-37.5	3	2%	N/A	13.18%	3.27%	30.13%
-37.5	3	5%	N/A	23.42%	16.02%	63.96%
-37.5	5	0%	N/A	0.00%	0.00%	0.00%
-37.5	5	1%	N/A	58.65%	4.74%	5.49%
-37.5	5	2%	N/A	16.91%	8.96%	14.15%
-37.5	5	5%	N/A	31.18%	5.53%	50.25%
-37.5	10	0%	N/A	0.00%	0.00%	0.00%
-37.5	10	1%	N/A	27.86%	2.94%	3.39%
-37.5	10	2%	N/A	56.31%	3.92%	11.02%
-37.5	10	5%	N/A	48.21%	5.18%	40.14%

Table 21. Approximated Inverse gradient(x100) as predicted by the Tyler Algorithm (Optimum)

Inverse Slope of Interface (x100)	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	-11.40	-14.61	-17.83	-21.73
0.00	3	1%	-11.20	-13.18	-14.76	-22.60
0.00	3	2%	-9.98	-11.99	-12.88	-27.42
0.00	3	5%	-9.42	-10.27	-14.35	-38.45
0.00	5	0%	-5.32	-6.27	-9.85	-22.24
0.00	5	1%	-5.64	-4.10	-16.50	-22.23
0.00	5	2%	-5.98	-11.19	-15.60	-31.57
0.00	5	5%	-11.16	-12.58	-17.38	-33.27
0.00	10	0%	-5.37	-6.96	-8.37	-24.21
0.00	10	1%	-5.54	-4.62	-16.46	-18.45
0.00	10	2%	-6.94	-5.92	-15.78	-22.91
0.00	10	5%	-11.33	-13.59	-14.28	-26.24
-18.75	3	0%	-22.85	-21.68	-20.49	-23.01
-18.75	3	1%	-20.15	-19.30	-17.74	-23.30
-18.75	3	2%	-17.83	-16.96	-17.79	-28.06
-18.75	3	5%	-11.77	-14.12	-24.11	-38.24
-18.75	5	0%	-18.00	-18.36	-15.78	-23.45
-18.75	5	1%	-18.18	-19.29	-18.38	-22.95
-18.75	5	2%	-18.10	-19.21	-18.06	-40.31
-18.75	5	5%	-14.98	-16.29	-18.41	-31.81
-18.75	10	0%	-17.74	-17.59	-17.25	-28.97
-18.75	10	1%	-17.62	-20.19	-22.08	-19.36
-18.75	10	2%	-18.27	-20.15	-18.14	-23.87
-18.75	10	5%	-15.51	-16.11	-17.08	-29.99
-37.5	3	0%	N/A	-30.21	-27.69	-23.62
-37.5	3	1%	N/A	-29.43	-27.89	-25.10
-37.5	3	2%	N/A	-26.88	-26.06	-29.90
-37.5	3	5%	N/A	-21.25	-27.75	-38.48
-37.5	5	0%	N/A	-35.76	-40.21	-39.91
-37.5	5	1%	N/A	-30.07	-25.06	-27.88
-37.5	5	2%	N/A	-27.71	-23.52	-44.43
-37.5	5	5%	N/A	-25.45	-28.14	-72.87
-37.5	10	0%	N/A	-34.50	-37.32	-42.36
-37.5	10	1%	N/A	-33.94	-30.47	-24.10
-37.5	10	2%	N/A	-29.39	-25.12	-29.42
-37.5	10	5%	N/A	-26.18	-23.07	-67.43

Table 22. Standard Deviations (x100) Associated with the Approximated Inverse Gradient as Predicted by the Tyler Algorithm (Optimum)

Inverse Slope of Interface (x100)	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	0.00	0.00	0.00	0.00
0.00	3	1%	5.56	6.17	5.63	6.77
0.00	3	2%	6.05	5.67	7.25	14.52
0.00	3	5%	2.61	5.98	27.10	83.05
0.00	5	0%	0.00	0.00	0.00	0.00
0.00	5	1%	3.33	18.70	3.44	30.12
0.00	5	2%	3.43	4.74	5.17	79.95
0.00	5	5%	17.35	4.55	9.16	94.91
0.00	10	0%	0.00	0.00	0.00	0.00
0.00	10	1%	2.24	11.36	5.47	8.13
0.00	10	2%	18.61	23.60	4.56	32.66
0.00	10	5%	2.24	4.38	6.17	71.86
-18.75	3	0%	0.00	0.00	0.00	0.00
-18.75	3	1%	2.94	6.64	6.33	6.98
-18.75	3	2%	4.52	5.60	8.21	15.03
-18.75	3	5%	2.52	4.62	43.68	86.28
-18.75	5	0%	0.00	0.00	0.00	0.00
-18.75	5	1%	2.23	3.20	2.72	30.50
-18.75	5	2%	2.32	3.53	4.38	76.58
-18.75	5	5%	2.72	3.74	9.56	414.21
-18.75	10	0%	0.00	0.00	0.00	0.00
-18.75	10	1%	1.76	2.13	5.12	8.40
-18.75	10	2%	1.75	2.74	3.97	33.10
-18.75	10	5%	1.94	2.37	5.83	78.23
-37.5	3	0%	N/A	0.00	0.00	0.00
-37.5	3	1%	N/A	1.85	4.29	7.65
-37.5	3	2%	N/A	3.80	8.39	16.76
-37.5	3	5%	N/A	6.62	47.01	90.78
-37.5	5	0%	N/A	0.00	0.00	0.00
-37.5	5	1%	N/A	3.73	3.60	17.31
-37.5	5	2%	N/A	1.99	3.76	66.62
-37.5	5	5%	N/A	4.00	7.71	114.09
-37.5	10	0%	N/A	0.00	0.00	0.00
-37.5	10	1%	N/A	3.27	3.49	8.39
-37.5	10	2%	N/A	2.54	4.01	33.81
-37.5	10	5%	N/A	3.24	5.56	102.23

Table 23. Approximated Inverse Gradient as Predicted by the Tyler Algorithm
(Predictive Optimum)

Inverse Slope of Interface (x100)	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	-11.40	-14.61	-36.47	-26.46
0.00	3	1%	-10.76	-13.18	-29.67	-25.40
0.00	3	2%	-9.07	-10.91	-29.00	-327.55
0.00	3	5%	-5.99	-10.27	-46.05	1238.18
0.00	5	0%	-5.32	-10.37	-9.85	-22.02
0.00	5	1%	-4.84	-7.70	-25.69	-29.29
0.00	5	2%	-4.72	-9.03	-25.58	-49.28
0.00	5	5%	-8.13	-9.99	-25.32	-212.46
0.00	10	0%	-5.60	-6.96	-8.37	-21.42
0.00	10	1%	-5.54	-8.30	-17.79	-22.71
0.00	10	2%	-7.45	-10.80	-17.13	-36.19
0.00	10	5%	-8.74	-13.13	-18.16	-107.10
-18.75	3	0%	-13.60	-21.68	-20.49	-27.38
-18.75	3	1%	-15.45	-17.36	-36.38	-25.90
-18.75	3	2%	-15.04	-14.90	-29.54	-328.24
-18.75	3	5%	-11.09	-11.32	-45.00	1187.78
-18.75	5	0%	-15.22	-13.10	-15.78	-22.30
-18.75	5	1%	-11.09	-9.24	-26.46	-29.82
-18.75	5	2%	-8.48	-13.92	-26.32	-49.59
-18.75	5	5%	-11.13	-13.14	-25.95	-212.66
-18.75	10	0%	-17.29	-17.55	-17.25	-21.61
-18.75	10	1%	-14.12	-11.60	-21.73	-23.70
-18.75	10	2%	-12.27	-17.41	-18.53	-36.70
-18.75	10	5%	-12.14	-17.04	-19.20	-106.93
-37.5	3	0%	N/A	-28.40	-26.24	-28.39
-37.5	3	1%	N/A	-25.09	-26.32	-27.52
-37.5	3	2%	N/A	-23.04	-31.88	-330.19
-37.5	3	5%	N/A	-17.39	-41.94	1096.42
-37.5	5	0%	N/A	-29.30	-30.45	-27.08
-37.5	5	1%	N/A	-27.05	-26.46	-31.80
-37.5	5	2%	N/A	-25.63	-24.17	-50.42
-37.5	5	5%	N/A	-21.45	-28.14	-172.35
-37.5	10	0%	N/A	-30.23	-38.76	-27.00
-37.5	10	1%	N/A	-33.10	-28.68	-26.10
-37.5	10	2%	N/A	-32.04	-25.12	-38.17
-37.5	10	5%	N/A	-31.96	-23.07	-106.60

Table 24. Standard Deviations (x100) Associated with the Approximated Inverse Gradient as Predicted by the Tyler Algorithm (Predictive Optimum)

Inverse Slope of Interface (x100)	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	0.00	0.00	0.00	0.00
0.00	3	1%	7.56	6.17	2.81	7.81
0.00	3	2%	7.11	6.13	5.76	75.27
0.00	3	5%	5.25	5.98	41.76	4051.88
0.00	5	0%	0.00	0.00	0.00	0.00
0.00	5	1%	6.14	3.64	1.23	15.77
0.00	5	2%	4.25	5.46	2.53	39.91
0.00	5	5%	38.63	7.89	7.64	1102.59
0.00	10	0%	0.00	0.00	0.00	0.00
0.00	10	1%	27.74	2.26	3.27	6.41
0.00	10	2%	37.87	4.02	2.10	31.93
0.00	10	5%	49.79	5.83	4.74	400.09
-18.75	3	0%	0.00	0.00	0.00	0.00
-18.75	3	1%	9.84	8.70	2.00	7.97
-18.75	3	2%	10.05	8.21	5.58	76.30
-18.75	3	5%	9.56	7.92	38.95	3995.60
-18.75	5	0%	0.00	0.00	0.00	0.00
-18.75	5	1%	23.78	5.86	1.18	15.83
-18.75	5	2%	9.78	7.27	2.48	40.70
-18.75	5	5%	26.89	9.25	7.65	1102.71
-18.75	10	0%	0.00	0.00	0.00	0.00
-18.75	10	1%	23.43	4.71	3.74	6.60
-18.75	10	2%	23.70	5.95	2.28	32.24
-18.75	10	5%	44.36	9.72	4.88	400.16
-37.5	3	0%	N/A	0.00	0.00	0.00
-37.5	3	1%	N/A	11.03	5.32	8.48
-37.5	3	2%	N/A	11.54	5.13	79.46
-37.5	3	5%	N/A	11.33	23.75	3894.68
-37.5	5	0%	N/A	0.00	0.00	0.00
-37.5	5	1%	N/A	51.89	4.98	16.08
-37.5	5	2%	N/A	15.61	8.95	41.24
-37.5	5	5%	N/A	26.87	7.71	682.22
-37.5	10	0%	N/A	0.00	0.00	0.00
-37.5	10	1%	N/A	32.05	2.69	7.15
-37.5	10	2%	N/A	42.60	4.01	31.42
-37.5	10	5%	N/A	37.96	5.56	400.42

Table 25. Optimum Summary for Tyler Regularization Algorithm using Five Measurements

	Uniformly Distributed Random Error			
	0%	1%	2%	5%
Mode	1.412E-05	1.556E-03	9.074E-03	2.940E-02
Median	8.235E-05	2.178E-03	9.074E-03	2.940E-02
Mean	4.448E-04	3.097E-03	1.135E-02	3.544E-02
STD	8.159E-04	3.512E-03	1.181E-02	2.540E-02
Skewness	2.324	2.654	2.241	0.914
Kurtosis	4.674	8.584	6.008	0.712
1-log_{1.8}(Mode)	20	12	9	7

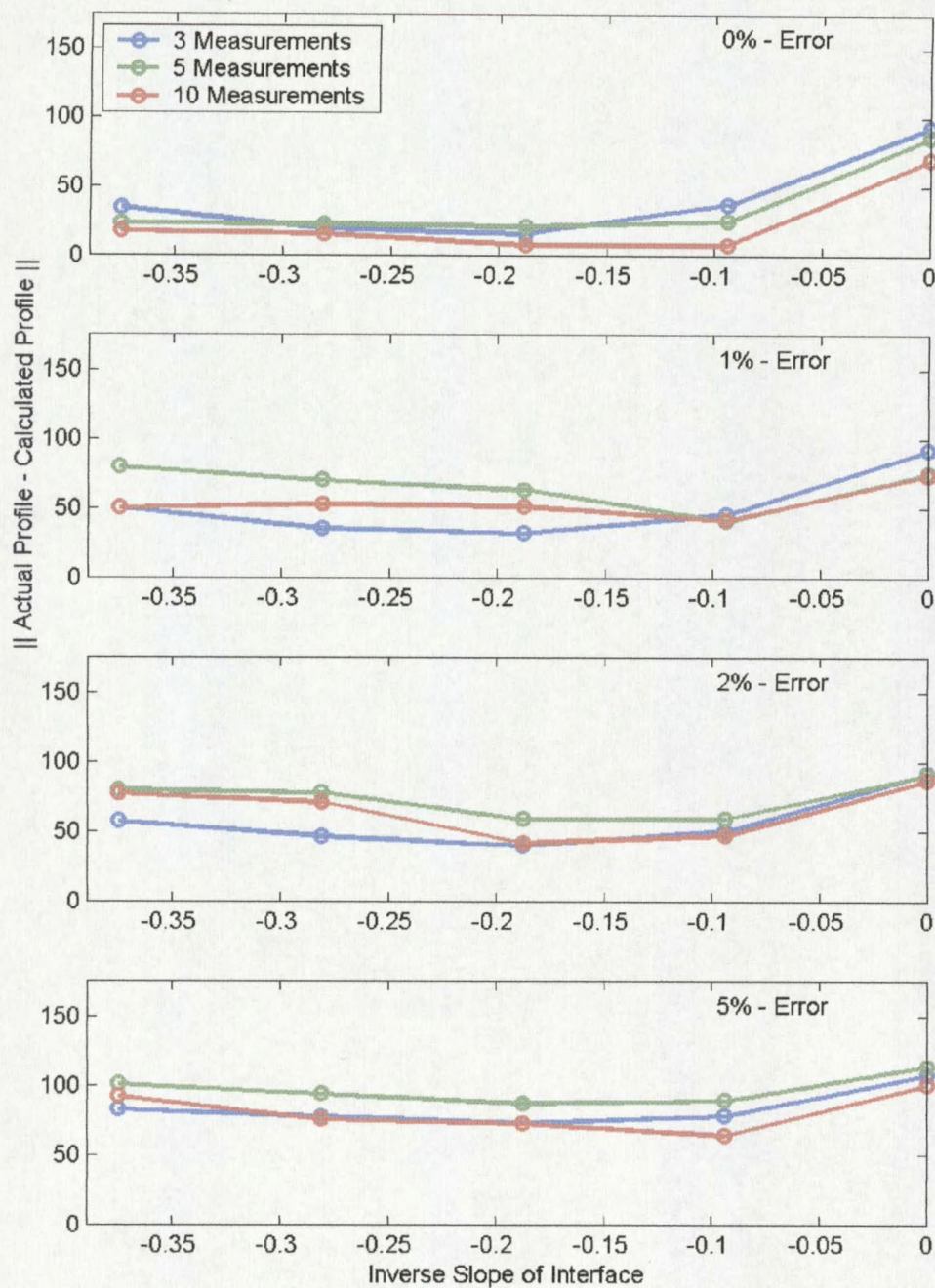


Figure 23. Mean Squared Error Predicted by Equation 31 for Regularization Algorithm with overlayer thickness equal to 15Å

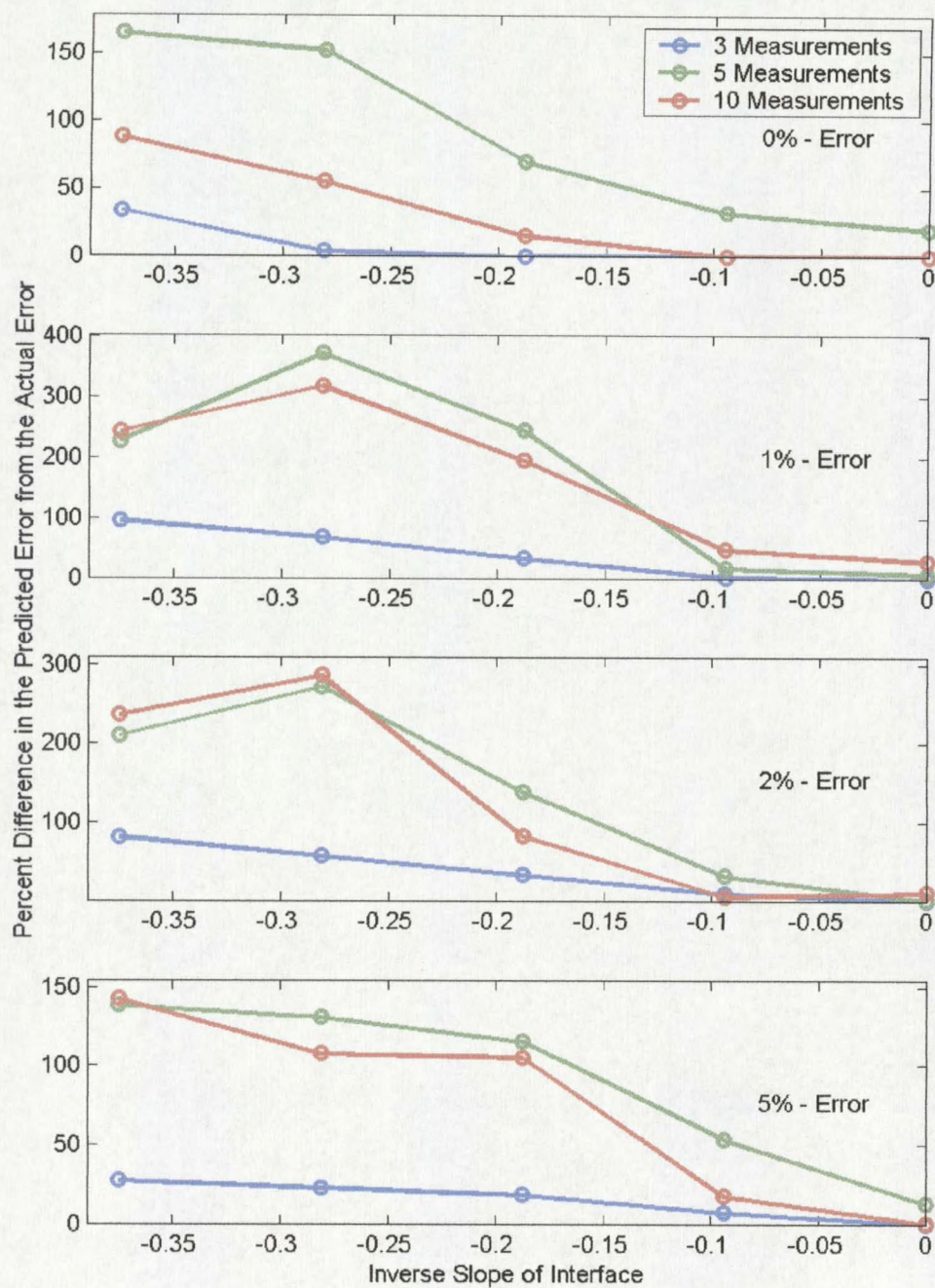


Figure 24. Percent Difference in the Predicted Error from the Mean Squared Error for Regularization Algorithm with overlayer thickness equal to 15Å

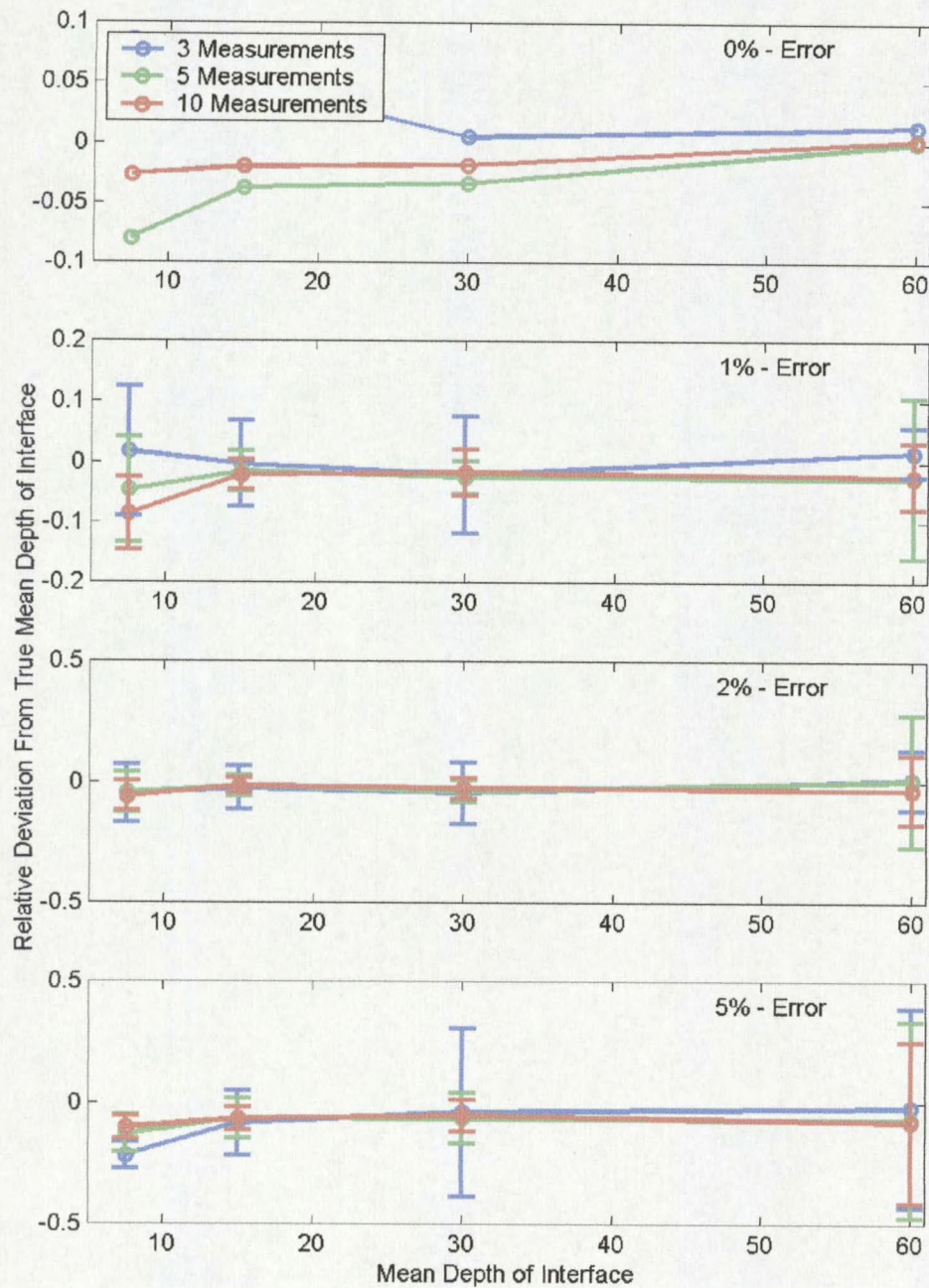


Figure 25. Relative Deviation from the True Mean Depth of the Interface as a Function of Interface Depth with Inverse Gradient of -18.75×10^{-2} (Error Bars = $\pm$ Relative Standard Deviation)

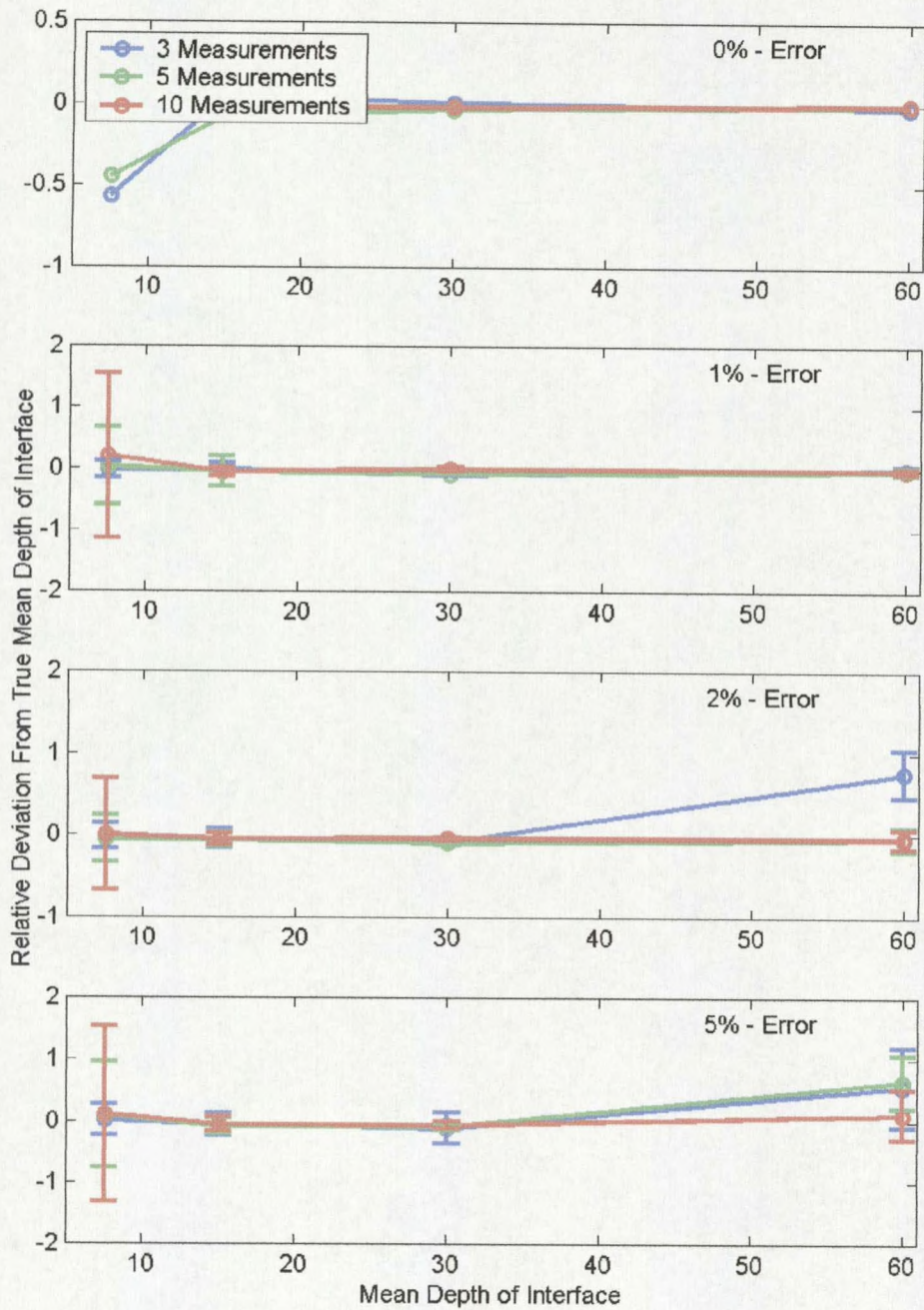


Figure 26. Predicted Relative Deviation from the True Mean Depth of the Interface as a Function of Interface Depth with Inverse Gradient of -18.75×10^{-2} (Error Bars = $\pm$ Relative Standard Deviation)

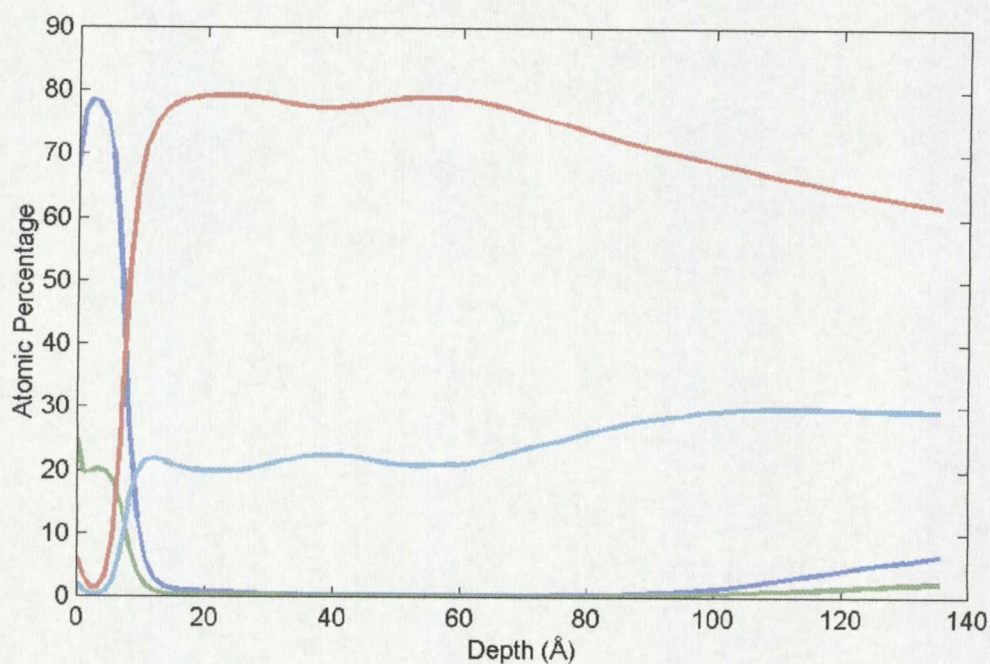


Figure 27. Approximated Profile using Tyler Regularization (Overlayther Thickness = $7.5\text{\AA}$, Inverse Gradient = 0, 5 Measurements, and 2% Random Error Introduced)

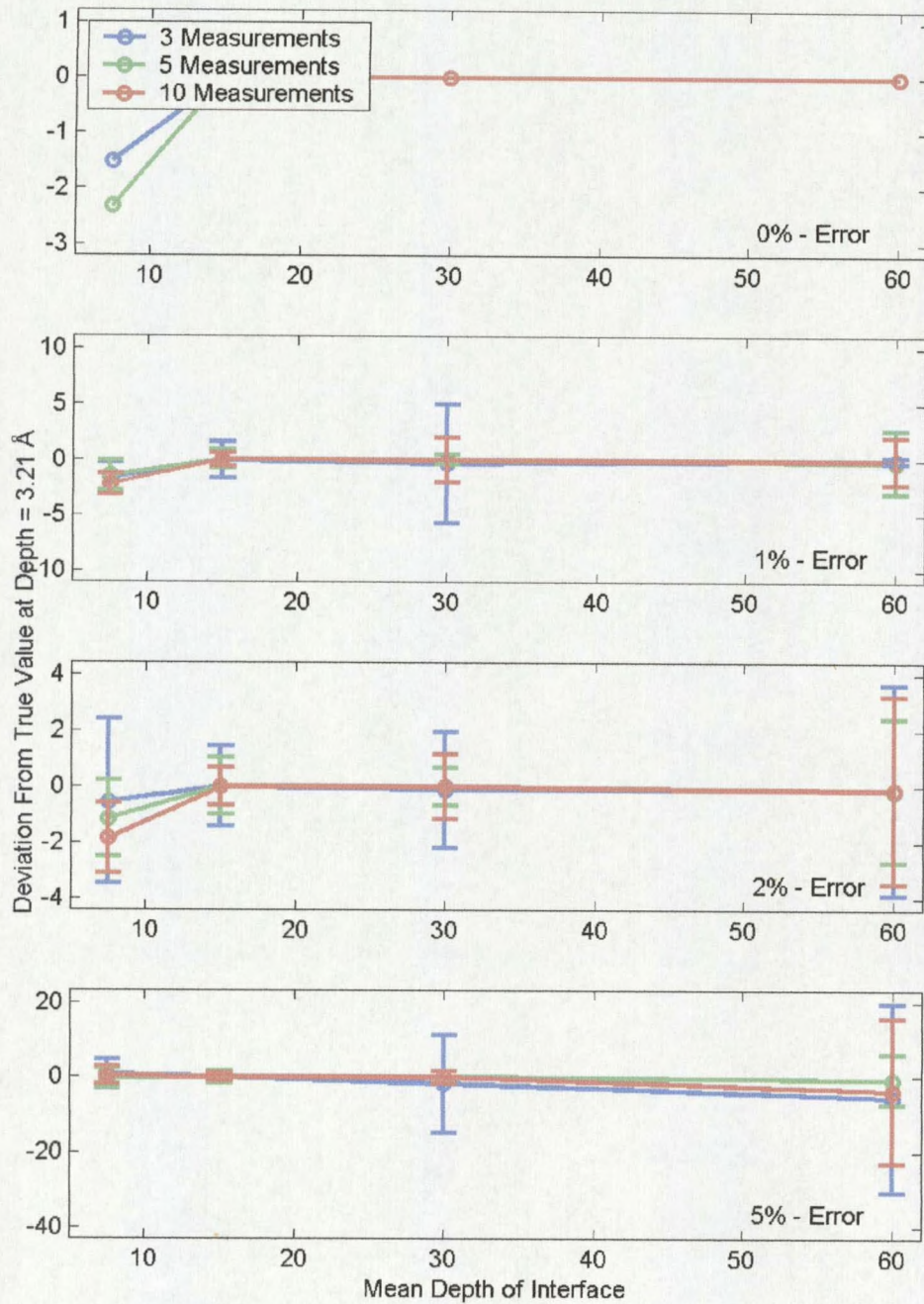


Figure 28. Deviation From True Value at Depth 3.21Å verses Mean Depth of Interface with an Inverse Gradient of -18.75×10^{-2}

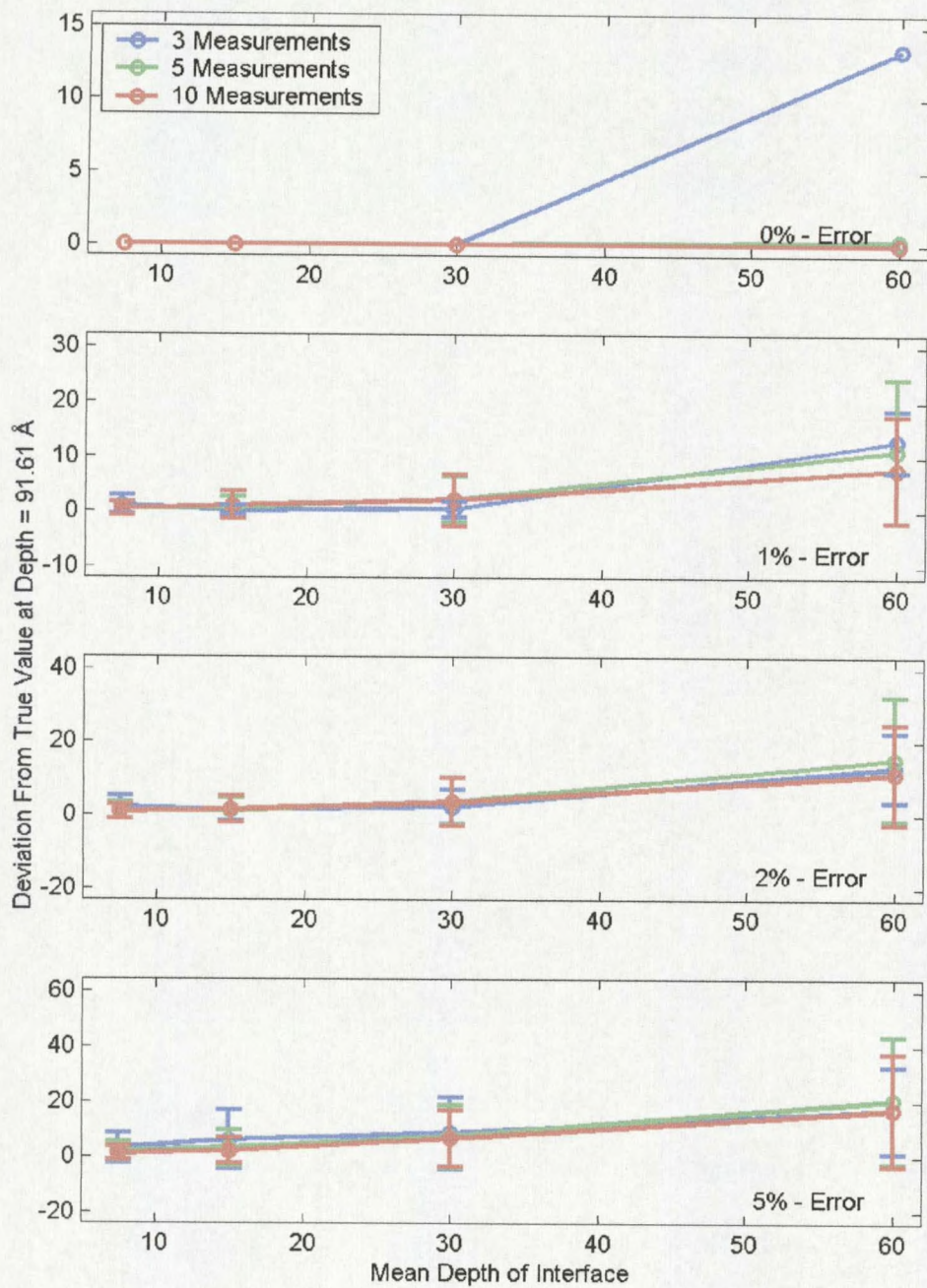


Figure 29. Deviation From True Value at Depth 91.61 Å versus Mean Depth of Interface with an Inverse Gradient of -18.75×10^{-2}

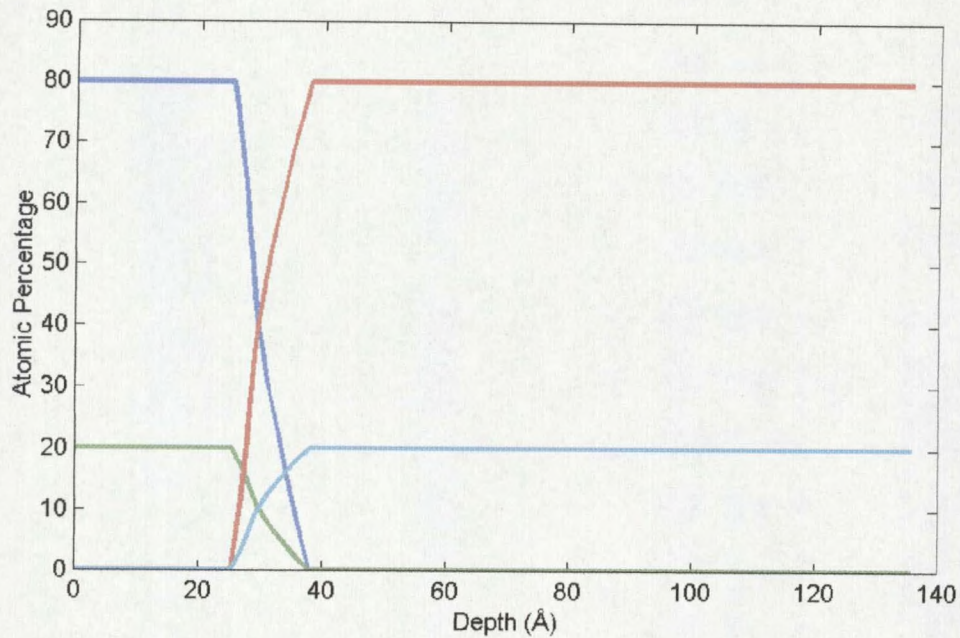


Figure 30. Approximated Profile using Five Measurements for Overlayer Thickness of 30 Å, Inverse Gradient of 0, and 0 Error

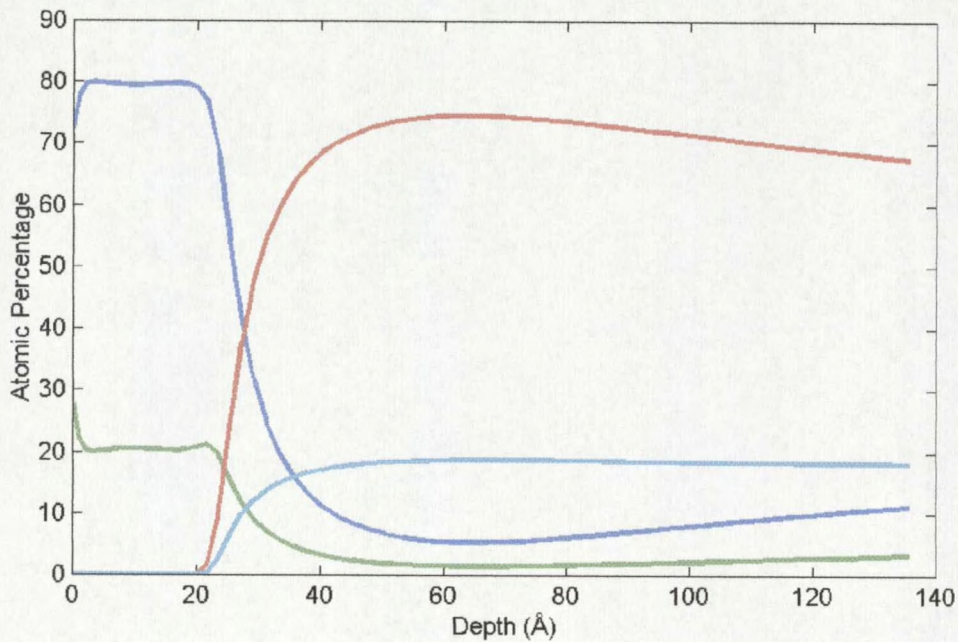


Figure 31. Approximated Profile using Five Measurements for Overlayer Thickness of 30 Å, Inverse Gradient of 0, and 0 Error

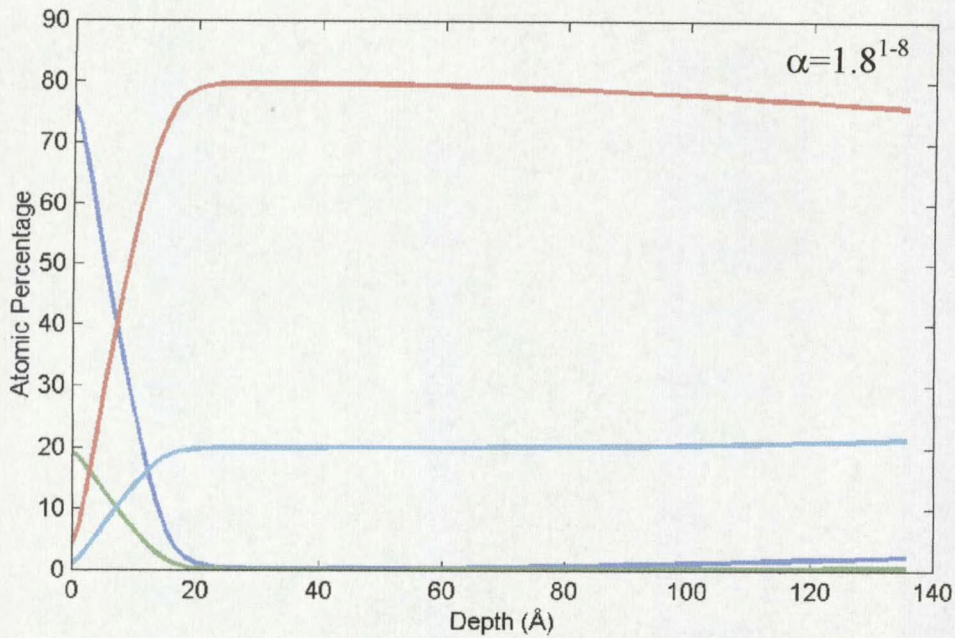


Figure 32. True Optimum Approximated Profile using Five Measurements for Overlayer Thickness of 7.5Å , Inverse Gradient of -18.75×10^{-2} , and 2 Error

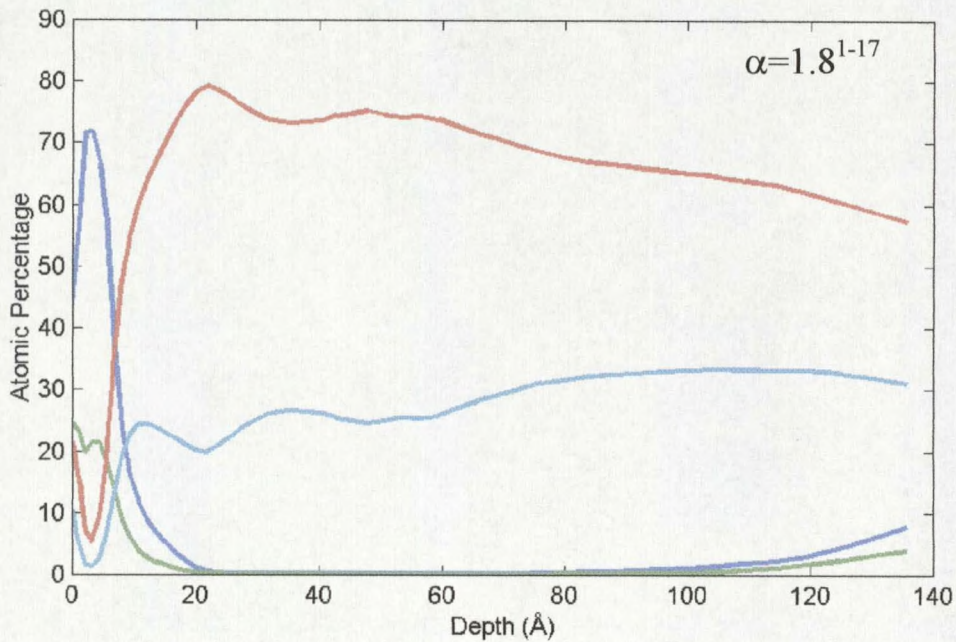


Figure 33. Predicted Optimum Approximated Profile using Five Measurements for Overlayer Thickness of 7.5Å , Inverse Gradient of -18.75×10^{-2} , and 2 Error

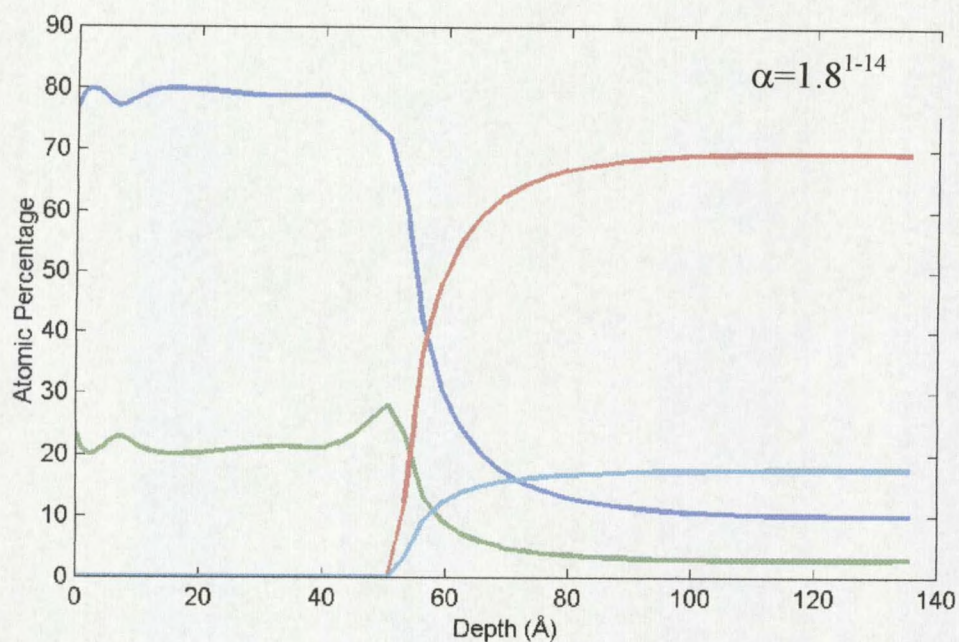


Figure 34. True Optimum Approximated Profile using Five Measurements for Overlayer Thickness of 60Å, Inverse Gradient of -18.75×10^{-2} , and 1 Error

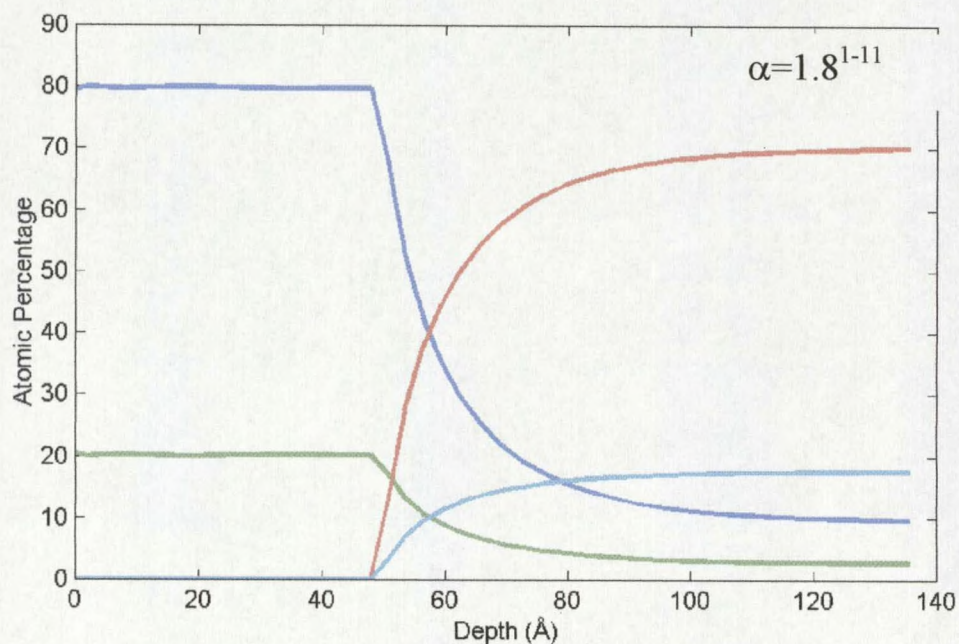


Figure 35. Predicted Optimum Approximated Profile using Five Measurements for Overlayer Thickness of 60Å, Inverse Gradient of -18.75×10^{-2} , and 1 Error

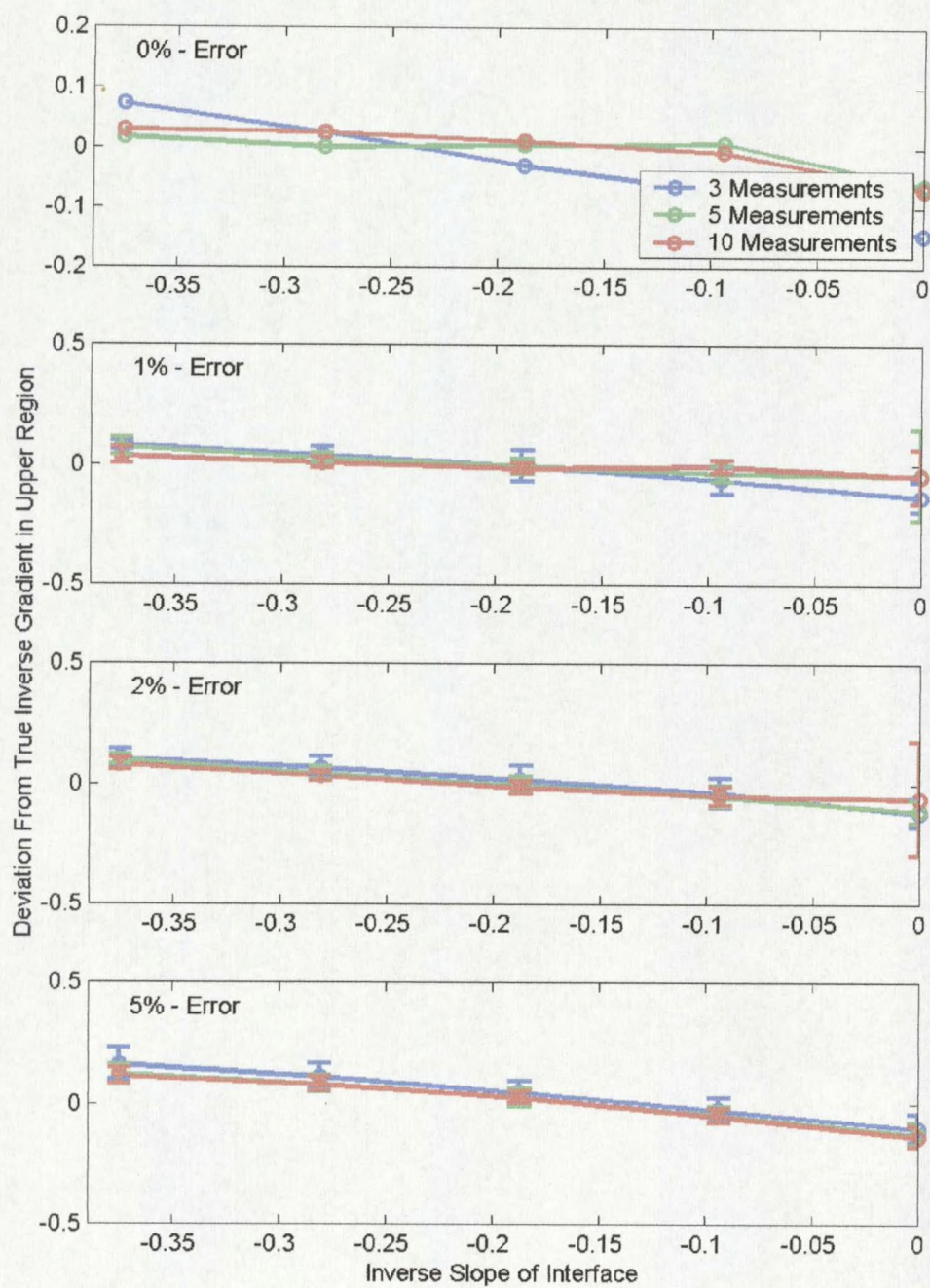


Figure 36. Deviation from the True Inverse Gradient as a function of Inverse Gradient for Depth of $7.5 \text{ \AA}$

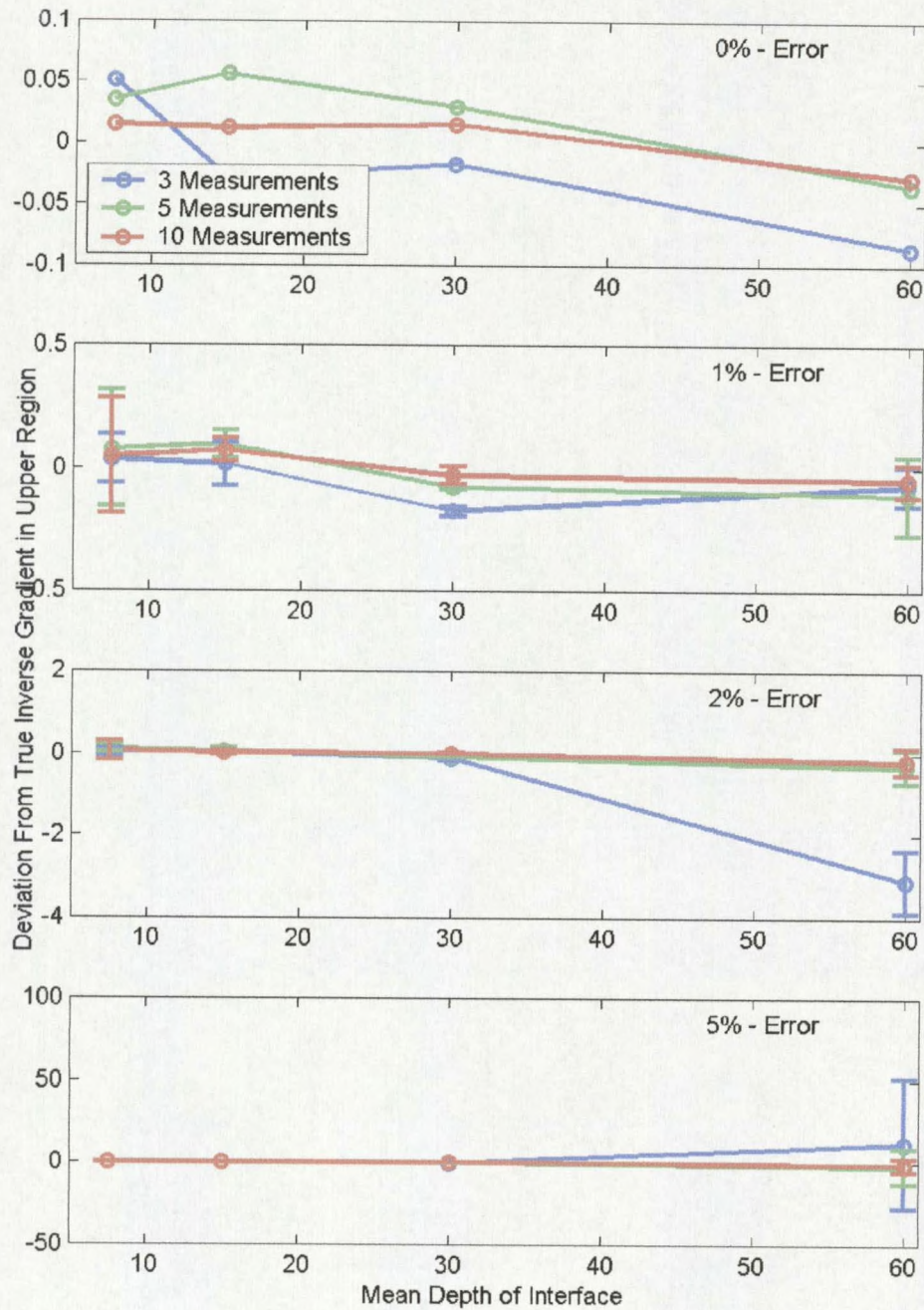


Figure 37. Deviation from the True Inverse Gradient as a function of Depth with True Inverse Gradient of -18.75×10^{-2}

CHAPTER 6

ACCURACY & RESOLUTION OF SINGULAR VALUE DECOMPOSITION

Evaluation of the Singular Value Decomposition algorithm will proceed similarly to that used with Tyler Regularization. The same four criteria for accuracy used in the previous chapter (actual error, deviation from the mean position of the interface, error from the actual value at different depths, and a qualitative evaluation of the approximated profile) will be used to assess the SVD algorithm. The resolution or algorithm's ability to distinguish between interface gradients will be evaluated using the inverse slope to include the interface with the infinite gradient. Again the inverse gradient will be evaluated in three regions: the upper region (75-50% of the maximum concentration), lower region (50-25% of the maximum concentration), and overall (75-25% of the maximum concentration). As in the previous chapters, examples will be primarily drawn from the three principal gradients (infinite, $-1/18.75$, and $-1/37.5$), however, any trends discussed apply to all gradients.

Mean Squared Error (Equation 30)

The mean squared error of the approximated profile is again used first in the discussion of accuracy because it assumes all points are equally important which enables the profile to be evaluated as a whole.

True Optimum Cases

Table 26 summarizes the mean squared error (Equation 30) for the approximated profiles generated using the Singular Value Decomposition algorithm. The most notable trend in the data set is that the error in the approximated profile increases with overlayer thickness (Figure 38), however, the relationship is still relatively flat when compared to that approximated using the Tyler Algorithm. This may be a preliminary indication that Singular Value Decomposition does not exhibit the tailing seen in the previous chapter or that the algorithm provides better accuracy and/or resolution deeper in the sample. Much like the Tyler Algorithm, the error in the approximated profile tends to reach a maximum at the sharpest interface (negative infinity).

Predicted Optimum

Data using the predictive optimum as the selection criteria can be found in Table 27. The data in Chapter 4 indicates that the predictive selection criteria typically selects the same number of singular values as the true optimum (~80%), however, in those cases where there is a discrepancy, the predictive method tends to underestimate the number of singular values needed. This discrepancy is typically only one singular value but it translates into errors of up to about 100% greater than those in the true optimum cases do. On a few occasions the predictive criteria selected one singular value. One singular value results in a homogeneous sample as seen in Figure 39. This forces one to question the validity of using the predictive method with this algorithm.

Relative Deviation from True Mean Overlayer Thickness

True Optimum

The Singular Value Decomposition data was again generated by calculating the depth at which the concentration is 50% of its maximum value (80%) and finding the relative deviation from that of true depth value. The data was then tabulated (Tables 28 & 29) and plotted as a function of depth, and inverse gradient of the interface.

Features observed with the data set include the observation that the relative deviation from the true mean overlayer thickness and its associated relative standard deviation is somewhat larger near the surface (Figure 40). Any bias toward estimation of the overlayer thickness as a function of mean depth of the interface is obscured by the large standard deviations at the surface and impairs the ability to draw any inference. The standard deviations in the data displays an insignificant relationship, if any, with the inverse gradient.

Also the SVD algorithm tends to underestimate the mean overlayer thickness for more gradual interfaces and improves as the interface sharpens or becomes abrupt. This is almost certainly a direct result of underestimating the inverse gradient and will be investigated. An example of the aforementioned trend is shown in Figure 41.

Predicted Optimum

Because of the dramatic impact of removing a singular value on the approximation of the profile, the number of optimum singular values for both the true and predicted optimum are identical for nearly all cases (~80%). The most notable exception

is in the cases with no uniform error introduced into the data where the discrepancy ranges between 1 and 3 singular values and appears to have no bias in the selection.

Discrepancies of 2 or 3 are only found in the cases using 10 measurements.

Understanding this, it is expected and has been confirmed that there are no appreciable differences in either the relative mean overlayer thickness or their corresponding standard deviations.

An unexpected feature found in the few discrepancies between the true and predictive optimum was that, when the overlayer was shallower than 30Å, the predicted optimum has a smaller deviation from the true value. At overlayers 30Å or thicker the true optimum has a smaller deviation from the true value. This may be an indication that the predictive criteria may in fact be more sensitive in the near surface region.

Error from Actual Value

The error from the actual atomic percentages at different depths in the sample (0, 3.21, 6.78, 16.68, 29.27, 45.29, 66.67, 91.60 Å) were tabulated as in the previous chapter. Again, because of the size of this data set the tabulated data are not included in the text, rather selected plots that illustrate important points and features will be provided. The full data is found in Appendix B. A qualitative evaluation of the algorithm in different regions of the sample will also be included in this section on accuracy.

True Optimum Value

The error in concentration at the specified depths has been plotted as a function of both inverse gradient and overlayer thickness. Much like the Tyler Algorithm the

deviation at the specified points is directly related to the point's distance from the interface. At depths close to the interface both the deviation and the associated standard deviation are much larger than at points further away from the interface (Figure 42). Therefore, a small change in the position of the interface results in large changes in the approximated concentration at that point. The bias in estimating the concentration is directly related to the algorithm resolution and will be discussed in the section on resolution.

Evaluation of the profiles at the surface, interface, and deep in the sample seem to provide for a clearer illustration of the features associated with the algorithm. Near the surface, the optimally selected cases still showed signs of the surface instability that appears to increase with error level in the original intensities. The increasing instability with error level can most likely be attributed to the fact that in most cases the number of singular values does not change as the error increases. The upper portion of the interface appears relatively sharp for most cases, however, it typically begins to round and in some instances tails at greater depths. Much like the Tyler algorithm, the Singular Value Decomposition algorithm tends to tail deeper in the sample, which also increases with the error level. These trends are illustrated in Figure 43 and 44.

Predicted Optimum Cases

Because in most cases the predictive optimum selects the same number of singular values, the relationships for accuracy are the same as those for the true optimum. That is, both the errors and the associated standard deviations are largest near the interface. As expected points deeper in the sample exhibit more error in the

approximated atomic percentages. Using three measurements quite often produces erratic points while both five and ten measurements show very comparable results.

The qualitative evaluative of the three regions (near surface, interface, and deep in the sample) exposes more subtle trends. The near surface region displayed less surface instability than the true optimum cases. This is typically a result of using fewer singular values than the true optimum. However, it was mentioned in Chapter 4 that there is no correlation between the number of singular values selected for the true optimum and those for the predicted optimum. In addition, it appears that the near surface region for the predictive optimum is always identical to or more accurate than the true optimum. This indicates that the predictive optimum is more sensitive in the near surface region.

This better sensitivity at the surface is offset by poorer resolution at the interface. This is demonstrated in comparing Figure 44 to Figure 45. While it appears that the initial portion of the interface in Figure 45 is as accurate or more accurate than that in Figure 44, the profile quickly begins to level or smooth out. Tailing is seen after the profile goes through a maximum or minimum in some of the cases using the true optimum, when the two cases are different, however, the approximated profiles only approach their true values. An interesting feature in this is that, while resolution is somewhat compromised, the accuracy deeper in the sample does not appear to be significantly affected.

Resolution

Next the resolution of the Singular Value Decomposition algorithm was evaluated. Again, resolution is defined as the ability to distinguish between interface gradients. Because of the algorithm's tendency to tail or level off, the analysis is divided into three parts: the upper region (75-50% of the maximum value before the interface), the bottom region (50-25% of the maximum value before the interface), and the total interface region (75-25% of the maximum value before the interface). Because of the volume of data used in the analysis, tables are not included for all data in this section. The full data set is in the complete table in Appendix B.

True Optimum Cases

Much like the Tyler algorithm the Singular Value Decomposition algorithm displayed considerable tailing, which translates into underestimating the gradient in the lower region enough so as to provide no useable information. This gross underestimation tends to increase with the overlayer thickness, carries over to the calculation of the total gradient, and therefore provides no significant information on the resolution of the algorithm.

Conversely, there do appear to be dominant trends in the data set for the upper gradient. The deviations from the true inverse gradients and their associated standard deviations were extracted (Tables 30 and 31). At gradual interfaces the predicted interface is considerably sharper than the true interface as seen in Figures 46. However, at sharp interfaces the algorithm underestimates the gradient of the interface. Secondly,

the error in the approximated gradient tends to increase with interface depth while the associated standard deviations decrease with interface depth (Figure 47). There does not appear to be any relationship between the sharpness of the interface and the standard deviations.

In nearly all cases, the absolute bias in the estimation of the inverse gradient was smaller using the Singular Value Decomposition Algorithm when comparing to that of the Tyler algorithm. This difference was reduced as the error in the data increased.

Predicted Optimum Cases

Again because the predictive optimum in most cases selects the same number of singular values the relationship is the same as for the predicted optimum as for the true optimum. Again, the full data set for the Singular Value Decomposition algorithm can be found in Appendix B if further validation is desired.

Optimum Values

In evaluating the algorithm with the simulated data sets it becomes evident that the optimum number of singular values is almost solely dependent on the error present in the data. It has also been determined that little additional information is obtained by collecting spectra at more than five take-off angles. Rather, the profile is better enhanced by reducing the noise in the data by achieving a better peak to noise ratio. Table 32 provides a Summary table for the optimum values at the various error levels. It is believed that the mode is the optimum value because high leverage points have little impact on its selection, however the mean and median are also displayed in the table.

Table 26. Mean Squared Error for True Optimum using Singular Value Decomposition Algorithm

Inverse Slope of Interface (x100)	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	118.6	145.5	141.0	112.6
0.00	3	1%	117.0	138.7	141.0	112.0
0.00	3	2%	117.8	138.0	143.2	112.5
0.00	3	5%	121.5	145.1	158.3	123.3
0.00	5	0%	74.4	60.5	52.7	110.8
0.00	5	1%	84.5	88.2	95.9	111.0
0.00	5	2%	86.1	96.3	95.7	112.0
0.00	5	5%	92.0	111.7	114.6	121.4
0.00	10	0%	40.7	61.1	58.0	68.6
0.00	10	1%	81.7	91.9	99.3	110.7
0.00	10	2%	81.4	90.1	95.7	111.1
0.00	10	5%	81.4	102.7	111.7	117.9
-18.75	3	0%	66.5	85.5	105.4	78.0
-18.75	3	1%	61.8	84.2	104.7	77.9
-18.75	3	2%	58.3	79.4	105.4	78.8
-18.75	3	5%	55.0	77.1	116.4	89.2
-18.75	5	0%	25.7	18.6	26.2	82.5
-18.75	5	1%	36.0	21.1	44.5	82.7
-18.75	5	2%	37.8	33.4	49.2	83.1
-18.75	5	5%	53.2	51.7	73.5	89.7
-18.75	10	0%	5.3	10.7	25.1	27.5
-18.75	10	1%	40.7	30.4	50.5	84.1
-18.75	10	2%	45.9	34.3	49.5	84.1
-18.75	10	5%	47.5	49.3	73.3	87.5
-37.5	3	0%	N/A	97.6	95.4	68.7
-37.5	3	1%	N/A	94.4	93.9	68.3
-37.5	3	2%	N/A	87.5	92.2	66.8
-37.5	3	5%	N/A	72.5	91.8	67.7
-37.5	5	0%	N/A	22.0	18.4	77.1
-37.5	5	1%	N/A	49.0	49.9	75.7
-37.5	5	2%	N/A	55.4	53.7	74.3
-37.5	5	5%	N/A	68.4	72.5	72.7
-37.5	10	0%	N/A	26.4	9.5	29.8
-37.5	10	1%	N/A	60.9	56.6	77.6
-37.5	10	2%	N/A	63.0	56.6	76.3
-37.5	10	5%	N/A	70.1	72.3	74.0

Table 27. Mean Squared Error for Predictive Optimum using Singular Value Decomposition Algorithm

Inverse Slope of Interface (x100)	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	118.6	145.5	141.0	112.6
0.00	3	1%	117.0	138.7	141.0	112.0
0.00	3	2%	117.8	138.0	143.2	112.5
0.00	3	5%	121.5	145.1	158.3	123.3
0.00	5	0%	74.4	94.8	52.7	110.8
0.00	5	1%	88.3	88.2	95.9	111.0
0.00	5	2%	86.1	96.3	95.7	112.0
0.00	5	5%	92.0	111.7	137.0	121.4
0.00	10	0%	76.4	96.1	61.6	110.7
0.00	10	1%	84.3	91.9	125.3	110.7
0.00	10	2%	92.1	90.1	125.6	111.1
0.00	10	5%	81.4	102.7	129.0	117.9
-18.75	3	0%	66.5	85.5	105.4	78.0
-18.75	3	1%	61.8	84.2	104.7	77.9
-18.75	3	2%	58.3	79.4	105.4	78.8
-18.75	3	5%	55.0	77.1	116.4	89.2
-18.75	5	0%	26.3	18.6	26.2	82.5
-18.75	5	1%	36.0	21.1	44.5	82.7
-18.75	5	2%	37.8	33.4	49.2	83.1
-18.75	5	5%	253.1	51.7	96.9	89.7
-18.75	10	0%	38.5	30.9	27.3	84.2
-18.75	10	1%	40.7	30.4	93.2	84.1
-18.75	10	2%	45.9	34.3	93.2	84.1
-18.75	10	5%	262.6	52.9	92.8	87.5
-37.5	3	0%	N/A	97.6	95.4	68.7
-37.5	3	1%	N/A	94.4	93.9	68.3
-37.5	3	2%	N/A	87.5	92.2	66.8
-37.5	3	5%	N/A	72.5	91.8	67.7
-37.5	5	0%	N/A	47.1	18.4	77.1
-37.5	5	1%	N/A	49.0	49.9	75.7
-37.5	5	2%	N/A	55.4	53.7	74.3
-37.5	5	5%	N/A	68.4	84.2	72.7
-37.5	10	0%	N/A	60.6	29.4	79.6
-37.5	10	1%	N/A	60.9	61.3	77.6
-37.5	10	2%	N/A	63.0	88.3	76.3
-37.5	10	5%	N/A	72.7	85.7	74.0

Table 28. Mean Relative Overlay Thickness for the True Optimum Cases using the Singular Value Decomposition Algorithm

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	22.28%	12.00%	5.32%	1.26%
0.00	3	1%	23.22%	12.81%	5.62%	1.32%
0.00	3	2%	24.68%	13.12%	6.07%	1.56%
0.00	3	5%	26.19%	14.58%	8.32%	3.00%
0.00	5	0%	2.39%	0.27%	2.21%	2.44%
0.00	5	1%	12.13%	1.06%	2.70%	2.39%
0.00	5	2%	12.20%	0.55%	4.17%	2.50%
0.00	5	5%	12.73%	4.29%	2.97%	3.41%
0.00	10	0%	-0.68%	0.93%	0.51%	0.81%
0.00	10	1%	7.09%	3.20%	2.53%	2.74%
0.00	10	2%	7.22%	0.91%	3.44%	2.79%
0.00	10	5%	7.54%	0.17%	6.35%	3.38%
-18.75	3	0%	0.53%	8.54%	3.41%	0.22%
-18.75	3	1%	1.15%	8.55%	3.64%	0.35%
-18.75	3	2%	3.59%	8.90%	4.09%	0.63%
-18.75	3	5%	12.06%	10.63%	6.33%	2.09%
-18.75	5	0%	-14.87%	4.35%	-3.27%	1.41%
-18.75	5	1%	3.94%	1.96%	0.84%	1.36%
-18.75	5	2%	0.20%	-0.87%	2.32%	1.46%
-18.75	5	5%	3.52%	-0.20%	1.41%	2.41%
-18.75	10	0%	1.01%	1.31%	-1.33%	-1.34%
-18.75	10	1%	10.70%	4.14%	0.91%	1.73%
-18.75	10	2%	6.69%	1.96%	1.31%	1.74%
-18.75	10	5%	-1.33%	-0.96%	4.06%	2.34%
-37.5	3	0%	N/A	-9.38%	-2.53%	-2.42%
-37.5	3	1%	N/A	-8.34%	-2.15%	-2.34%
-37.5	3	2%	N/A	-7.51%	-1.71%	-2.06%
-37.5	3	5%	N/A	-3.73%	0.50%	-0.49%
-37.5	5	0%	N/A	-7.35%	-3.25%	-1.77%
-37.5	5	1%	N/A	2.24%	-4.15%	-1.75%
-37.5	5	2%	N/A	-0.36%	-3.47%	-1.57%
-37.5	5	5%	N/A	-5.88%	-2.93%	-0.57%
-37.5	10	0%	N/A	-6.80%	1.64%	-4.57%
-37.5	10	1%	N/A	3.59%	-3.67%	-1.52%
-37.5	10	2%	N/A	2.50%	-3.72%	-1.38%
-37.5	10	5%	N/A	-16.61%	-2.44%	-0.73%

Table 29. Relative Standard Deviation for the True Optimum Cases using the Singular Value Decomposition Algorithm

Inverse Slope of Interface	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	0.00%	0.00%	0.00%	0.00%
0.00	3	1%	7.21%	4.78%	2.52%	1.34%
0.00	3	2%	14.24%	9.59%	5.06%	2.63%
0.00	3	5%	27.92%	22.52%	13.12%	6.63%
0.00	5	0%	0.00%	0.00%	0.00%	0.00%
0.00	5	1%	2.74%	9.65%	2.68%	1.07%
0.00	5	2%	5.15%	16.73%	7.27%	2.27%
0.00	5	5%	12.59%	9.19%	20.23%	5.90%
0.00	10	0%	0.00%	0.00%	0.00%	0.00%
0.00	10	1%	1.28%	4.72%	1.51%	0.77%
0.00	10	2%	2.63%	10.15%	3.46%	1.67%
0.00	10	5%	6.80%	17.16%	20.02%	4.44%
-18.75	3	0%	0.00%	0.00%	0.00%	0.00%
-18.75	3	1%	5.09%	4.81%	2.47%	1.36%
-18.75	3	2%	12.44%	9.72%	5.02%	2.60%
-18.75	3	5%	30.41%	22.66%	13.05%	6.51%
-18.75	5	0%	0.00%	0.00%	0.00%	0.00%
-18.75	5	1%	10.43%	5.94%	2.41%	1.14%
-18.75	5	2%	12.84%	13.42%	6.91%	2.24%
-18.75	5	5%	12.23%	8.87%	20.15%	5.80%
-18.75	10	0%	0.00%	0.00%	0.00%	0.00%
-18.75	10	1%	7.97%	2.66%	1.52%	0.85%
-18.75	10	2%	11.85%	6.88%	3.12%	1.68%
-18.75	10	5%	5.78%	5.02%	17.97%	4.34%
-37.5	3	0%	N/A	0.00%	0.00%	0.00%
-37.5	3	1%	N/A	5.46%	2.45%	1.17%
-37.5	3	2%	N/A	10.73%	4.93%	2.47%
-37.5	3	5%	N/A	24.37%	12.79%	6.24%
-37.5	5	0%	N/A	0.00%	0.00%	0.00%
-37.5	5	1%	N/A	3.23%	1.65%	0.97%
-37.5	5	2%	N/A	7.43%	4.98%	2.06%
-37.5	5	5%	N/A	16.34%	21.33%	5.43%
-37.5	10	0%	N/A	0.00%	0.00%	0.00%
-37.5	10	1%	N/A	2.46%	1.20%	0.71%
-37.5	10	2%	N/A	4.83%	2.60%	1.55%
-37.5	10	5%	N/A	4.03%	10.01%	4.03%

Table 30. Approximated Inverse Gradient (x100) as Predicted by the Singular Value Decomposition Method (Optimum)

Inverse Slope of Interface (x100)	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	-3.76	-4.72	-18.39	-19.45
0.00	3	1%	-4.58	-6.41	-18.74	-19.38
0.00	3	2%	-5.31	-7.34	-19.30	-20.23
0.00	3	5%	-7.10	-11.61	-22.82	-25.34
0.00	5	0%	-9.83	-15.11	-6.07	-16.29
0.00	5	1%	-10.66	-13.01	-14.47	-17.22
0.00	5	2%	-5.85	-10.75	-13.22	-17.95
0.00	5	5%	-6.42	-9.56	-17.69	-21.90
0.00	10	0%	-9.88	-14.09	-8.04	-16.43
0.00	10	1%	-10.48	-13.86	-13.23	-16.80
0.00	10	2%	-10.85	-11.95	-13.58	-17.21
0.00	10	5%	-6.89	-9.14	-14.65	-19.90
-18.75	3	0%	-5.90	-7.03	-19.01	-20.33
-18.75	3	1%	-6.13	-6.54	-18.78	-19.84
-18.75	3	2%	-6.61	-7.49	-19.34	-20.75
-18.75	3	5%	-8.99	-11.83	-22.75	-25.78
-18.75	5	0%	-22.48	-19.07	-11.10	-17.23
-18.75	5	1%	-17.97	-17.79	-15.88	-17.69
-18.75	5	2%	-17.20	-14.78	-14.35	-18.39
-18.75	5	5%	12000.00	-9.93	-18.00	-22.31
-18.75	10	0%	-24.30	-17.48	-10.40	-16.57
-18.75	10	1%	-21.41	-17.24	-13.97	-17.14
-18.75	10	2%	-19.94	-15.90	-14.08	-17.74
-18.75	10	5%	12000.00	-11.18	-15.04	-20.26
-37.5	3	0%	N/A	-6.78	-18.63	-21.25
-37.5	3	1%	N/A	-7.50	-18.73	-21.44
-37.5	3	2%	N/A	-8.55	-19.27	-22.28
-37.5	3	5%	N/A	-13.23	-22.53	-27.12
-37.5	5	0%	N/A	-24.68	-38.92	-18.13
-37.5	5	1%	N/A	-24.08	-19.87	-18.95
-37.5	5	2%	N/A	-22.70	-18.34	-19.77
-37.5	5	5%	N/A	-18.98	-19.09	-23.41
-37.5	10	0%	N/A	-22.55	-28.29	-17.72
-37.5	10	1%	N/A	-22.34	-17.16	-18.35
-37.5	10	2%	N/A	-21.79	-15.56	-18.96
-37.5	10	5%	N/A	-18.62	-16.23	-21.44

Table 31. Standard Deviations (x100) Associated with Approximated Inverse Gradient as Predicted by the Singular Value Decomposition Method (Optimum)

Inverse Slope of Interface (x100)	Number of Measurements	Percent Error	Mean Depth of Interface			
			7.5 Å	15 Å	30 Å	60 Å
0.00	3	0%	0.00	0.00	0.00	0.00
0.00	3	1%	0.75	0.90	1.22	1.68
0.00	3	2%	1.60	2.00	2.79	3.70
0.00	3	5%	3.43	7.42	8.52	11.12
0.00	5	0%	0.00	0.00	0.00	0.00
0.00	5	1%	0.29	5.55	2.57	1.24
0.00	5	2%	0.59	6.37	4.39	2.70
0.00	5	5%	1.59	2.16	11.59	8.17
0.00	10	0%	0.00	0.00	0.00	0.00
0.00	10	1%	0.21	3.37	1.54	0.78
0.00	10	2%	0.47	5.11	3.12	2.11
0.00	10	5%	1.19	5.67	21.97	5.58
-18.75	3	0%	0.00	0.00	0.00	0.00
-18.75	3	1%	0.54	0.86	1.24	1.60
-18.75	3	2%	1.42	2.02	2.73	3.77
-18.75	3	5%	4.26	7.54	8.47	11.27
-18.75	5	0%	0.00	0.00	0.00	0.00
-18.75	5	1%	7.06	5.24	2.51	1.29
-18.75	5	2%	7.93	7.66	4.58	2.67
-18.75	5	5%	1.50	2.08	13.04	8.16
-18.75	10	0%	0.00	0.00	0.00	0.00
-18.75	10	1%	6.21	2.75	1.42	0.98
-18.75	10	2%	9.81	4.99	3.12	2.01
-18.75	10	5%	0.98	1.37	18.40	5.65
-37.5	3	0%	N/A	0.00	0.00	0.00
-37.5	3	1%	N/A	0.88	1.13	2.06
-37.5	3	2%	N/A	2.22	2.57	4.04
-37.5	3	5%	N/A	8.49	8.17	11.88
-37.5	5	0%	N/A	0.00	0.00	0.00
-37.5	5	1%	N/A	2.62	2.01	1.37
-37.5	5	2%	N/A	6.68	4.71	2.90
-37.5	5	5%	N/A	10.00	23.78	8.34
-37.5	10	0%	N/A	0.00	0.00	0.00
-37.5	10	1%	N/A	1.23	1.27	0.84
-37.5	10	2%	N/A	3.17	2.79	2.13
-37.5	10	5%	N/A	1.31	9.26	5.90

Table 32. Optimum Summary for Singular Value Decomposition using Five Measurements

	Uniformly Distributed Random Error			
	0%	1%	2%	5%
Mode	4	3	2	2
Median	4	3	2	2
Mean	3.417	2.750	2.458	2.250
STD	0.881	0.608	0.509	0.442
Skewness	-0.975	0.158	0.179	1.233
Kurtosis	-0.986	-0.347	-2.156	-0.531

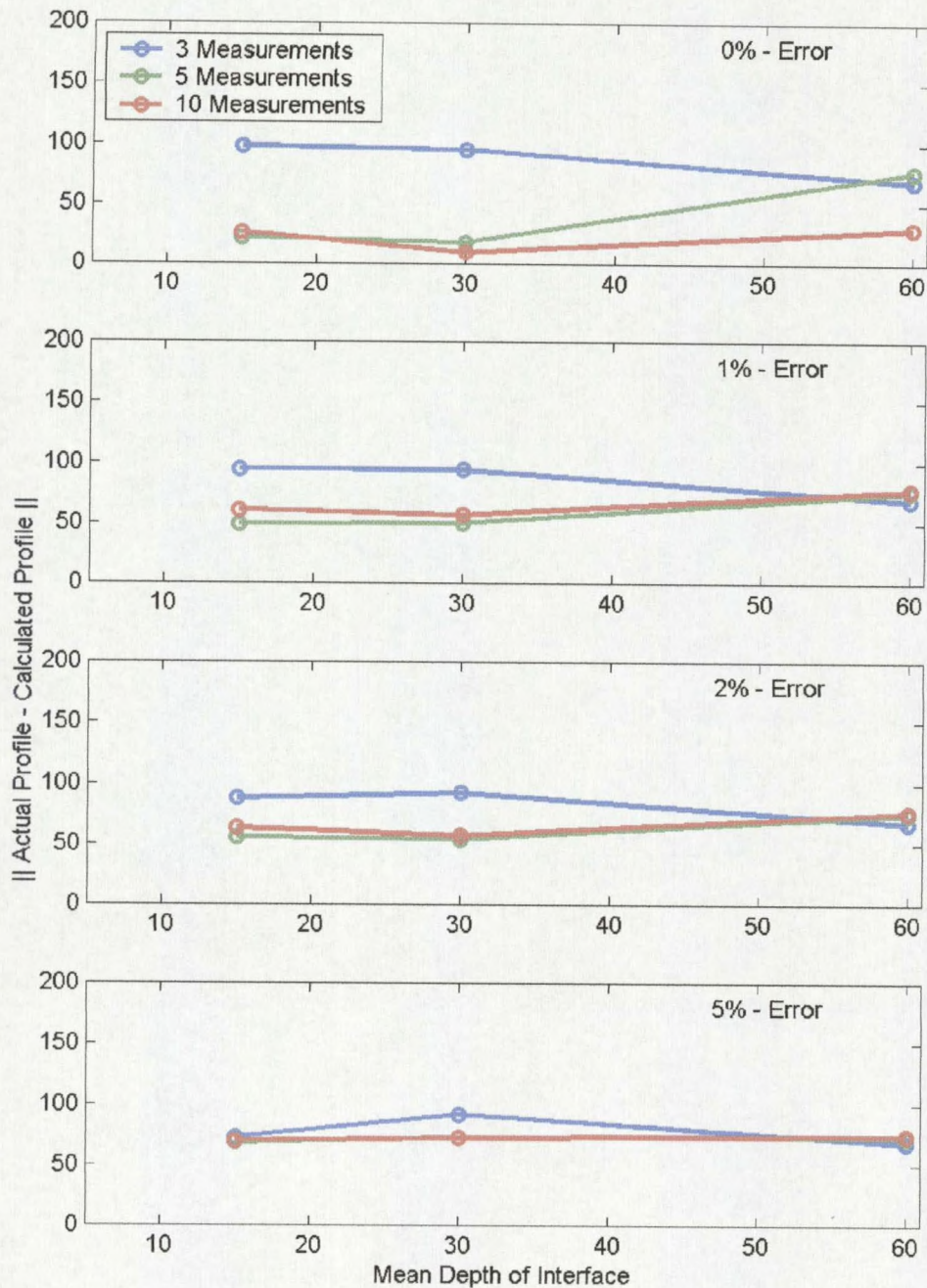


Figure 38. Mean Squared Error vs. Overlayer Thickness for True Optimum Cases Using Singular Value Decomposition (Inverse Gradient of -37.5×10^{-2})

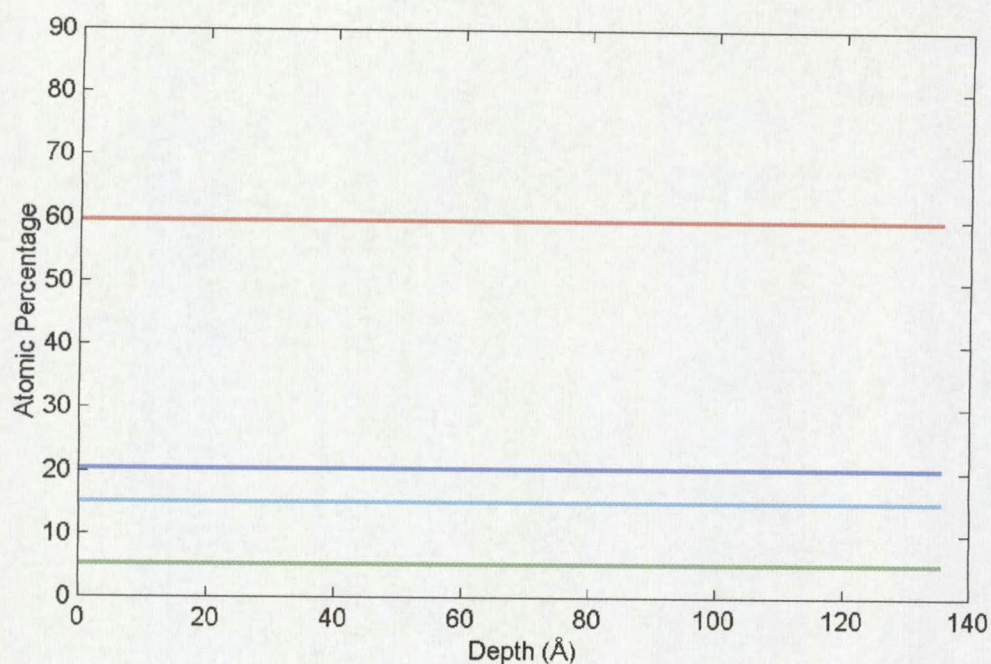


Figure 39. Approximated Profile Using SVD Algorithm (Overlayer Thickness = $7.5\text{\AA}$, Inverse Gradient = 18.75×10^{-2} , 5 Measurements, and 5% Random Error Introduced)

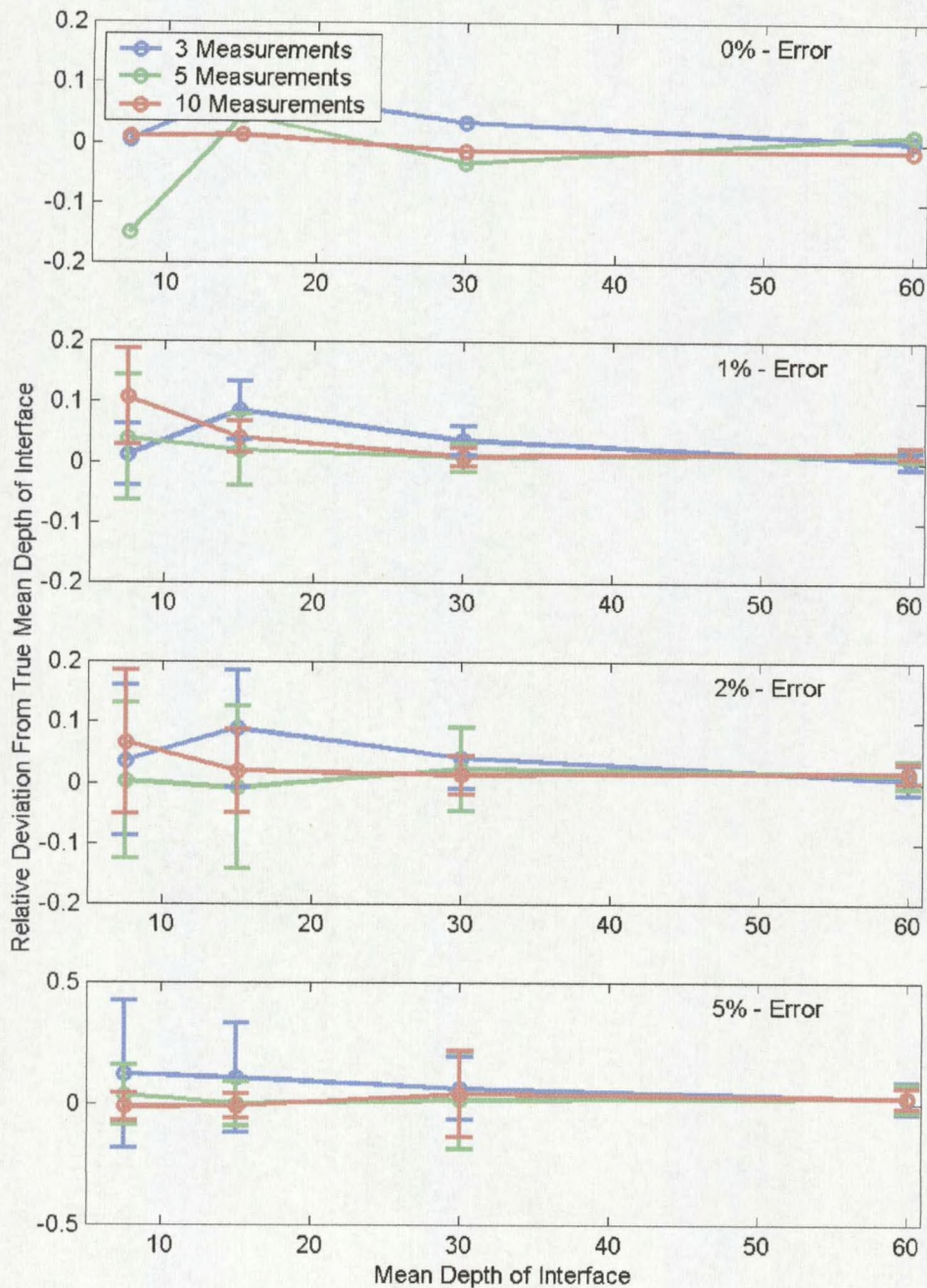


Figure 40. Relative Deviation from the True Mean Depth of the Interface as a Function of Interface Thickness with Inverse Gradient of -18.75×10^{-2} (Error Bars = $\pm$ Relative Standard Deviation)

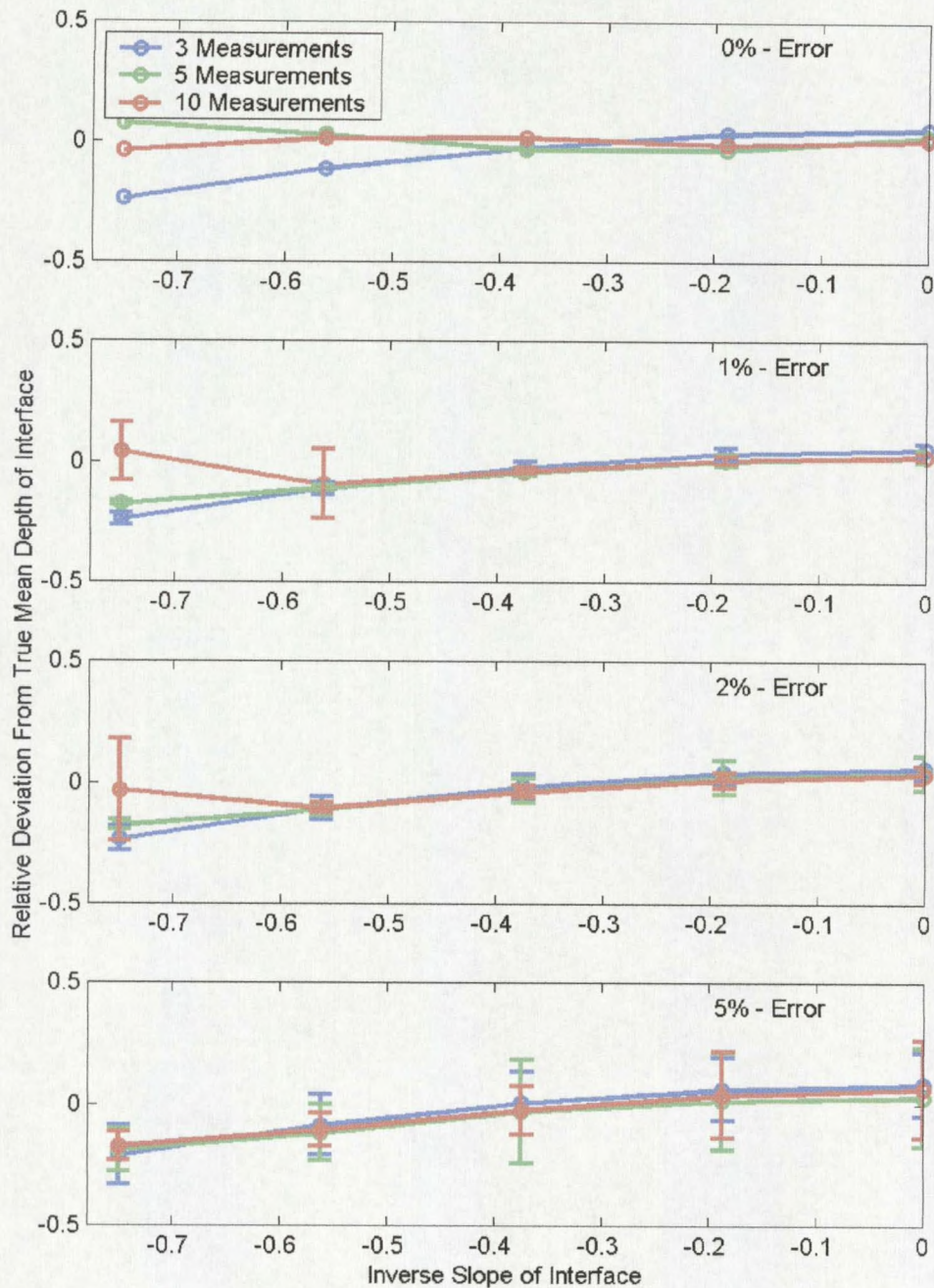


Figure 41. Relative Deviation from the True Mean Depth of the Interface as a Function of Inverse Gradient with Overlayer Thickness of $30\text{\AA}$ (Error Bars = $\pm$ Relative Standard Deviation)

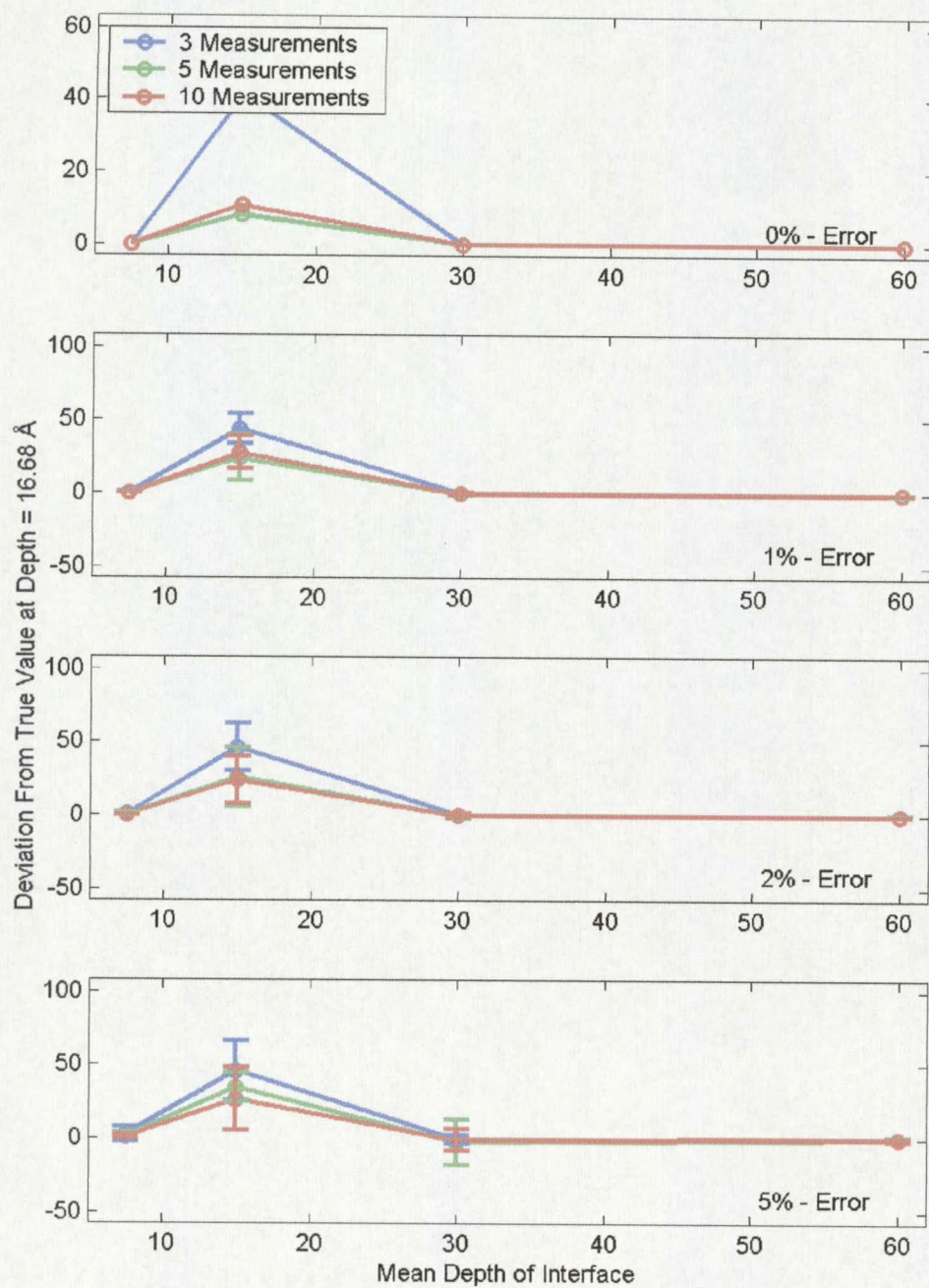


Figure 42. Deviation from Actual Atomic Percentage at Depth of 16.68Å with Inverse Gradient of 0

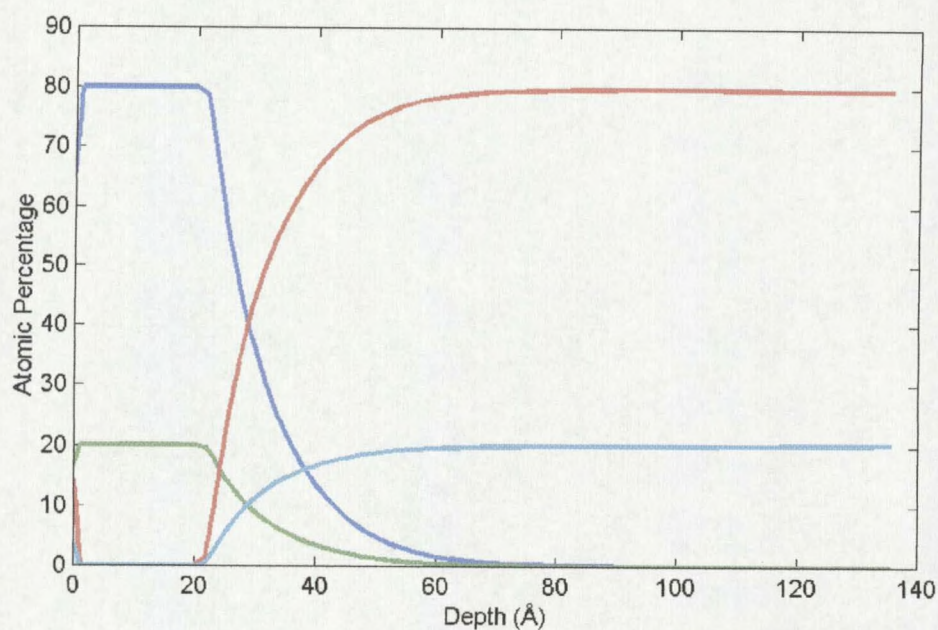


Figure 43. Approximated Profile Using SVD Algorithm with 3 Singular Values (Overlayer Thickness = $30\text{\AA}$, Inverse Gradient = 37.5×10^{-2} , 5 Measurements, and 1% Random Error Introduced)

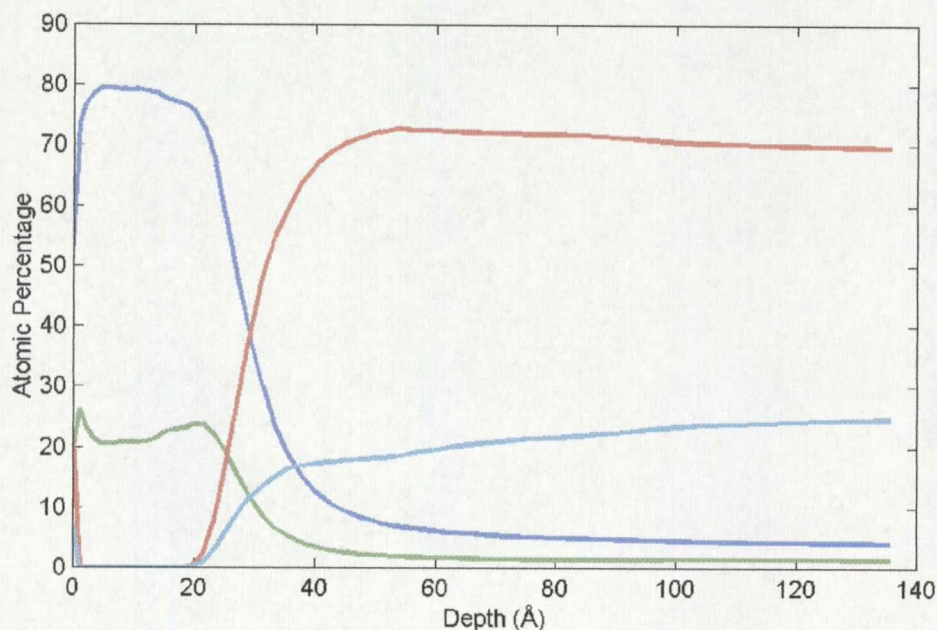


Figure 44. Approximated Profile Using SVD Algorithm with 3 Singular Values (Overlayer Thickness = $30\text{\AA}$, Inverse Gradient = 37.5×10^{-2} , 5 Measurements, and 5% Random Error Introduced)

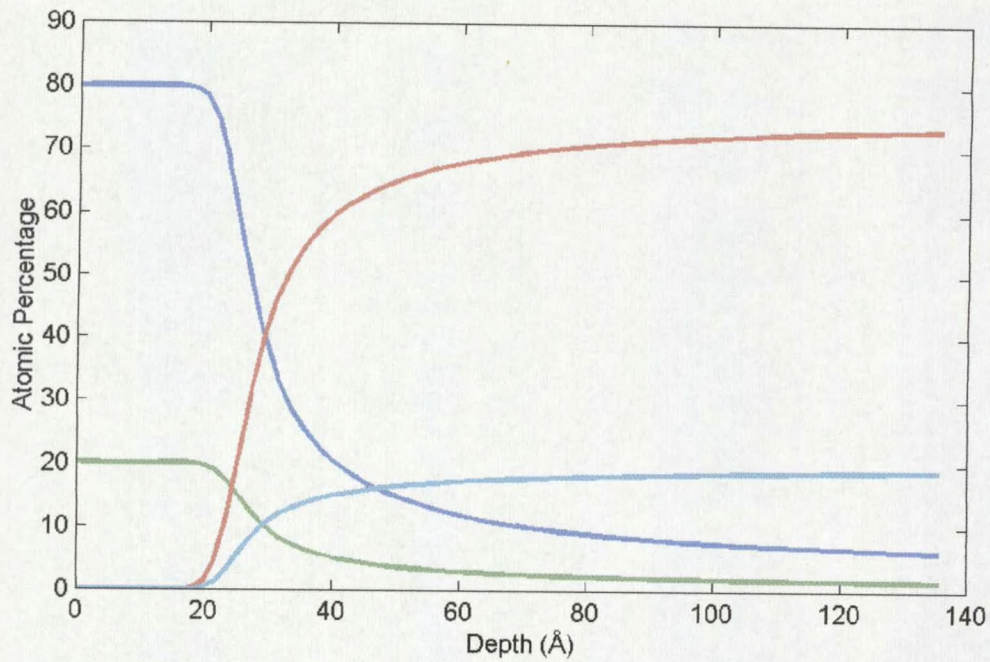


Figure 45. Approximated Profile Using SVD Algorithm with 2 Singular Values (Overlayer Thickness = $30\text{\AA}$, Inverse Gradient = 37.5×10^{-2} , 5 Measurements, and 5% Random Error Introduced)

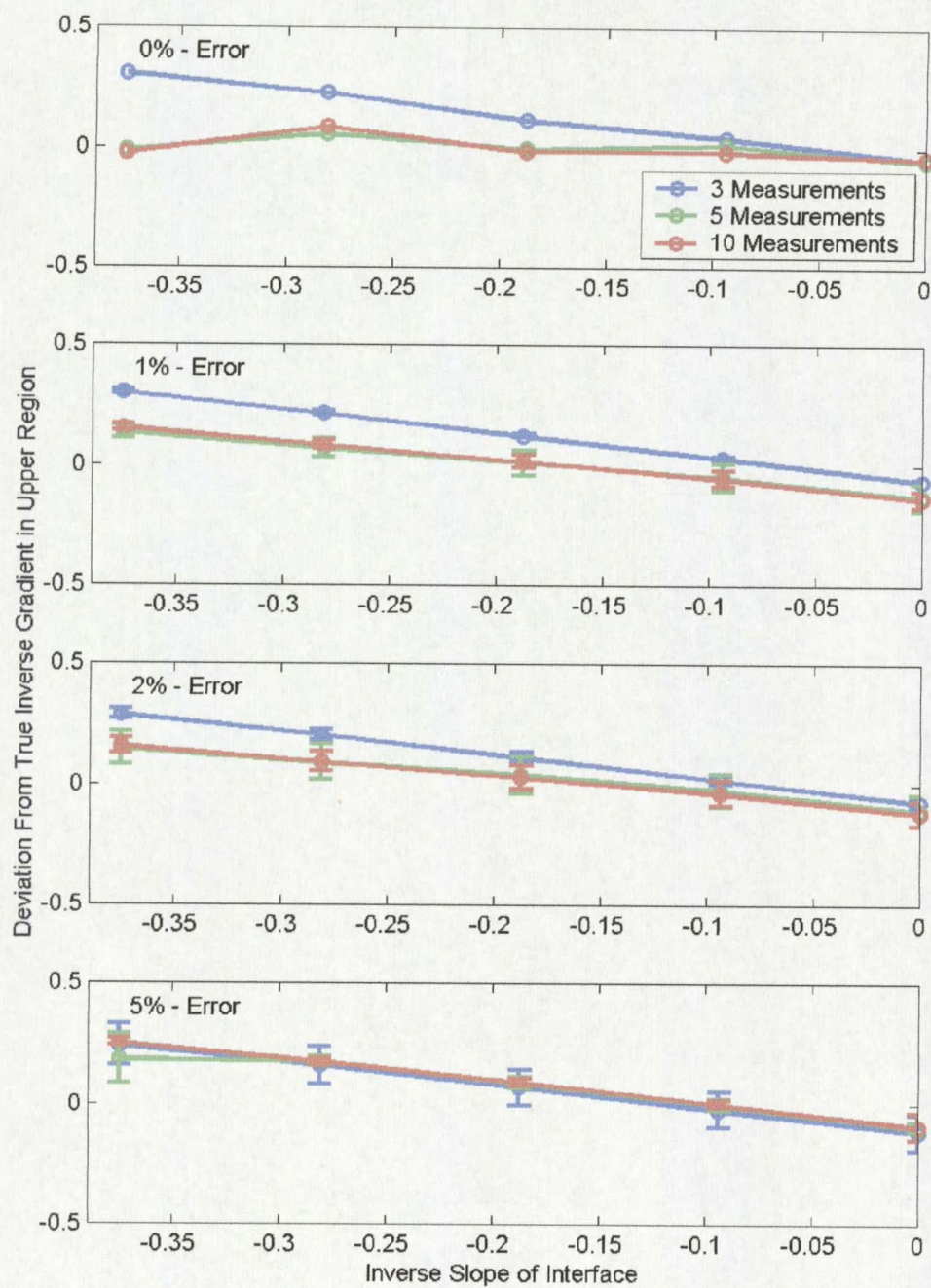


Figure 46. Deviation from True Inverse Gradient at Depth of 15 Å (Optimum)

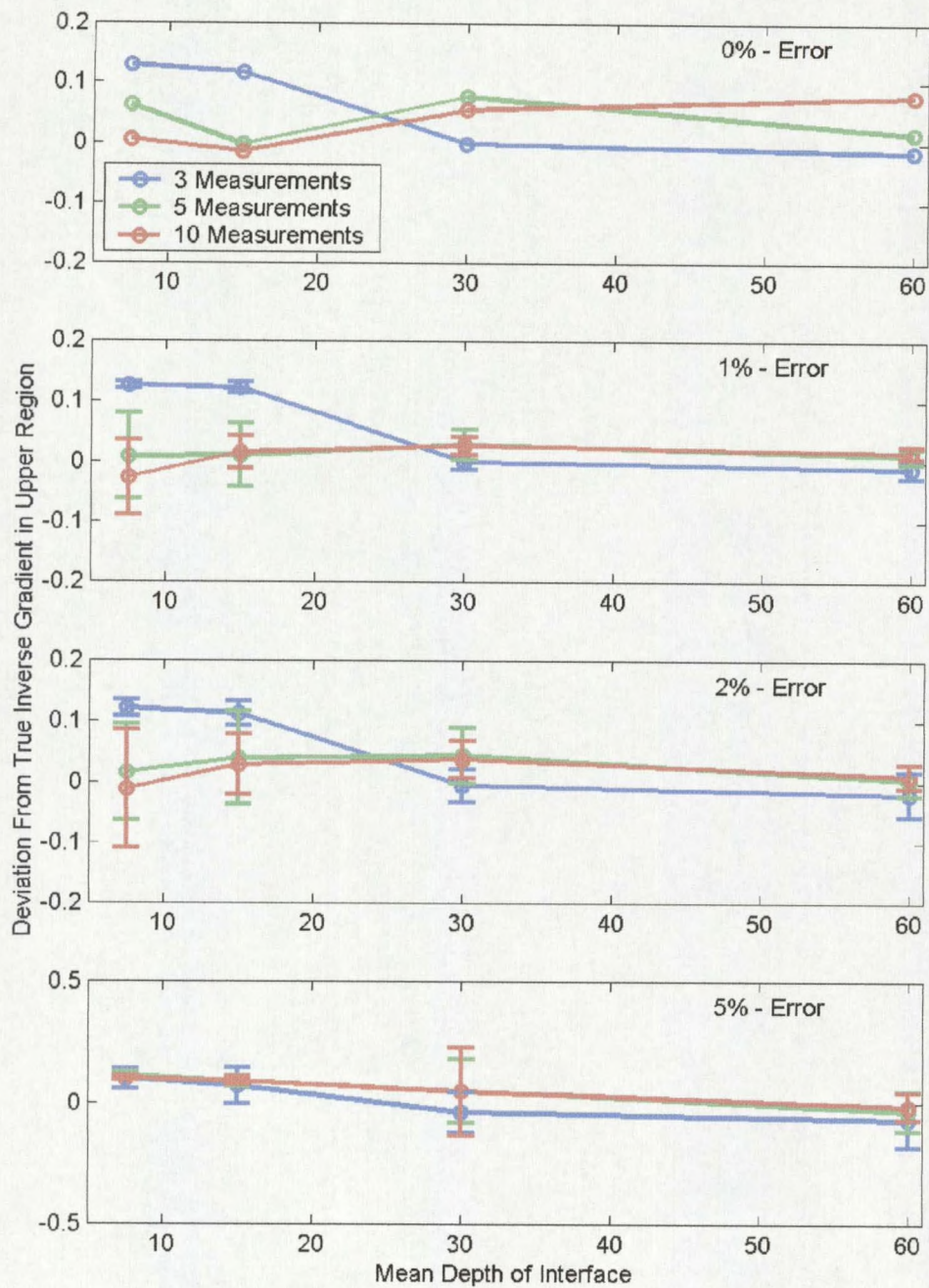


Figure 47. Deviation from True Inverse Gradient with Inverse Gradient of 18.75×10^{-2} (Optimum)

CHAPTER 7

EFFECTS OF SURFACE ROUGHNESS

It has already been established that using more than 5 measurements provides little additional information. It appears more advantageous to increase the signal to noise ratio (reduce error in the measurement) as opposed to taking more measurements. The question that now begs asking is, do the take-off angles at which the measurements are taken influence how surface roughness affects the approximated profile? It is expected that as the cosine of the take-off angle is decreased the surface roughness will contribute more to the measured intensity. The objective of the rough simulated surface analysis is to determine how roughness affects the measurements at various take-off angles.

Angle resolved XPS data were collected for three assorted length alkanethiols (C8, C12, and C16). The topography of each sample was then determined as described in Chapter 3. A maximum roughness (surface area : projected surface area) value was then determined and fifteen corresponding roughness values ranging from 1 to 1.019 were then selected to generate the "egg-carton" like surface. These values correspond to the experimentally collected data, and thus allow for testing on a sample of a known topography and concentration depth profile.

The arbitrarily chosen concentration depth profile for use in this analysis is a homogenous overlayer of 80% A and 20%B 30Å (1λ) thick over a homogenous substrate

comprised of 80%C and 20%D. Core level photoelectrons from A, B, C, and D all have the same inelastic mean free path (30Å). Data was simulated for “egg-carton” surface of varying amplitude by generating a mesh surface according to the following equation:

$$H = A \cos(x) \cos(y) \Big|_{x=0 \dots 2\pi, y=0 \dots 2\pi} \quad (24)$$

where H is the height of the surface and A is an adjustable parameter that varies the amplitude. The x and y gradients were then calculated and the appropriate adjustments were then made to the take-off angle to impose a 1λ overlayer on the surface. This was done as follows:

$$\phi = a \tan\left(\frac{\partial H}{\partial x}\right), \quad \beta = a \tan\left(\frac{\partial H}{\partial y}\right) \quad (25 \text{ \& } 26)$$

$$\theta_{\text{actual}} = \frac{1}{\sqrt{1 + \tan^2(\theta + \phi)} \sqrt{1 + \tan^2(\beta)}} \quad (27)$$

where θ_{actual} is the actual angle between the x-ray source and surface normal. The corresponding intensities, $F(\theta_{\text{actual}})$, were then calculated for each point on the 150x150 wavelike grid. The average intensity for each take-off angle was then calculated. Fourteen amplitude (A) values for Equation 24 were chosen (0.02, 0.04...0.28). These values were chosen by taking the ratio of the surface area to the projected area of the experimentally collected AFM data. Collection of this data is discussed in detail in Chapter 8 on the experimentally collected data. The amplitudes were chosen so as to have the simulated data's ratio of the surface area to the projected surface area correspond to the experimentally collected data. This ratio was calculated as follows:

$$\frac{SA}{PSA} = (2\pi)^{-2} \iint \sqrt{(-A \sin(x) \cos(y))^2 + (-A \cos(x) \sin(y))^2 + (-1)^2} dy dx \quad (28)$$

In order to determine the effect of the surface roughness on the generated intensities, a ratio of the intensities with surface roughness to those without the generated surface roughness was determined. A surface plot was then generated displaying the results for both the overlayer and the substrate (Figures 48 and 49).

These results are consistent with the expected behavior of the system. The results indicate that the signal generated from the substrate is considerably more intense at glancing angles. This is undoubtedly a result of the effective sampling depth being altered more considerably by the roughness at these glancing angles. This, combined with a less intense signal in the overlayer, translates into a false indication of having both components C and D in the overlayer and a gradual transition to the substrate.

These trends are even more apparent as the overlayer thickness increases. The apparent tail or instability seen in Figure 48 is a result of the numerical integration and not an artifact of surface roughness. Using the mode values determined in Chapters 5 and 6, the calculated concentration depth profiles from both the Tyler Regularization and Singular Value Decomposition algorithms are shown using five measurements and the determined optimum values corresponding to 0% error at roughness of 1 (flat), 1.002, 1.008, and 1.019 (Figures 50 & 51). If the algorithms did not converge the smoothing parameter was increased systematically as follows until it converged

$$\alpha = 1.8^{N-\text{optimum}} \quad \text{where} \quad N = \text{Optimum}, \text{Optimum}-1, \dots, 1 \quad (32)$$

or the number of singular values was decreased monotonically until convergence.

From these plots it can be seen that the surface roughness in both algorithms makes elements deeper in the sample appear closer to the surface by changing the angle between the x-ray and surface normal. In addition, it appears that although the SVD algorithm converged at a roughness of 1.019 (Figure 51) it is most definitely unstable and therefore some prior knowledge as to the general shape of the depth profile is needed.

One possible improvement is to change the photoelectron take-off angles at which the measurements are taken. Therefore, the data for the "egg-carton" like surface was regenerated with three new data sets (Table 33). These new data sets remove the measurements at 80° and other glancing angles to varying extremes. Due to the enormous number of possible combinations of measurements the discussion will be restricted to the selected three.

Table 33. Trial Data Sets for Improvements on Rough Surface Analysis

Photoelectron Take-off Angles (degrees)					
Data Set 1	10	20	40	50	60
Data Set 2	10	20	40	50	70
Data Set 3	10	20	40	60	70

Of all the data sets, Data Set 1 most closely resembles the original set of five measurements. The measurement at 80° was replaced with one at 50° . The results of this replacement can be seen in the Figures 52 and 53. It is apparent that some of the effects of the roughness are dampened, however, some surface instability is still present.

Qualitatively evaluating the results using Data Set 1, it appears that removing both the measurements at 70° and 80° compromises both resolution and accuracy near the surface. This being the case it might be beneficial to include the measurement at 70° .

Data Set 2 qualitatively improves the accuracy in the near surface region over the original data set and Data Set 1 (Figures 54 & 55) when the surface is rough. More importantly, Data Set 2 does not compromise much in the way of either accuracy or resolution over the original data set on a perfectly flat surface. The final data set was evaluated and considered to be significantly more unstable in the near surface region. Therefore, the optimum set of measurements discussed here are those in Data Set 2.

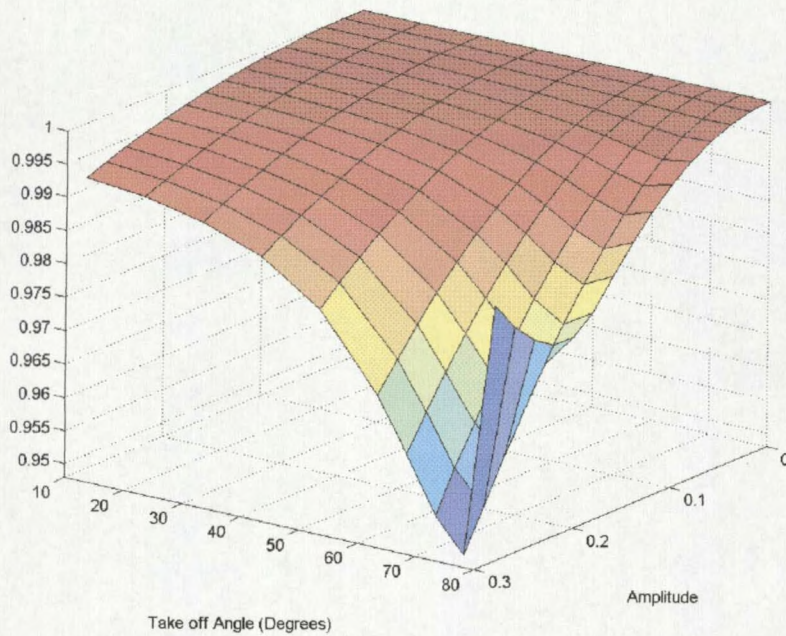


Figure 48. Ratio of Simulated Intensities with Surface Roughness to Simulated Intensities with no Roughness for Component A and B with 1λ overlayer

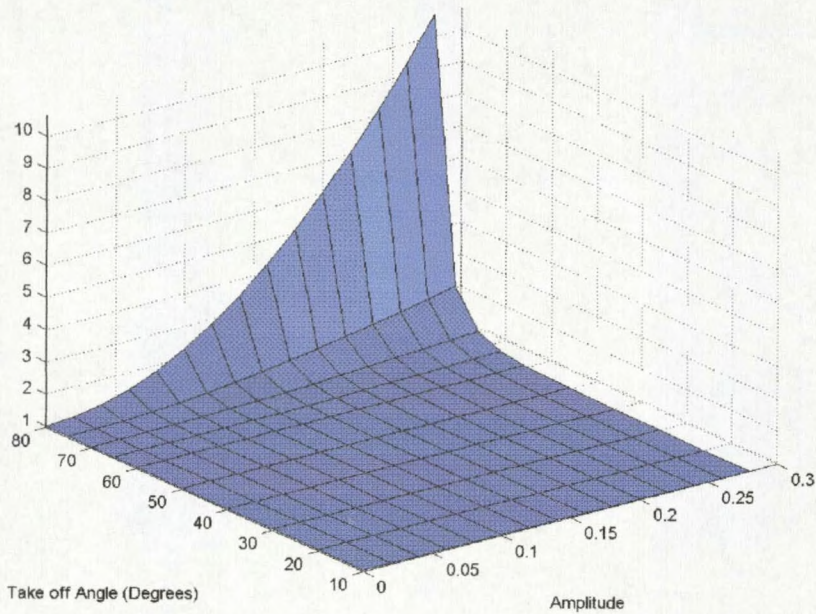


Figure 49. Ratio of Simulated Intensities with Surface Roughness to Simulated Intensities with no Roughness for Component C and D with 1λ overlayer

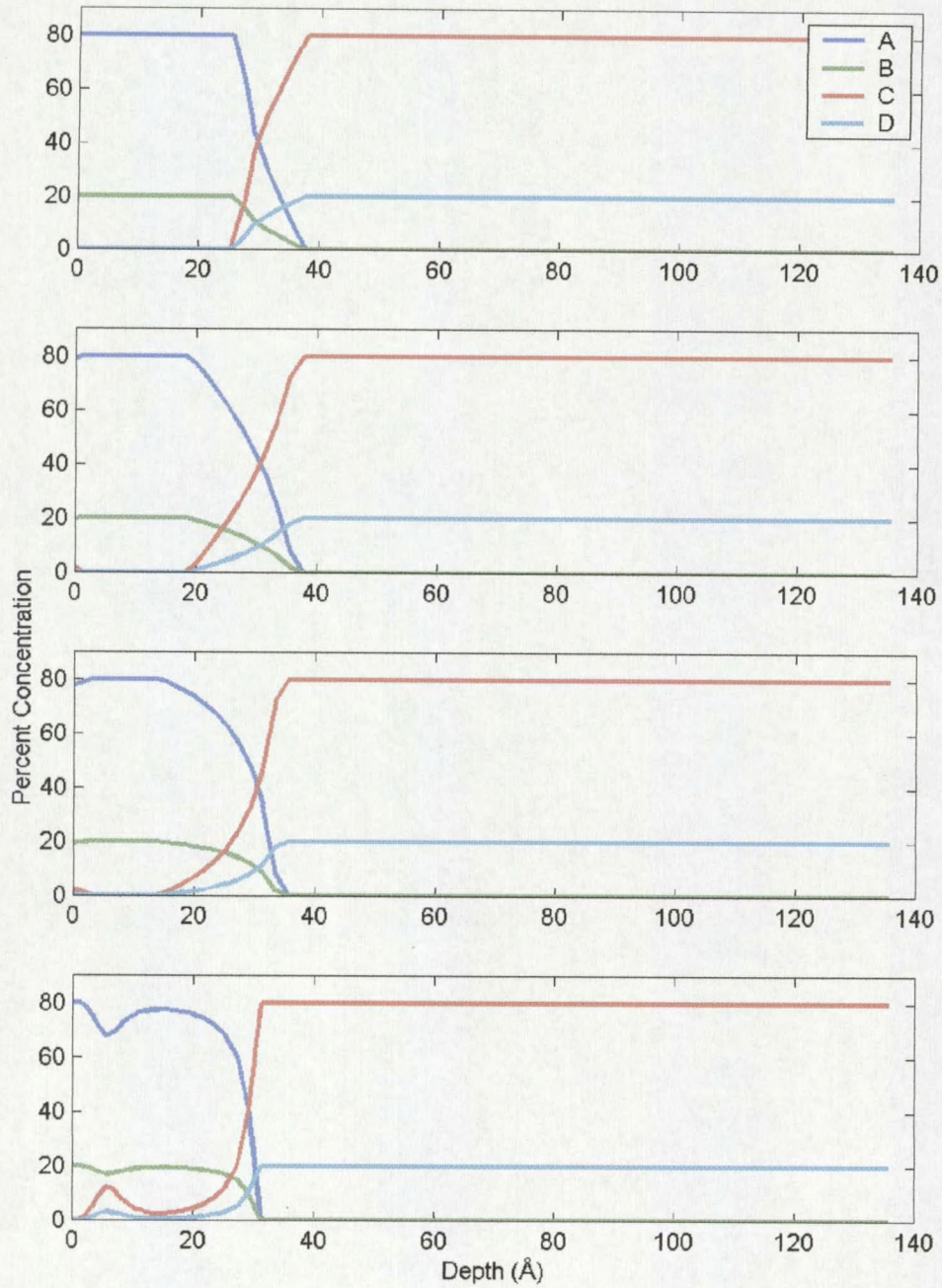


Figure 50. Calculated Concentration Depth Profile for 1λ overlayer with $\alpha=1.8^{1-20}$
 Roughness = a) 1, b) 1.002, c) 1.008, and d) 1.019

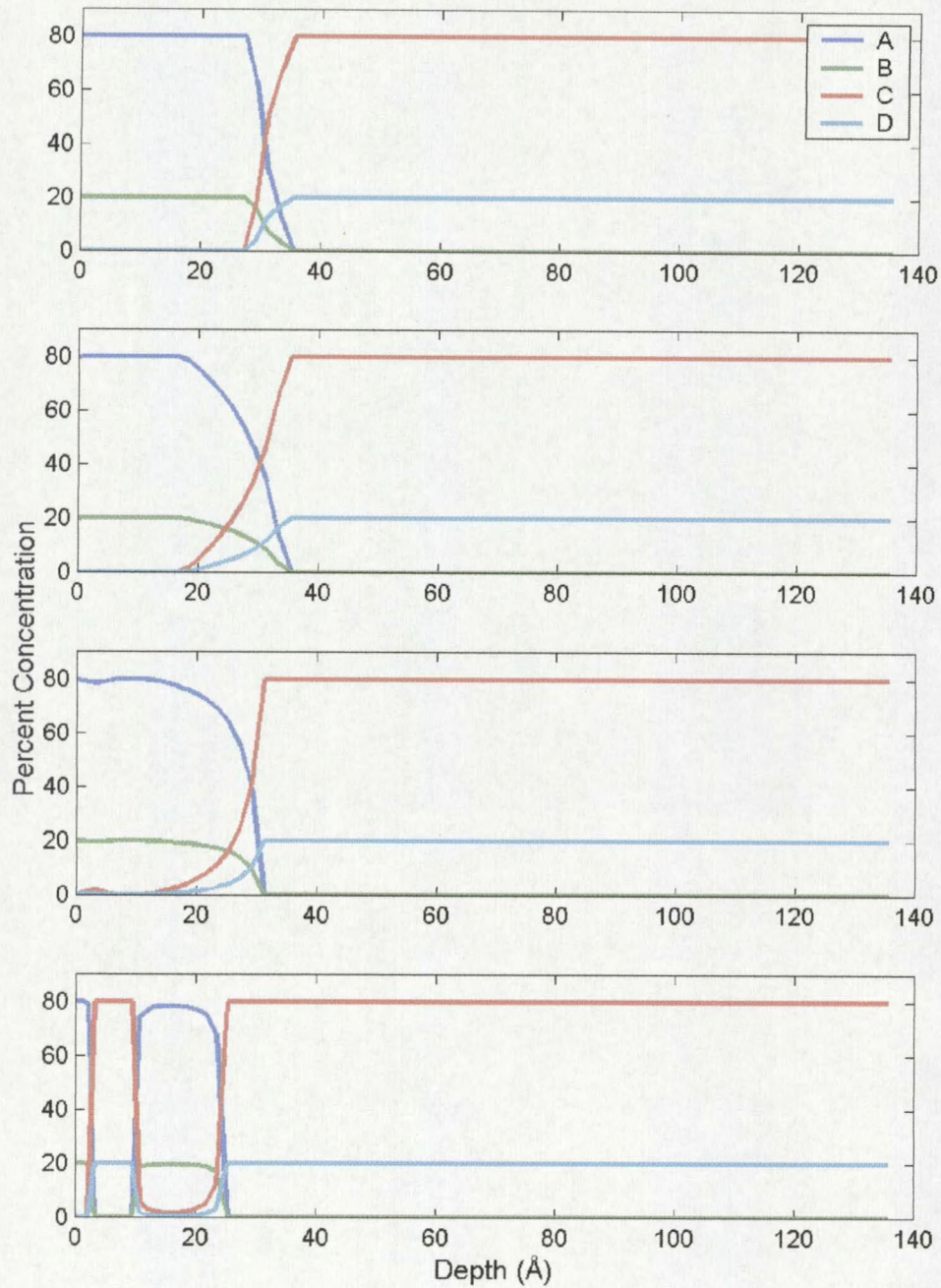


Figure 51. Calculated Concentration Depth Profile for 1λ overlayer with 4 Singular Values - Roughness = a) 1, b) 1.002, c) 1.008, and d) 1.019

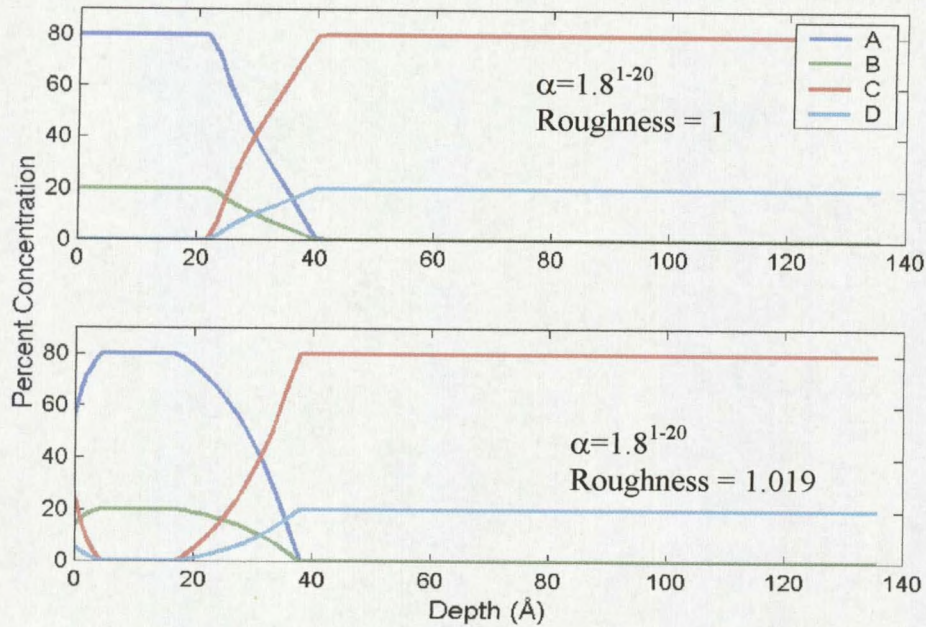


Figure 52. Calculated Concentration Depth Profile on Data Set 1 for 1 λ overlayer using Tyler Algorithm

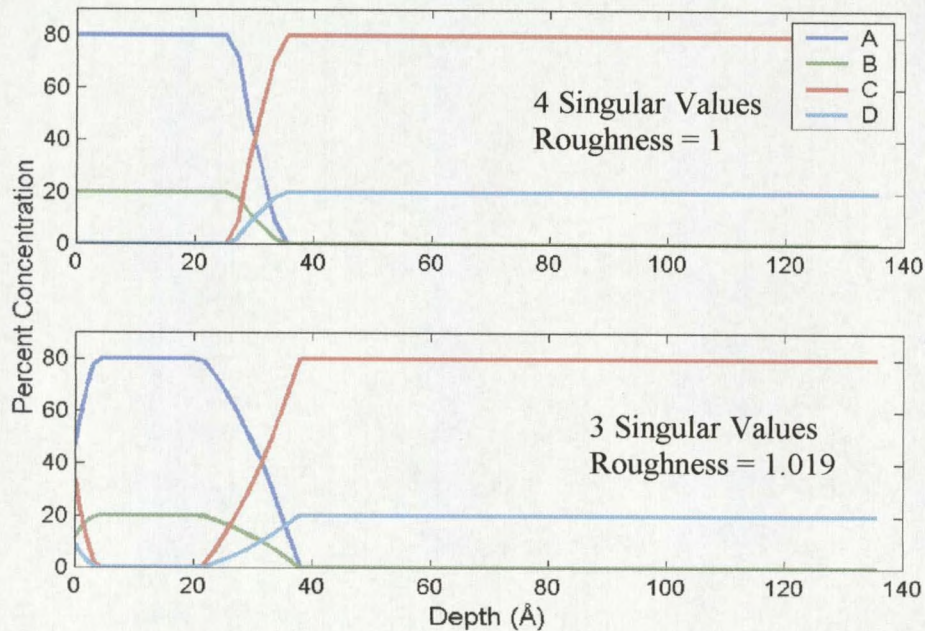


Figure 53. Calculated Concentration Depth Profile on Data Set 1 for 1 λ overlayer Using Singular Value Decomposition

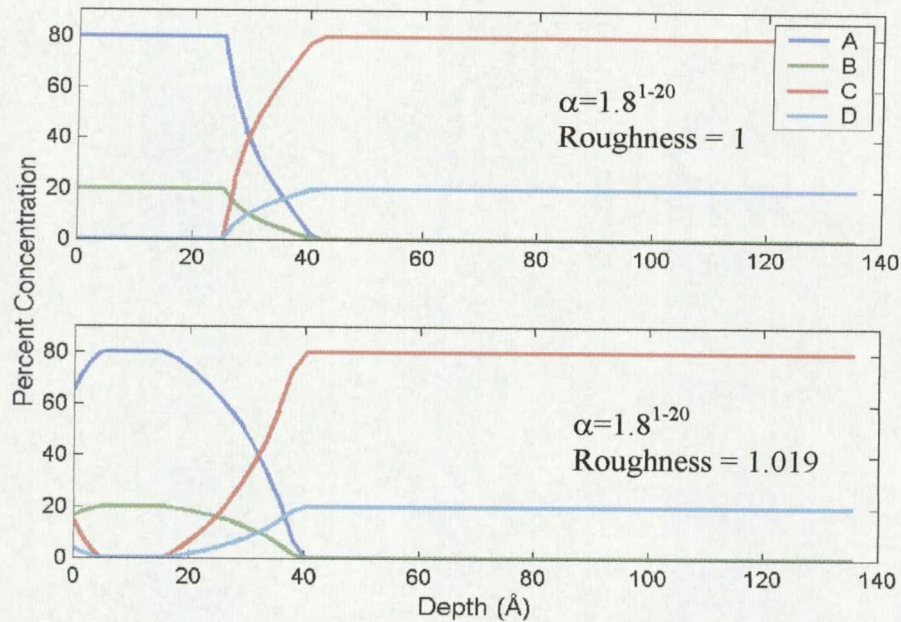


Figure 54. Calculated Concentration Depth Profile on Data Set 2 for 1λ overlayer Using Tyler Algorithm

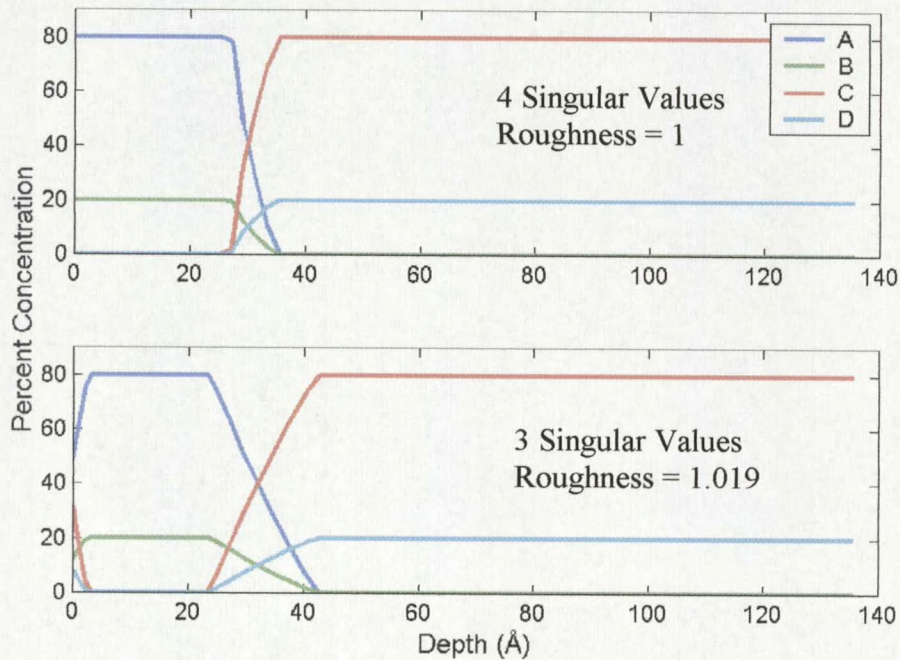


Figure 55. Calculated Concentration Depth Profile on Data Set 2 for 1λ overlayer using Singular Value Decomposition

CHAPTER 8

EXPERIMENTALLY COLLECTED DATA

Angle resolved XPS data were collected for three assorted length alkanethiols (C8, C12, and C16). The topography of each sample was determined as described in Chapter 3. The roughness (surface area: projected surface area) of the samples was determined. This data was used to test both the Tyler Regularization and SVD algorithms.

Topography of Experimentally Collected Data

The topography of a total of six samples consisting of three-chain length alkanethiols (C8, C12, and C16) adsorbed on gold was determined using atomic force microscopy as described in Chapter 3. A reasonable maximum roughness (surface area : projected surface area) was selected and the corresponding maximum amplitude value for the "egg-carton" like surface was calculated according to Equation 28.

AFM scans were performed for scan sizes of $1\mu\text{m}^2$, $100\mu\text{m}^2$, and $2500\mu\text{m}^2$. An example of each can be seen in Figures 56-58. Images for all scans can be found in Appendix D. The corresponding surface areas and roughness values for each sample scan is displayed in Table 34. The absent data for the C8b and C12b $1\mu\text{m}^2$ scan and the C16b $2500\mu\text{m}^2$ scan is due to an inability to gather reliable data. It appeared the gold had

pulled away from the mica substrate and made it impossible to collect data. Several attempts to find an adequate scan area were made, however, scans became subsequently worse with each attempt. Other samples were then scanned to verify the integrity of the equipment.

Depth Profiles Calculated for Experimental ARXPS Data

As mentioned in Chapter 3 the data were collected using a monochromatized 0.2mm aluminum $K\alpha$ X-ray source at 300 watts. The pass energies used for all elements during data acquisition were 117.40eV. It can be expected that roughly 1% error is encountered under these conditions. The XPS spectra were then integrated using MultiPak[®] Version 2.2 distributed by Physical Electronics to produce the signal intensities needed (Table 35). The data were normalized under the assumptions of equal inelastic mean free paths and constant density for all data sets such that:

$$SF_i = \frac{\cos(\theta_i) * \sum_{j=50^\circ, 40^\circ, 30^\circ \text{ Elements}} F(\theta_j)}{3 * \sum_{\text{Elements}} F(\theta_i)} \quad (32)$$

where SF is the normalization factor for take-off angle i . The normalization factors are given in Table 36. Both algorithms were then used to approximate the depth profile for each experiment using five measurements at the predetermined optimum take-off angles (10° , 20° , 40° , 50° , and 70°). The inelastic mean free path used for each element is as follows: carbon = $32\text{\AA}$, sulfur = $36\text{\AA}$, and gold = $36\text{\AA}$.

The variance between σ_{ij}, ψ and λ_{ij} in Equation 2 between elements is

$$F_{i,j}^*(\theta) = \frac{A \cdot \sigma_{i,j} \cdot \Psi}{\sin \phi} \cdot \int_0^{\infty} \eta_j(x) \cdot e^{\frac{-x}{\lambda_{i,j} \cdot \cos \theta}} dx \quad (2)$$

compensated for in the MultiPak[®] software. However, the variance in $A \cdot \psi / \sin(\phi)$ between angles in Equation 2 is not accounted for. Variation in the sample position because of the automation involved in the sample position causes this discrepancy. Therefore, the data were also normalized independently as follows to better account for this variation:

$$SF_i = \frac{\cos(\theta_i)}{\sum_{Elements} F(\theta_i)} \quad (33)$$

Figures 59 and 60 display how normalizing the data independently removes this variation in the approximated profiles. Therefore, the experimental data will be presented independently normalized.

Tyler Regularization

The profiles from all experimental data sets were calculated for the optimum smoothing parameter at 1%, 2%, and 5% error. The mean values of the position of the interface were then calculated by finding the depth at which carbon drops below 50% in concentration and taking the mean from the four replicate samples. This is typically where carbon and gold intersect. The three (upper, lower, and total) mean gradients were also calculated in a similar fashion. Tables 37 & 38 summarize this data.

The data in Table 37 indicates that the profiles are highly reproducible and the associated standard deviations are on the low end of those found in the simulated data. However, Table 38 reveals that the interface becomes significantly more gradual and

therefore indicates the data optimized for 1% error is most probably the best smoothing parameter for a general set of data. Figures 61-63 display the approximated depth profile for each data set at this value.

Evaluating the plots for the C16 thiols it is obvious that at least some crude prior information is needed to determine if the approximated profile is plausible. If not, the smoothing parameter must be adjusted accordingly. Typically if the profile appears to be oscillatory or has large unanticipated features the system is under-smoothed and the smoothing parameter should be increased to verify that the features are not artifacts of the algorithm.

Singular Value Decomposition

The profiles from all experimental data sets were calculated for 1 and 2 singular values. The mean position of the interface and mean value of the gradient was again calculated as described above and displayed in Tables 39 and 40.

From the above Tables 39 and 40, it again appears that the cases optimized for 1% error are the general optimum. The cases that converge with three singular values display a considerable amount of instability at the surface when evaluating the approximated profiles qualitatively. Therefore, the best generalization that can be made about data of this type is to use two singular values in the approximations. The approximated depth profiles for the experimental data sets using the Singular Value Decomposition algorithm optimized for 2 % or 5% error are displayed in Figures 64-66.

While the above plots don't display any indication of undersmoothing, the user must remain aware of the possibility of oversmoothing. While it is anticipated that 2

singular values is the general optimum, because of the dramatic difference in smoothing between 2 and 3 singular values it is recommended that the other is routinely investigated.

Experimental Summary

Both algorithms produced highly reproducible results with the standard deviations at the low end of what was observed in the simulated data. The algorithms appear complementary to one another. The Tyler Algorithm displays considerable surface instability but has considerably better interface resolution. The SVD algorithm accurately displays the overlayer concentration but sacrifices resolution. Therefore, it may be beneficial to obtain profiles from both algorithms and extract semi-quantitative results from each.

Table 34. Experimentally Collected Topography Data

Sample	Scan Size	Vertical Range (nm)	Surface Area (mm)	Roughness
C8a	1 μm	8.590	1.011	1.011
	10 μm	63.444	100.260	1.003
	50 μm	72.470	2500.800	1.000
C8b	1 μm	Unable to Collect Data		
	10 μm	55.035	100.910	1.009
	50 μm	58.263	2507.500	1.003
C12a	1 μm	7.899	1.004	1.004
	10 μm	7.432	100.040	1.000
	50 μm	73.038	2500.000	1.000
C12b	1 μm	Unable to Collect Data		
	10 μm	34.296	100.540	1.005
	50 μm	170.170	2501.000	1.000
C16a	1 μm	4.704	1.005	1.005
	10 μm	50.716	100.040	1.000
	50 μm	142.960	2500.100	1.000
C16b	1 μm	7.756	1.017	1.017
	10 μm	13.870	100.030	1.000
	50 μm	Unable to Collect Data		
Max		170.170	2507.500	1.017
Min		4.704	1.004	1.000
Median		50.716	100.260	1.003
Mean		51.376	874.350	1.004

Table 35. Experimental Signal Intensities

Sample		Take-Off Angle (Degrees)	Measured Intensity					
			Carbon	Sample A Gold	Sulfur	Carbon	Sample B Gold	Sulfur
C 8 T h i o l	E x p e r i m e n t 1	80	28730	195512	4178	29459	190738	3650
		75	35299	337964	6226	38743	345485	5630
		70	44418	568278	8302	46512	568769	7716
		65	48371	796489	9782	51434	810358	8772
		60	58269	1113769	12406	59164	1132989	11739
		50	70703	1788929	15375	71878	1797954	14440
		40	77649	2507530	17260	81912	2561754	16496
		30	93750	3519456	21040	90959	3455627	18705
		20	103143	4368044	24842	105854	4319537	20972
		10	113727	5199735	26164	115547	5144268	23530
	E x p e r i m e n t 2	80	26531	195137	3742	30081	193178	3554
		75	33317	324970	5646	37497	329877	5299
		70	43375	555606	7729	46196	561454	7838
		65	45303	739785	9052	49959	790607	9165
		60	53970	1077379	12095	56608	1109603	10970
		50	64486	1732397	14099	67863	1758726	13488
		40	65718	2270641	16350	78262	2468438	15979
		30	82504	3256505	18896	88042	3232317	18065
		20	85234	3823128	20033	94470	3921692	19265
		10	95488	4387824	23047	102880	4624777	23354
C 1 2 T h i o l	E x p e r i m e n t 1	80	39716	128819	2819	38677	136497	2672
		75	51082	249383	4490	49704	261667	4310
		70	63404	442950	6062	62160	466792	6364
		65	67387	673791	7731	63855	691421	7915
		60	82853	968709	9425	75219	988567	8880
		50	98267	1562398	11680	92395	1609919	12144
		40	110385	2275154	13540	103265	2320422	14313
		30	121578	3040681	16175	123436	3189597	16542
		20	138700	3918636	18140	135300	4008002	19532
		10	154011	4724457	21719	144638	4670169	21423
	E x p e r i m e n t 2	80	39168	129269	2519	38996	134400	2548
		75	50255	242399	4102	46069	245142	4103
		70	63215	440319	6149	57705	444702	5883
		65	67030	647840	7549	59532	636395	7265
		60	76675	957037	8954	71667	933365	8774
		50	94472	1540417	11971	84085	1528209	11494
		40	105127	2134678	12838	89598	2021781	12140
		30	111526	2762358	14530	109596	2854926	14505
		20	118615	3388218	15809	125146	3742880	17651
		10	131927	4050034	17032	136804	4471163	19305

Table 35 – Continued

Sample		Take-Off Angle (Degrees)	Measured Intensity					
			Sample A			Sample B		
			Carbon	Gold	Sulfur	Carbon	Gold	Sulfur
C 1 6	E	80	45154	84362	1673	47570	89486	1883
	x	75	58370	172024	3100	58608	185420	3307
	p	70	74580	334472	4631	71983	352182	4977
	e	65	81758	533253	6169	86026	560888	6709
	r	60	98141	785424	7643	96101	815855	8018
	i	50	119797	1354492	10137	113491	1354950	10094
	m	40	141497	2005559	13229	143921	2032906	12537
	e	30	168887	2805941	15345	164969	2848786	14804
	n	20	185354	3589825	17734	185839	3658599	18124
	t	10	205465	4336445	18570	203885	4432155	18931
T h i o l	E	80	42548	80594	1640	44524	86640	2026
	x	75	55226	167109	3038	61141	176080	3388
	p	70	71765	322469	4554	76436	337663	4791
	e	65	77460	503904	6003	84314	535068	5758
	r	60	94975	771201	7820	95442	791134	8214
	i	50	108294	1285851	9837	110525	1308947	9998
	m	40	134533	1929685	11816	137748	1963734	12116
	e	30	160051	2705165	14023	160540	2787858	14692
	n	20	180526	3464091	15828	180336	3556103	17489
	t	10	194162	4179911	17154	191015	4154539	17814

Table 36. Normalization Factors used for Experimental Data

Angle	80°	75°	70°	65°	60°
Factor	0.9013	0.9723	0.9330	0.9627	0.8930
Angle	50°	40°	30°	20°	10°
Factor	0.8398	0.7819	0.6911	0.6278	0.5725

Table 37. Accuracy Summary for Tyler Algorithm on Experimental Data

	Smoothing Parameter	Depth					
		Concentration = 25%		Concentration = 50%		Concentration = 75%	
		Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.
C8 Thiol	1.56E-03	14.294	0.457	12.620	0.173	7.682	0.763
	9.07E-03	18.012	0.749	12.117	0.660	5.802	0.199
	2.94E-02	17.524	0.507	13.330	0.872	5.380	0.557
C12 Thiol	1.56E-03	16.375	0.792	15.113	0.636	12.292	1.505
	9.07E-03	21.940	0.340	16.249	0.914	10.232	0.702
	2.94E-02	20.560	0.416	17.294	0.709	11.949	1.736
C16 Thiol	1.56E-03	23.499	2.312	20.845	1.105	14.649	1.663
	9.07E-03	30.065	0.601	21.267	0.597	14.072	0.282
	2.94E-02	28.773	1.154	22.995	0.563	15.676	1.305

Table 38. Resolution Summary for Tyler Algorithm on Experimental Data

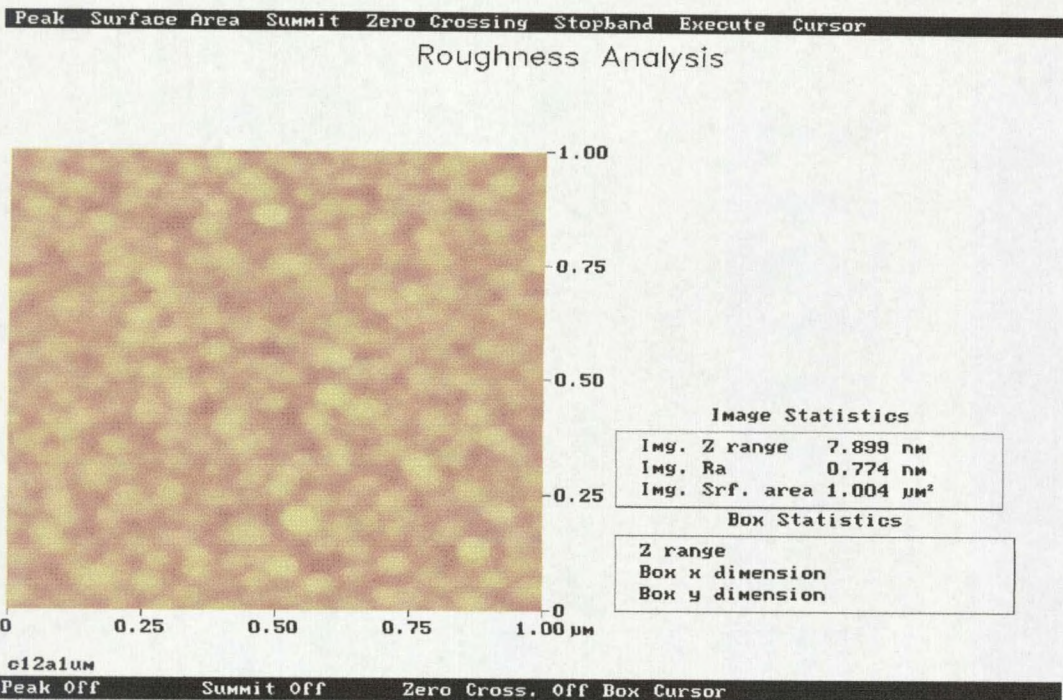
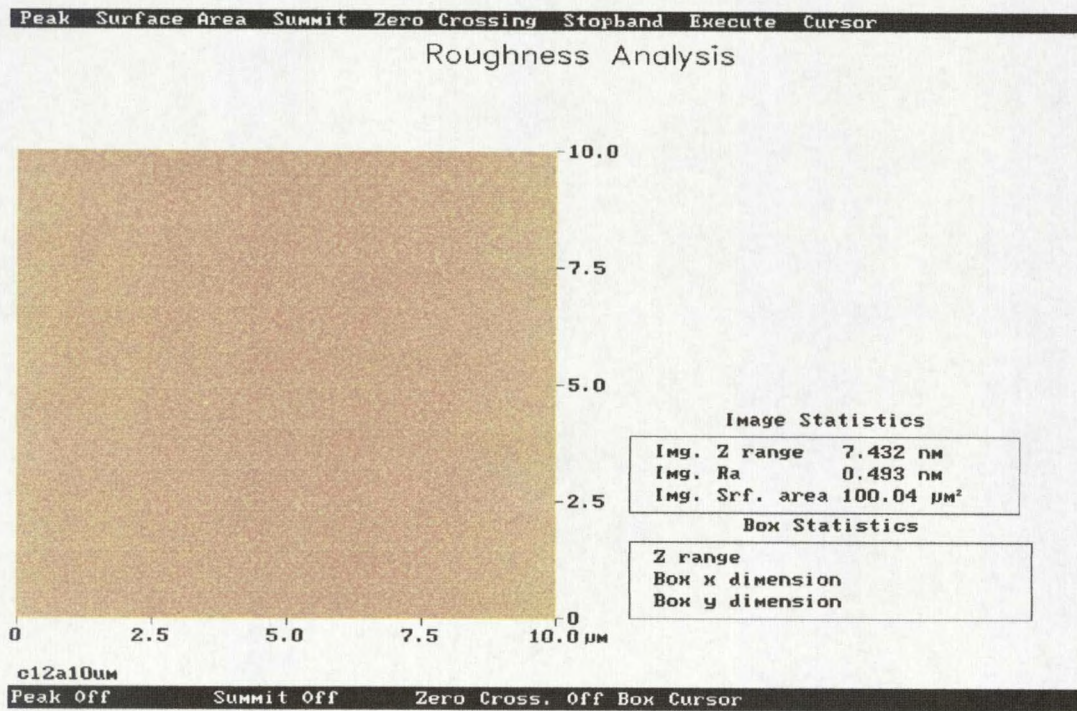
	Smoothing Parameter	Inverse $\times 10^2$					
		Upper Gradient		Lower Gradient		Total Gradient	
		Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.
C8 Thiol	1.56E-03	-19.752	3.460	-6.694	1.719	-13.223	2.411
	9.07E-03	-25.261	2.824	-23.579	0.735	-24.420	1.509
	2.94E-02	-31.800	4.894	-16.773	2.275	-24.287	1.409
C12 Thiol	1.56E-03	-11.283	5.476	-5.048	1.789	-8.165	3.487
	9.07E-03	-24.067	0.959	-22.763	2.514	-23.415	0.917
	2.94E-02	-21.381	4.175	-13.066	4.372	-17.224	4.251
C16 Thiol	1.56E-03	-24.786	10.431	-10.614	4.989	-17.700	7.704
	9.07E-03	-28.779	2.916	-35.195	2.664	-31.987	1.713
	2.94E-02	-29.275	3.502	-23.111	5.793	-26.193	4.639

Table 39. Accuracy Summary for Singular Value Decomposition on Experimental Data

	Singular Values	Depth					
		Concentration = 25%		Concentration = 50%		Concentration = 75%	
		Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.
C8 Thiol	3	16.549	0.533	11.815	1.538	9.166	3.137
	2	16.631	0.417	11.984	1.209	10.004	1.479
C12 Thiol	3	16.711	6.578	14.018	4.485	12.503	3.680
	2	21.644	0.683	16.841	0.733	14.882	0.765
C16 Thiol	3	26.620	1.743	22.733	0.608	19.530	0.490
	2	28.948	0.166	21.786	0.158	19.313	0.165

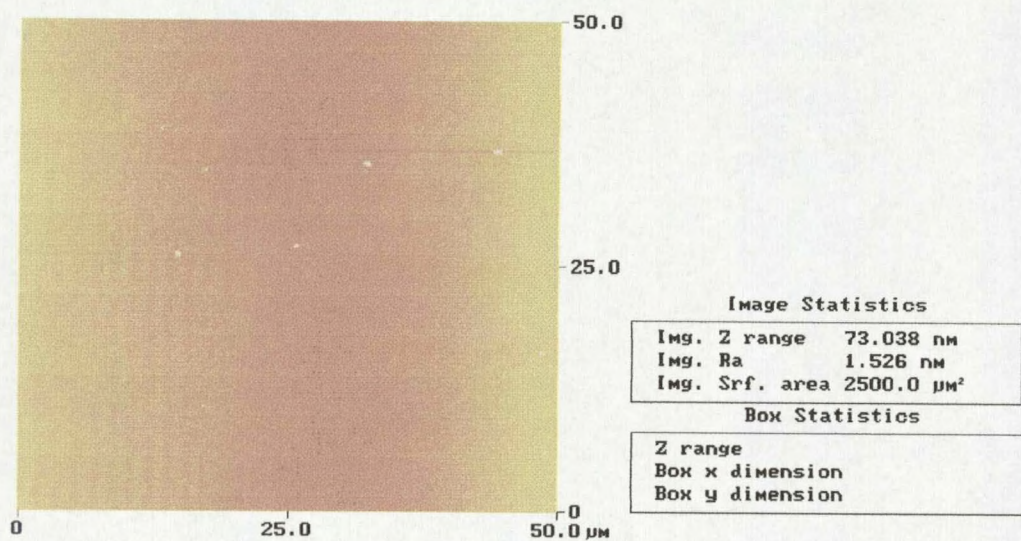
Table 40. Resolution Summary for Singular Value Decomposition on Experimental Data

	Singular Values	Inverse x 10 ²					
		Upper Gradient		Lower Gradient		Total Gradient	
		Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.
C8 Thiol	3	-10.596	6.470	-18.936	4.363	-14.766	5.412
	2	-7.922	1.131	-18.586	3.668	-13.254	2.399
C12 Thiol	3	-6.062	3.228	-10.769	9.943	-8.416	6.243
	2	-7.835	0.445	-19.210	0.734	-13.523	0.587
C16 Thiol	3	-12.816	2.900	-15.548	9.164	-14.182	4.048
	2	-9.889	0.157	-28.650	0.350	-19.270	0.248

Figure 56. $1\mu\text{m}^2$ Scan of C12a Alkanethiol on GoldFigure 57. $100\mu\text{m}^2$ Scan of C12a Alkanethiol on Gold

Peak Surface Area Summit Zero Crossing Stopband Execute Cursor

Roughness Analysis



c12a50um

Peak Off Summit Off Zero Cross. Off Box Cursor

Figure 58. $2500\mu\text{m}^2$ Scan of C12a Alkanethiol on Gold

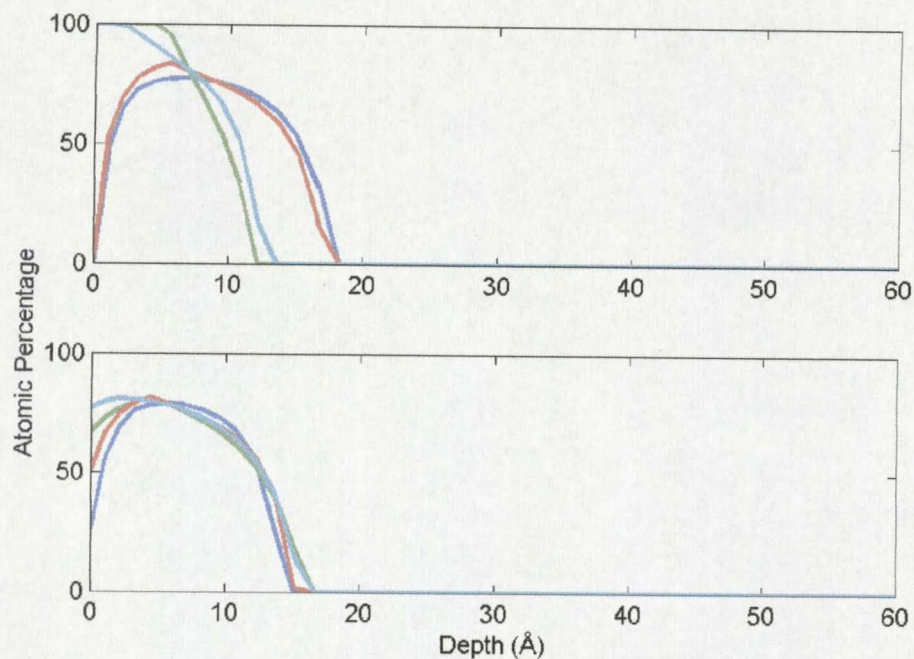


Figure 59. Approximated Carbon Profile using Tyler Regularization algorithm with $\alpha = 1.8^{1-12}$. a) Normalized Using Factors in Table 36. b) Independently Normalized

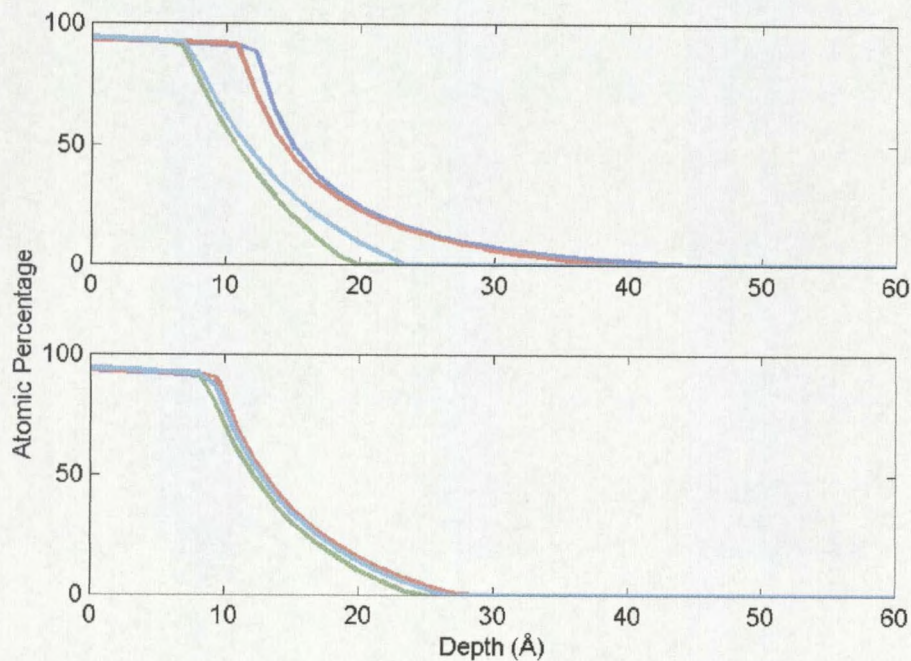


Figure 60. Approximated Carbon Profile Using SVD Algorithm with 2 Singular Values. a) Normalized Using Factors in Table 36. b) Independently Normalized.

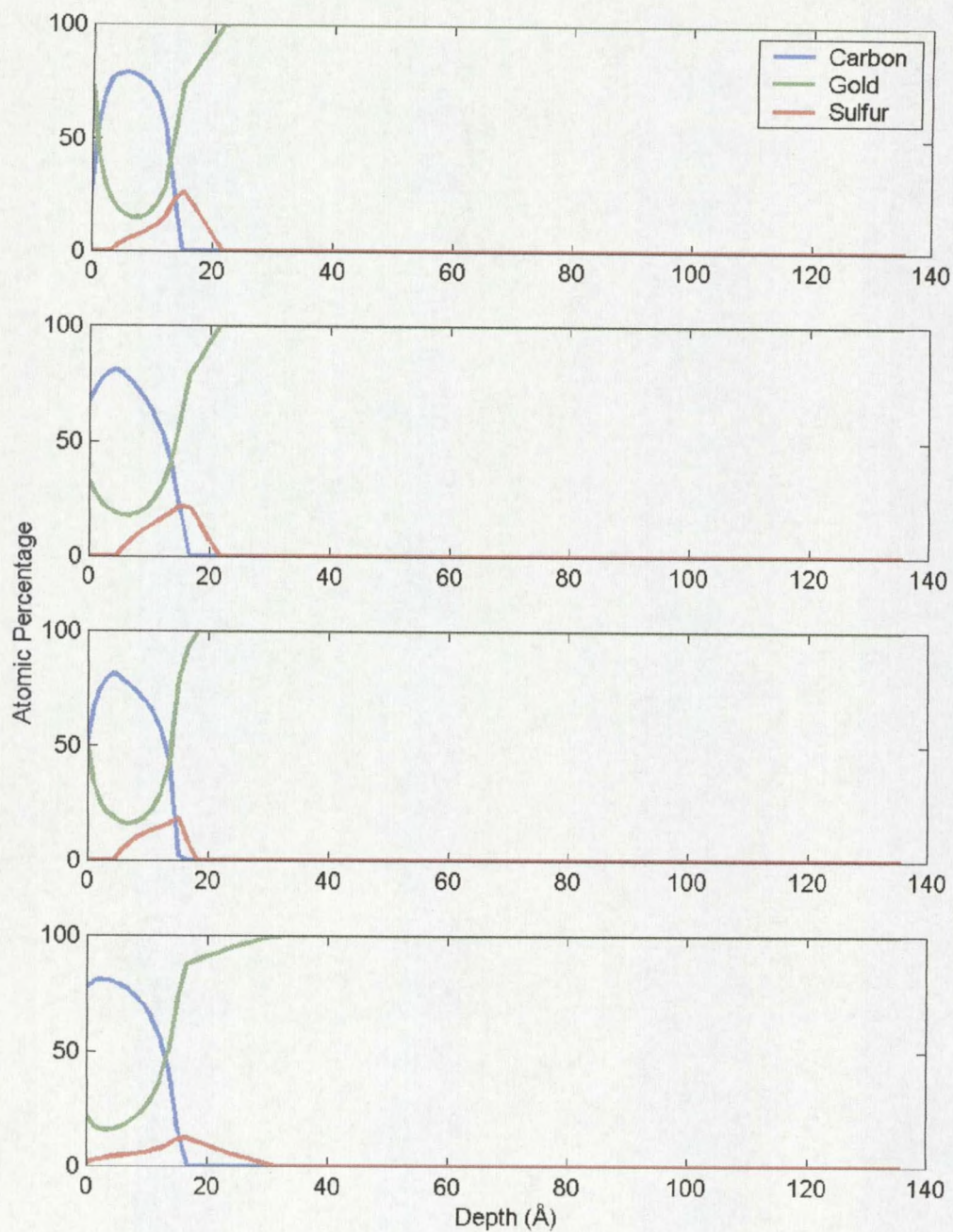


Figure 61. Approximated Depth Profile for C8 Alkanethiol on Gold using Tyler Algorithm ($\alpha=1.8^{1-12}$)

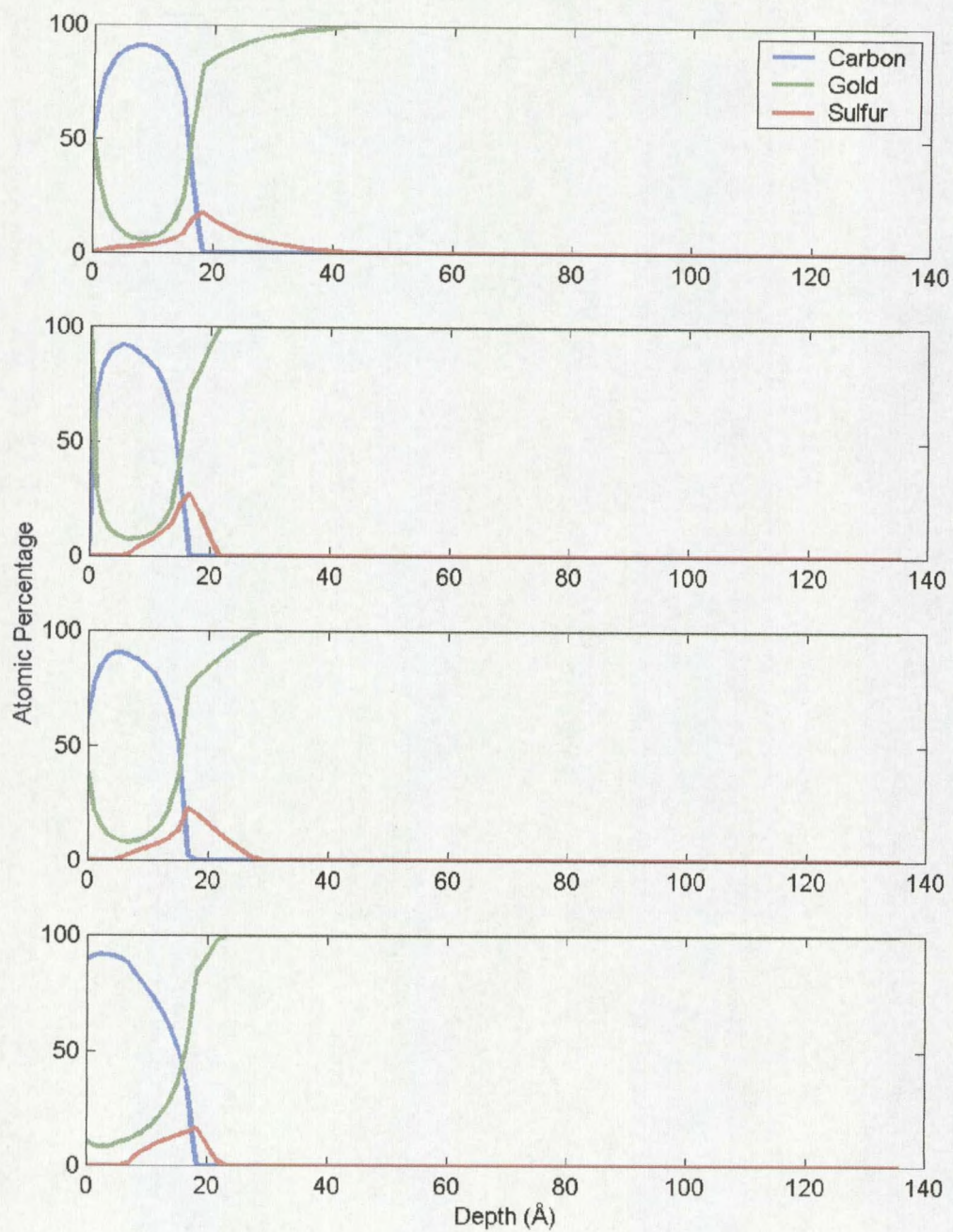


Figure 62. Approximated Depth Profile for C12 Alkanethiol on Gold using Tyler Algorithm ($\alpha=1.8^{1-12}$)

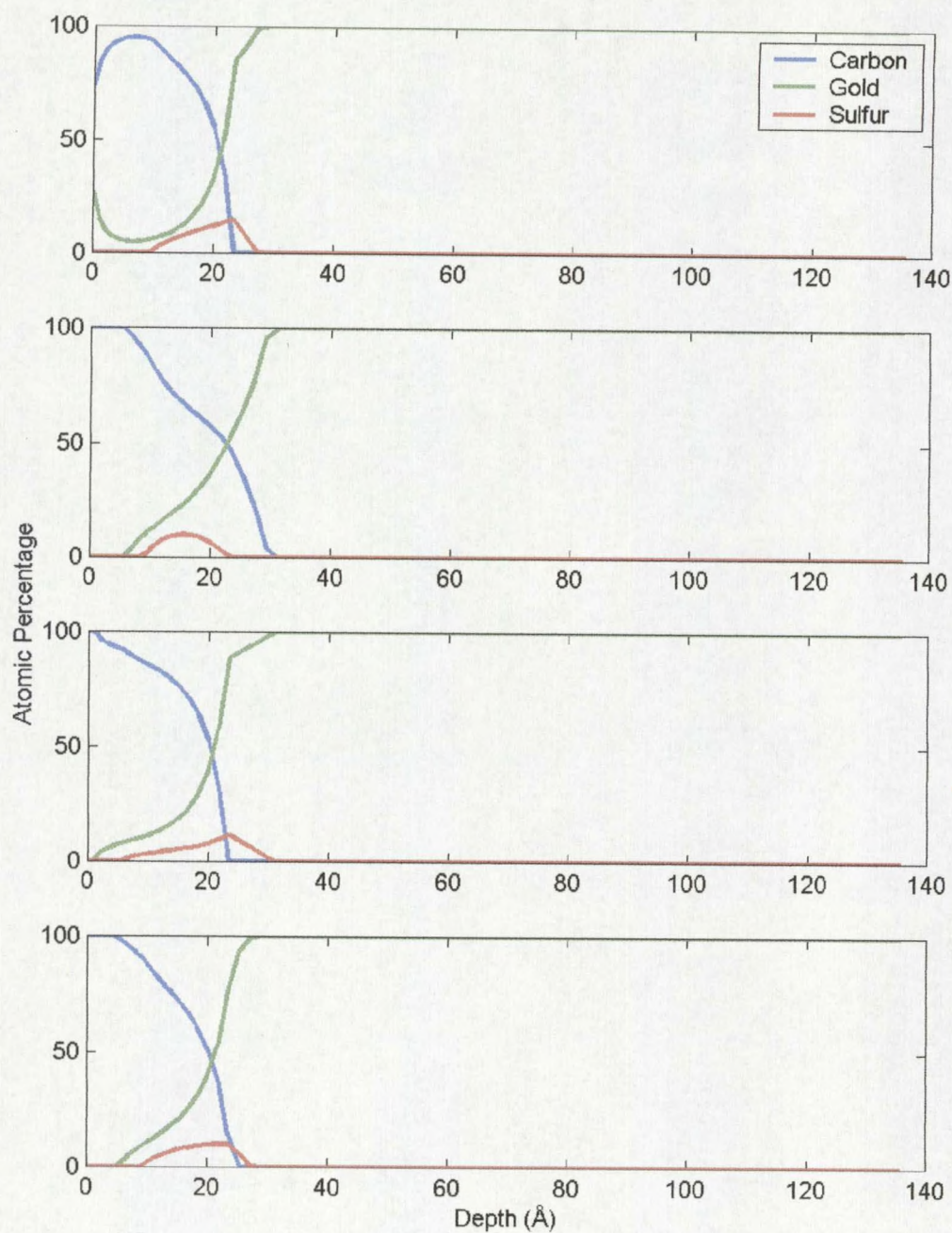


Figure 63. Approximated Depth Profile for C16 Alkanethiol on Gold using Tyler Algorithm ($\alpha=1.8^{1-12}$)

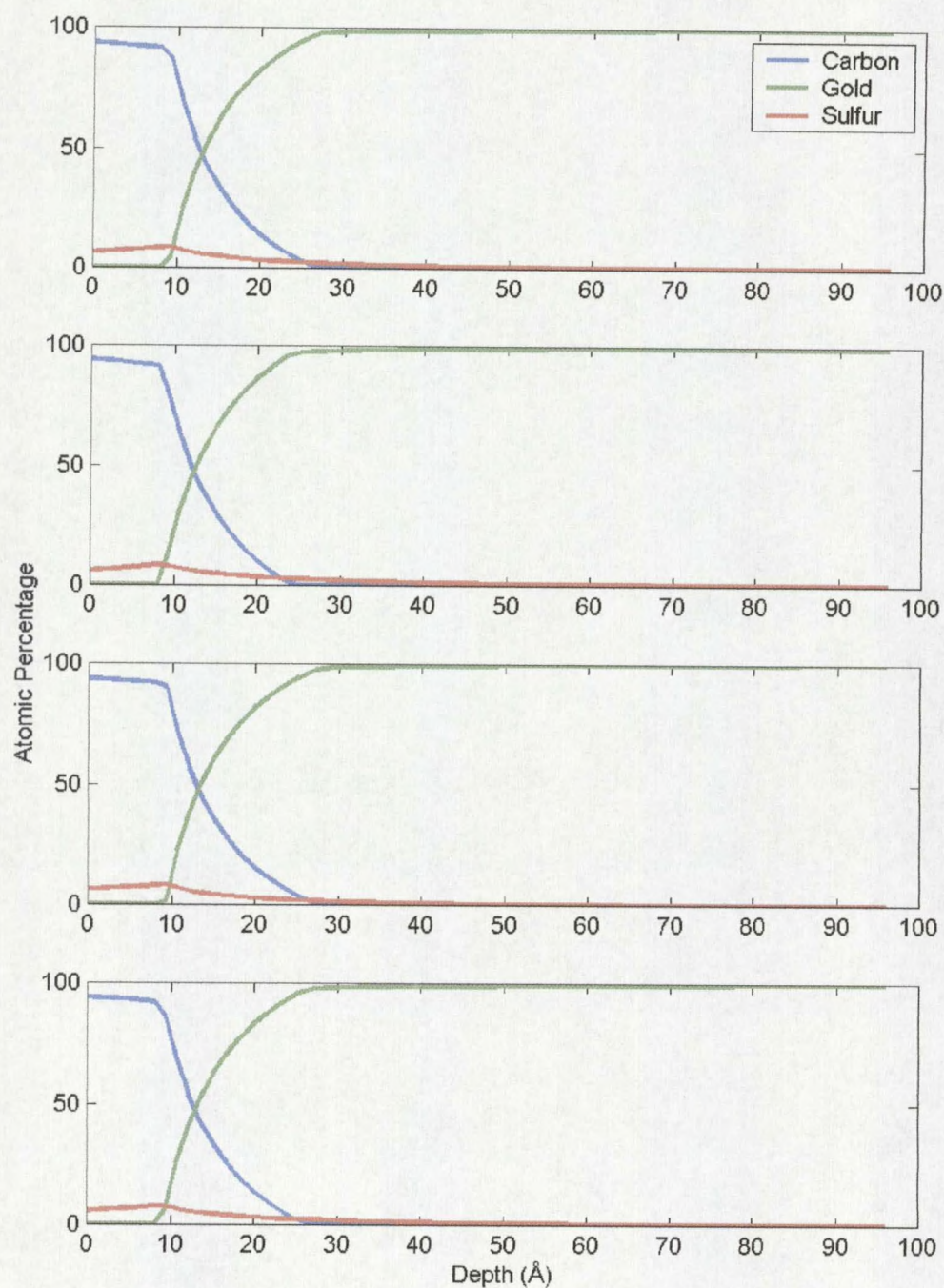


Figure 64. Approximated Depth Profile for C8 Alkanethiol on Gold using Singular Value Decomposition (Number of Singular Values = 2)

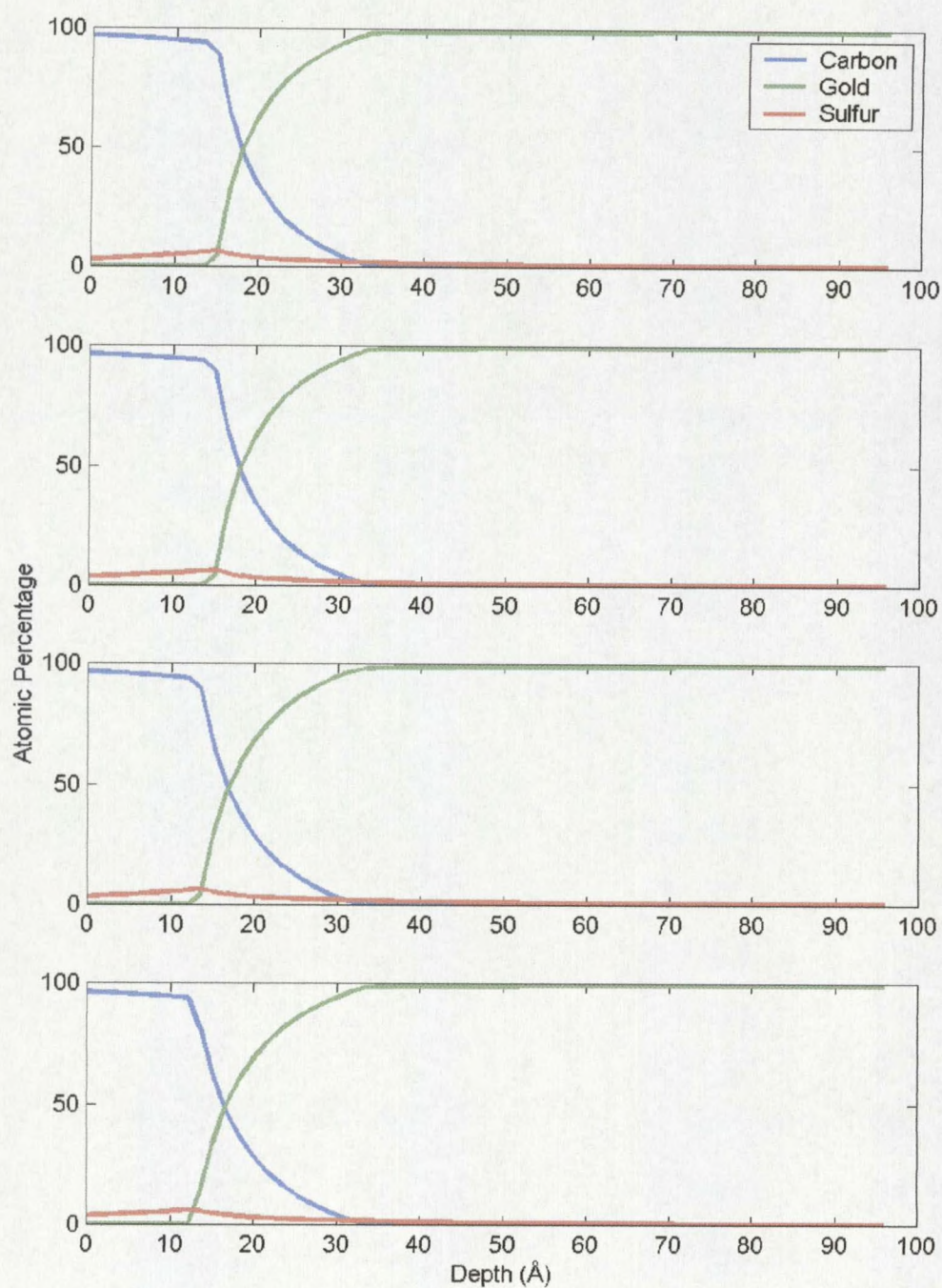


Figure 65. Approximated Depth Profile for C12 Alkanethiol on Gold using Singular Value Decomposition (Number of Singular Values = 2)

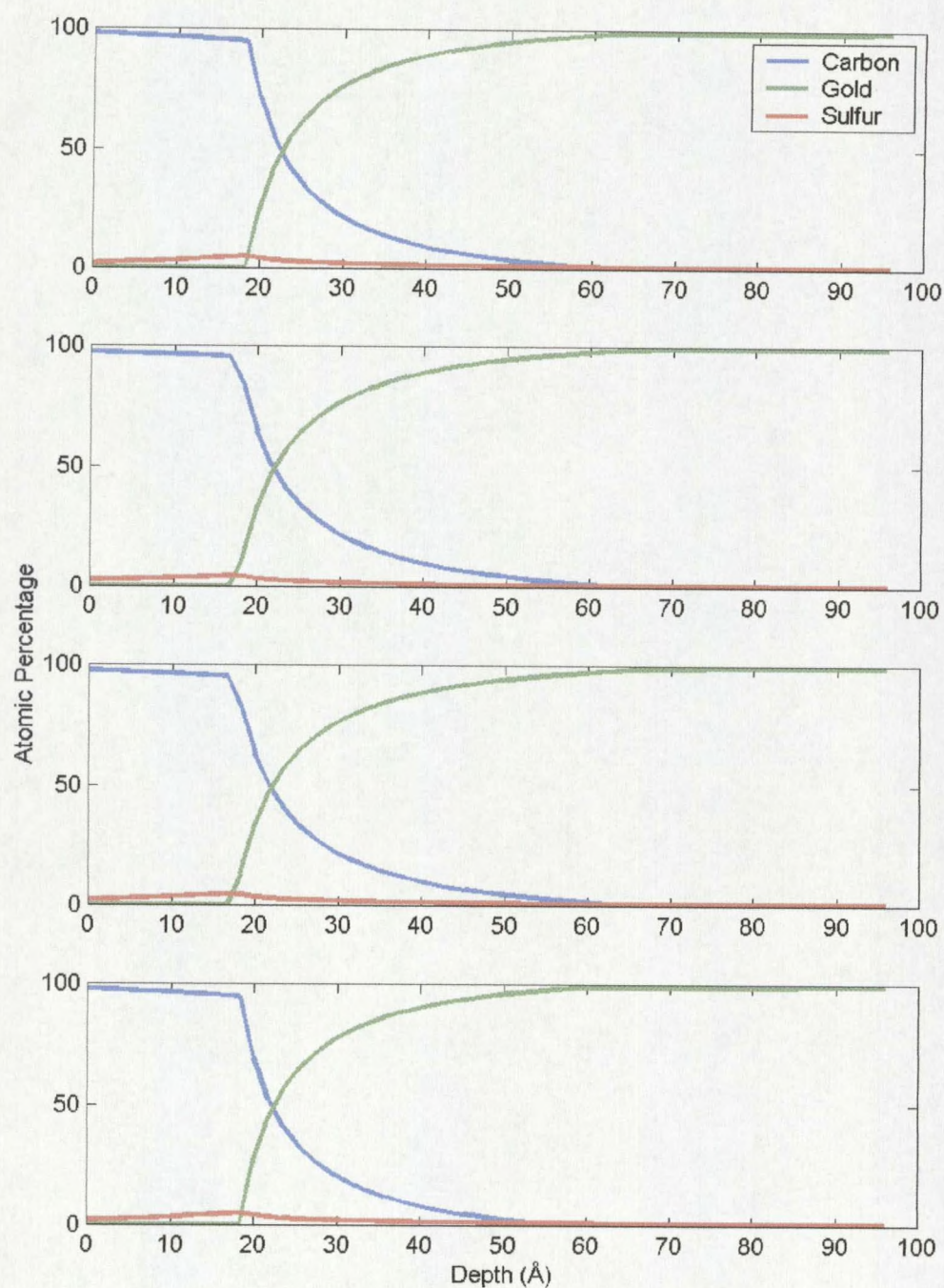


Figure 66. Approximated Depth Profile for C16 Alkanethiol on Gold using Singular Value Decomposition (Number of Singular Values = 2)

CHAPTER 9

CONCLUSIONS

Calculating depth/concentration profiles is a mathematically unstable problem. Therefore, conventional methods cannot be used to determine error propagation. Rather, simulating XPS data with known amounts of error allows for an upper bound to be put on the error propagation but in no way makes this a well-posed problem. During the course of this study, it has become increasingly apparent that there is no single solution to improve the approximation of the depth/concentration profiles. The following sections summarize the modifications to both algorithms and/or how the measurements are taken or simulated in an attempt to improve results.

Changing the Approximating Function

Both the Tyler Regularization Algorithm and the Singular Value Decomposition Algorithm have historically used the kernel (Equation 13) as the approximating function in the algorithm. Modifications were made to both algorithms to replace the approximating function with power function (Equation 14), cosine function (Equation 15), and a Legendre polynomial function (Equation 16). It was readily apparent that the

$$n(x) = \max \left[0, \sum_i^n c_i K(x, \theta_i) \right], \quad (13)$$

$$n(x) = \max \left[0, \sum_i^n c_i x^i \right], \text{ or} \quad (14)$$

$$n(x) = \max \left[0, \sum_i^n c_i \cdot x \cdot \cos(\omega) \right] \quad \text{where} \quad \omega = \frac{\pi}{180 \cdot 2^i}, \text{ or} \quad (15)$$

$$n(x) = \max \left[0, \sum_i^n c_i \sum_{m=0}^M \frac{(2i-2m)!}{2^i m! (i-m)! (i-2m)!} x^{i-2m} \right] \quad (16)$$

solution for both the cosine and the Legendre polynomial approximating functions were highly unstable and results, when obtained, were oscillatory. The power approximating function provided very good results, however it had an extremely narrow region of convergence. This narrow region of convergence is most likely a result of the magnitude ratio between the largest and smallest terms ($c \cdot x^n$: $c \cdot x$) in Equation 14. This will cause the matrix **M** in Equation 18 to approach singularity and thus the solution to be highly oscillatory. Even in the cases where the ratio is at its smallest (3 measurements) the stability data is not favorable. Therefore, the only stable approximating function used in this study was the kernel as used by Tyler, Tikhonov, Phillips, and Twomey.

Observed Trends

- Noise or error in the signal intensities has a considerable impact on the smoothing and thus the calculated depth/concentration profile. Therefore, efforts should be made to reduce any error other than systematic error, which will not greatly affect the approximated profile.
- Little additional information is gained by taking more than five measurements. It appears to be more beneficial to increase the signal to noise ratio.
- The algorithms are consistent with other findings in that it is unable to resolve gradients narrower than the mean overlay thickness.

- Erroneous concentrations in the upper $\sim 5\text{-}10\text{\AA}$, depending on overlayer thickness, are sometimes calculated due to the surface instability.
- Tailing is commonly observed deep in the sample. This typically occurs between 30-60 $\text{\AA}$ into the substrate.
- Small errors in the approximated position of the interface produce large error in the approximated profile at points near the interface. This error is amplified as the interface becomes sharper.
- The predictive criterion does an adequate job of estimating the necessary smoothing parameter. However, when used with the Tyler algorithm it tends to undersmooth for interfaces thicker than approximately 30 $\text{\AA}$ and oversmooth for thicker overlayers.
- Both algorithms tend to underestimate the inverse gradient for overlayers $< 30\text{\AA}$. Meaning, if a sharp interface is calculated it is probable that the actual interface is sharp. However, if the interface is more gradual it may be reasonable to assume, given some prior knowledge, that the interface may be sharper than approximated.
- An adequate starting point in the selection of a smoothing parameter can be made if the error in the data can be approximated and is as follows: 0% Error $\Rightarrow \alpha = 1.412\text{E-}05$, 1% Error $\Rightarrow \alpha = 1.556\text{E-}03$, 2% Error $\Rightarrow \alpha = 9.074\text{E-}03$, 5% Error $\Rightarrow \alpha = 2.940\text{E-}02$. However, this is still a highly unstable problem and even crude information as to the general shape of the depth profile is helpful.
- An adequate starting point in the selection for the number of singular values can be made if the error in the data can be approximated and is as follows: 0% Error $\Rightarrow \text{NSV} = 4$, 1% Error $\Rightarrow \text{NSV} = 3$, 2% Error $\Rightarrow \text{NSV} = 2$, 5% Error $\Rightarrow \text{NSV} = 2$. Again, prior information about the depth profile is helpful.
- The algorithms appear complementary to one another. The Tyler Algorithm displays considerable surface instability but has considerably better interface resolution. The SVD algorithm accurately displays the overlayer concentration but sacrifices resolution. Therefore, it may be beneficial to obtain profiles from both algorithms and extract semi-quantitative results from each.

Surface Roughness

- As the cosine of the take-off angle is decreased, the surface roughness contributes more to the measured intensity by changing the effective take-off angle at which the data is collected.

- By removing the measurement at 80° from the surface normal the effect of surface roughness is dampened without significantly impacting the approximated profile in the near surface region.
- The optimum set of measurements evaluated on surfaces with a maximum roughness value of 1.019 was as follows: take-off angles (10° , 20° , 40° , 50° , and 70°). This set of measurements provides the best compromise of dampening the effects of surface roughness and providing surface accuracy.

Experimental Samples

- All experimentally collected data provided consistent results to the known chemical structure of each sample. Each data set had data collected at take-off angles of 10° , 20° , 40° , 50° , and 70° . The predetermined optimum smoothing parameter for 1% error (1.8^{1-12}) and number of singular values for 2% error (2).
- Normalizing the signal intensities to correct for a systematic error stemming from instability in the instrument significantly affects the calculated profile. In this study, the normalization assumed constant density and equal inelastic mean free path for all elements.

Future Work and Recommendations

Because little additional information is provided from taking ten measurements over five, instrument time is utilized more efficiently by taking five measurements at 10° , 20° , 40° , 50° , and 70° from the surface normal and reducing the signal to noise ratio. The optimum parameters for use with the algorithms appear to be a smoothing parameter of 1.8^{1-12} and 2 singular values.

Because the experimental profiles are significantly affected by the normalization process, recommendations for further work are to investigate how the scaling function affects the calculated profile, and to determine ways to minimize its effects, both numerical and instrumental.

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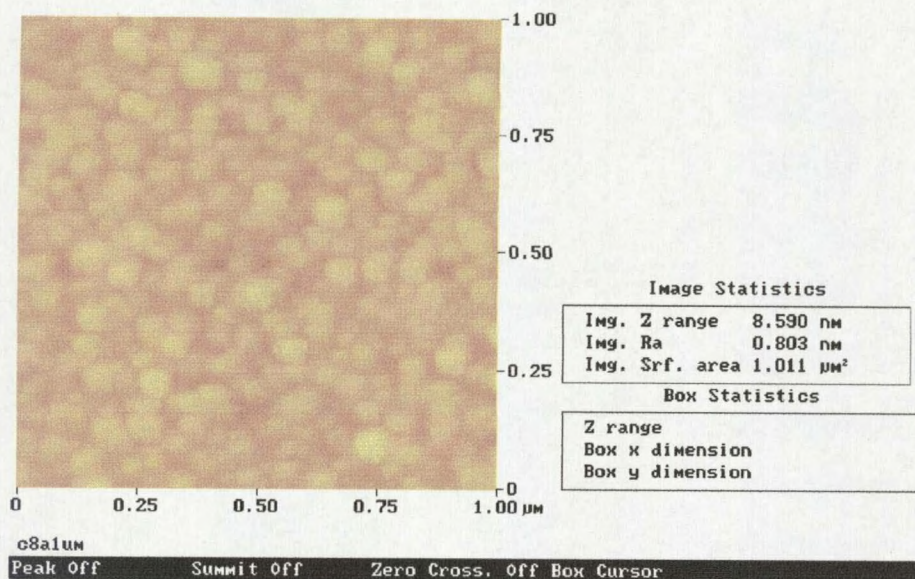
APPENDICES

APPENDIX C

Atomic Force Microscopy Data

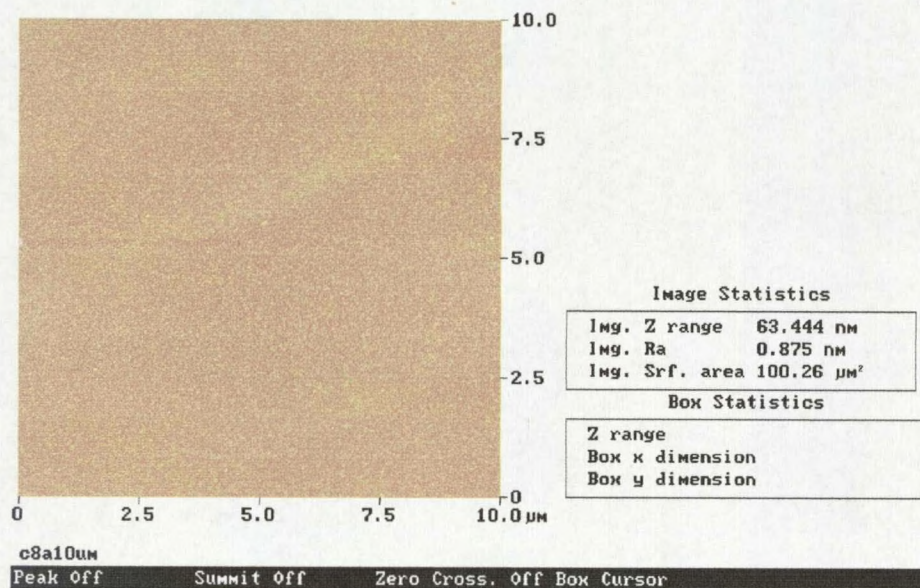
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Roughness Analysis



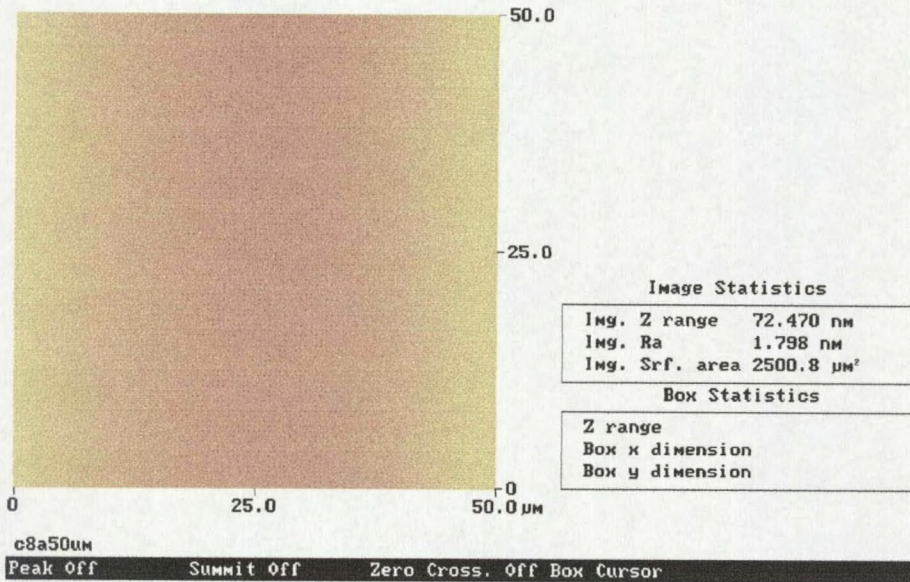
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Roughness Analysis



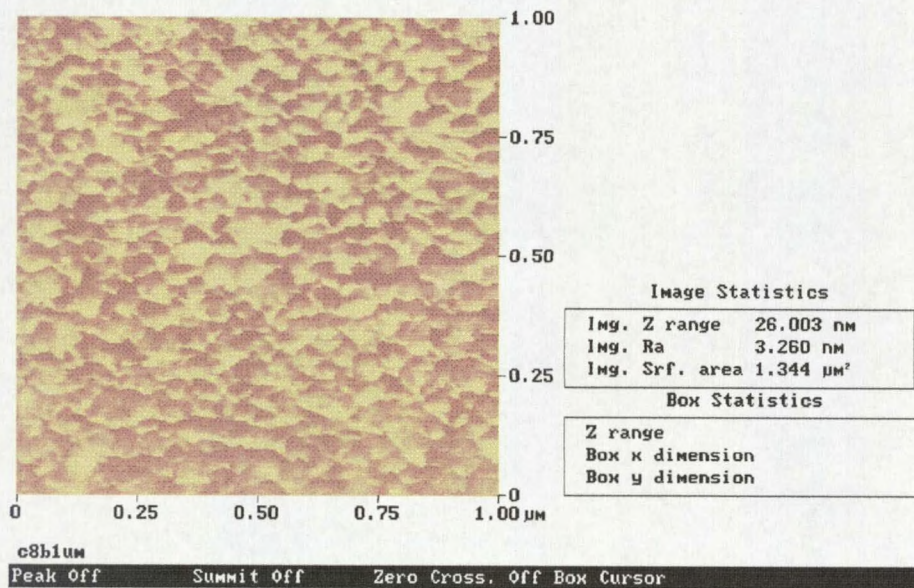
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Roughness Analysis



Peak Surface Area Summit Zero Crossing Stopband Execute Cursor

Roughness Analysis



Peak Surface Area Summit Zero Crossing Stopband Execute Cursor

Roughness Analysis

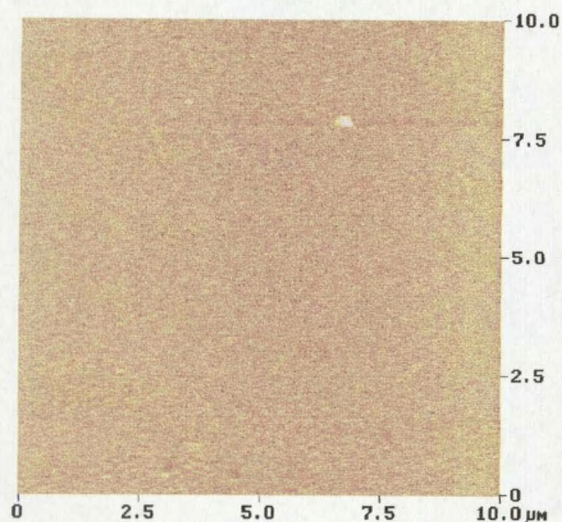


Image Statistics

Img. Z range	55.035 nm
Img. Ra	1.418 nm
Img. Srf. area	100.91 μm^2

Box Statistics

Z range
Box x dimension
Box y dimension

c8b10um

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Peak Surface Area Summit Zero Crossing Stopband Execute Cursor

Roughness Analysis

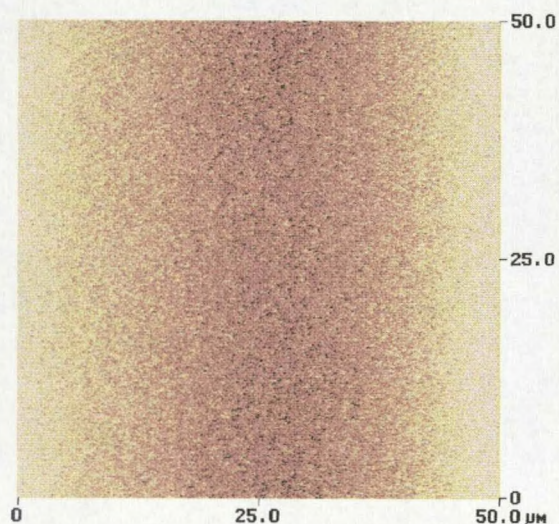


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Box Statistics

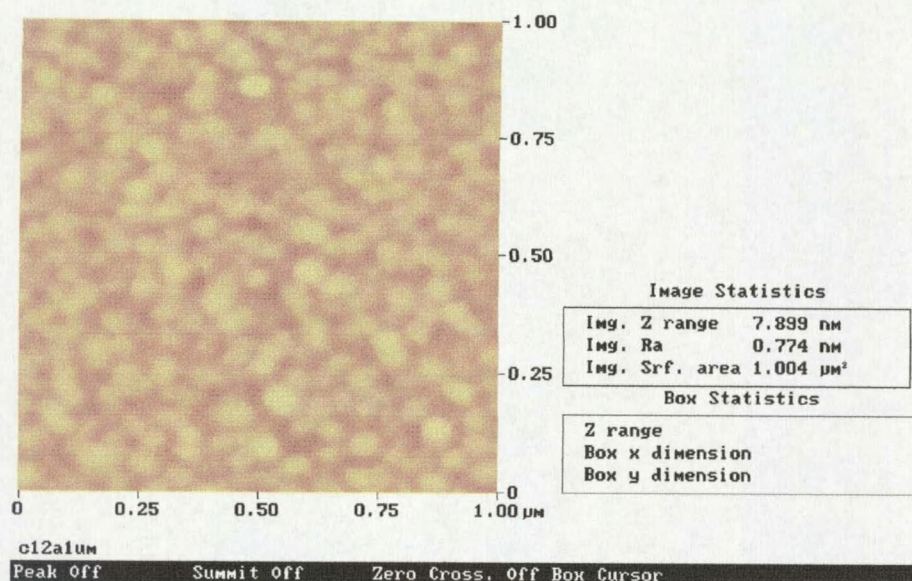
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Box x dimension
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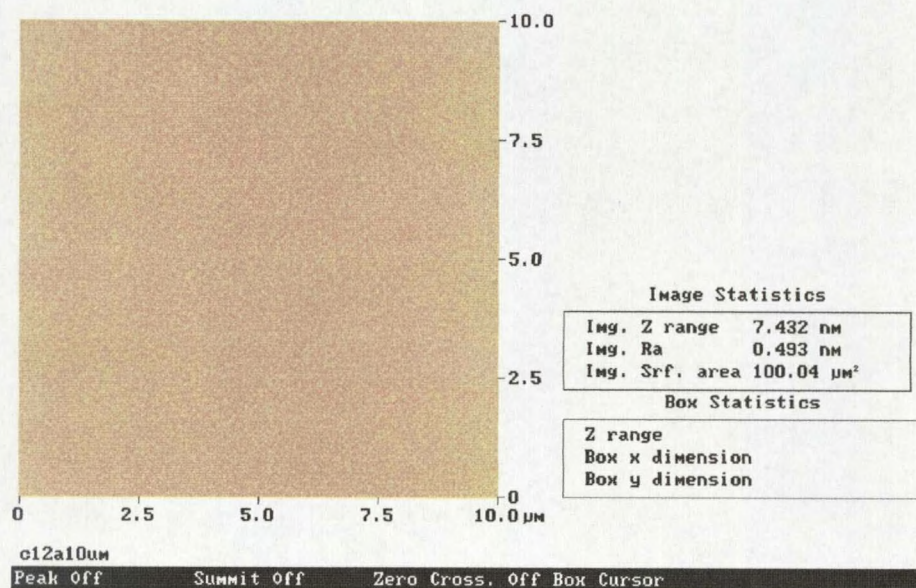
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Roughness Analysis



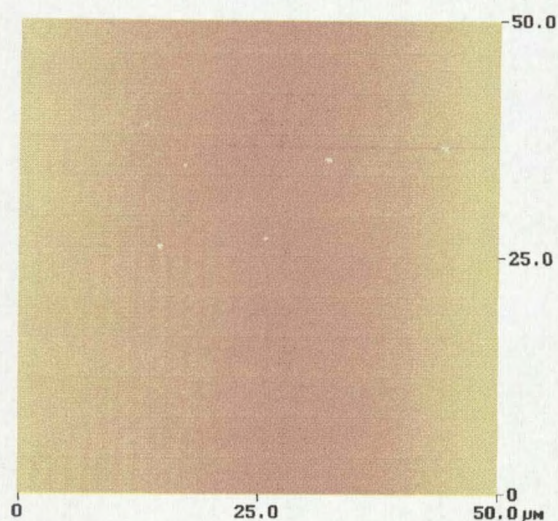
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Roughness Analysis



Peak Surface Area Summit Zero Crossing Stopband Execute Cursor

Roughness Analysis



c12a50um

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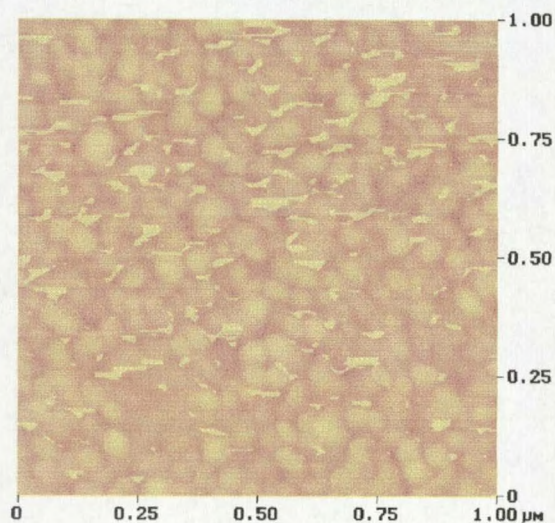
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 Img. Ra 1.526 nm
 Img. Srf. area 2500.0 μm²

Box Statistics

Z range
 Box x dimension
 Box y dimension

Peak Surface Area Summit Zero Crossing Stopband Execute Cursor

Roughness Analysis



c12blum

Peak Off Summit Off Zero Cross. Off Box Cursor

Image Statistics

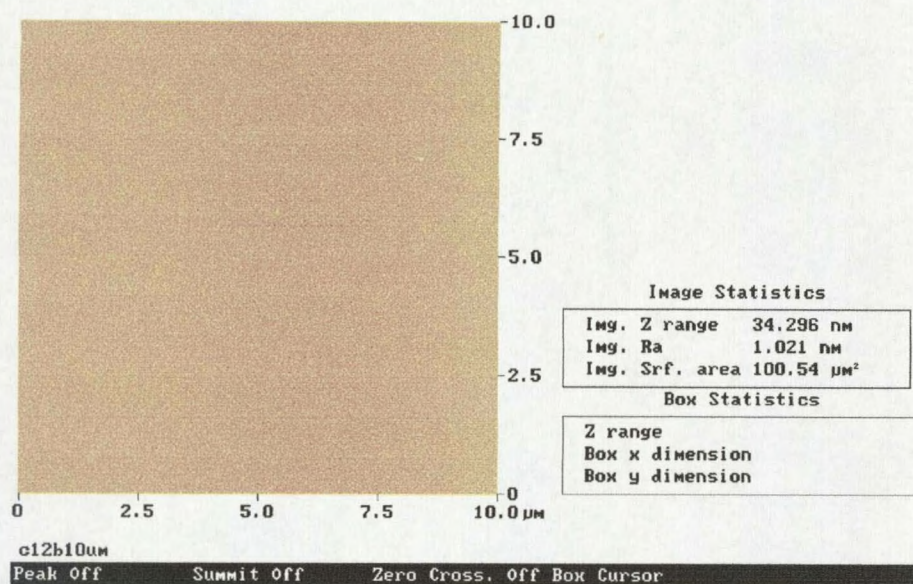
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Box Statistics

Z range
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 Box y dimension

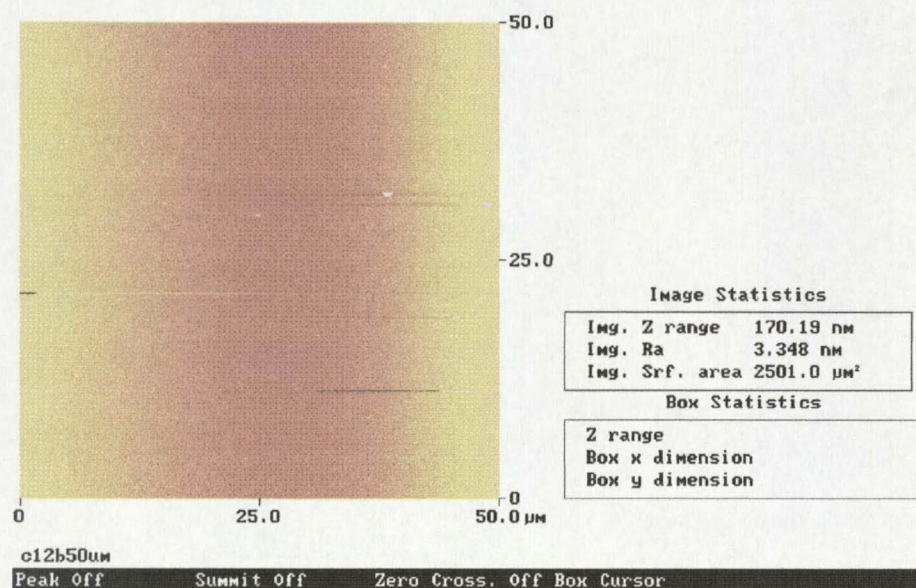
Peak Surface Area Summit Zero Crossing Stopband Execute Cursor

Roughness Analysis



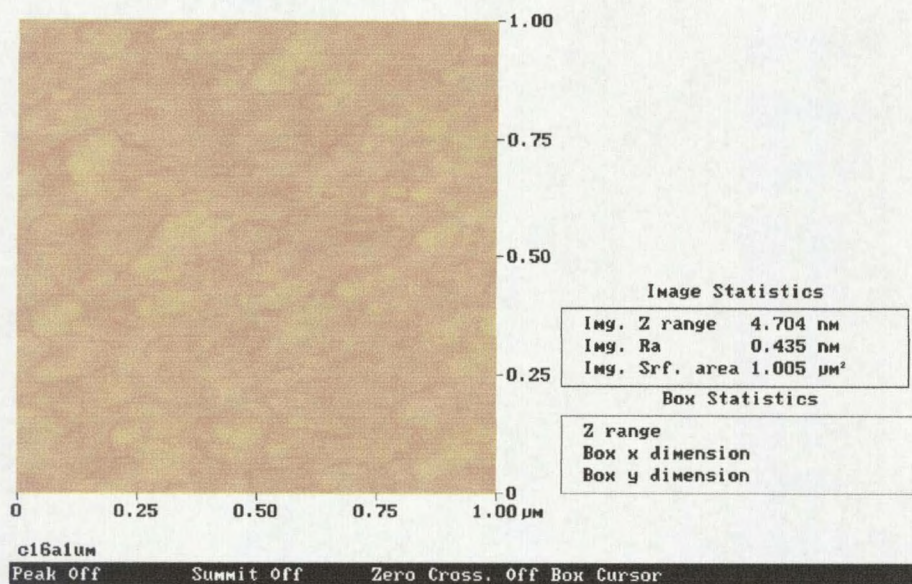
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Roughness Analysis



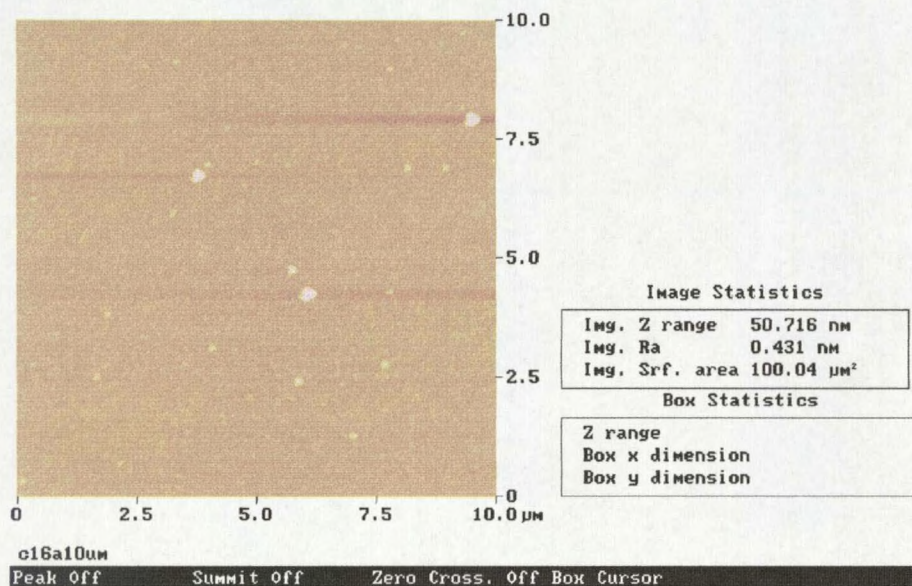
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Roughness Analysis



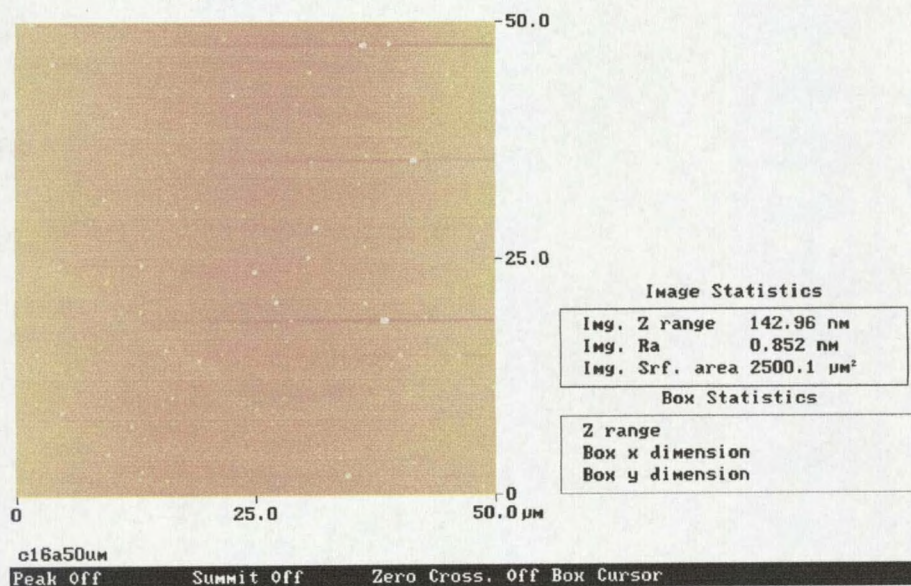
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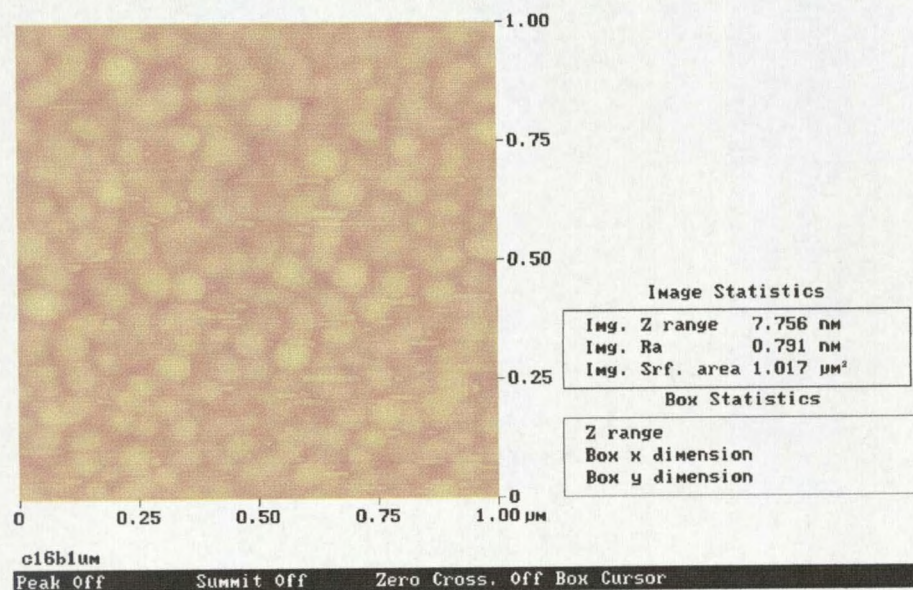
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Roughness Analysis



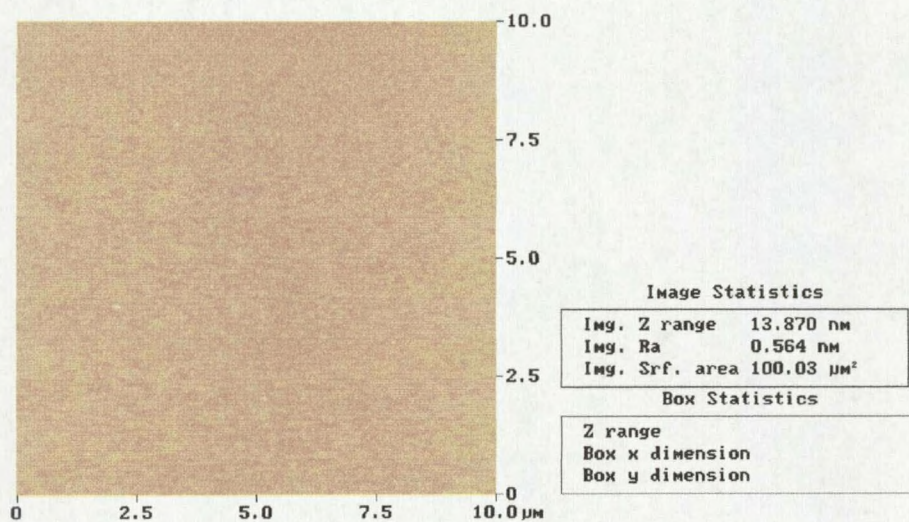
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Roughness Analysis



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Roughness Analysis



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Circulation. Take the separate
jewel case with you.~~