# Matrix-based approach for the inversion of ARXPS data

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## ARTICLE INFO

## ABSTRACT

A matrix-based analytical solution to the inversion and regularization of ARXPS data is presented and its characteristics are explored. For each of the 4 different input concentration depth profiles tested, 50 different sets of noisy ARXPS data are simulated. The profiles are subsequently recovered using both the novel matrix-based solution and conventional numerical methods. It is observed that the matrix-based method was several orders of magnitude faster, and capable of generating profiles equivalent to those obtained by numerical means, under almost all conditions.

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## 1. Introduction

Angle-resolved X-ray photoelectron spectroscopy (ARXPS) is a non-destructive method capable of assessing concentration depth profiles at a sample surface [1]. An XPS analysis is undertaken at a number of different photoemission angles, defined as the angle between the normal to a sample surface and the axis of the analyzer optics. Since electrons are attenuated as they travel through the sample, increasing the angle, which increases the photoelectron escape path length, has the effect of pushing the sampling volume towards shallower depths. Results obtained from a range of different angles can then be used to reconstruct the concentration depth profile through a series of mathematical manipulations.

The recovery of such profiles, however, is equivalent to the inversion of a Laplace transform, a famously unstable "ill-conditioned" problem [2–4], in which even small amounts of noise can cause large and physically unsound spikes in the profile, resulting from the "over-fitting" of the ARXPS data. The common approach to combatting this issue is regularization [2–4], which seeks to find a solution that simultaneously complies with the input data and an assumption about the smoothness of the extracted depth profile. More precisely, regularization involves finding a profile which minimizes the so-called "joint function":

$$\min\{\text{residual norm} + \alpha \text{ solution norm}\} \qquad (1)$$

In this joint function, the residual norm is the sum of the squared differences between the input data and the intensity or intensity ratio obtained from the proposed profile, a smaller residual norm indicating a better fit to the ARXPS data, while the solution norm is a measure of the smoothness of the proposed profile, a smaller solution norm signifying a smoother or flatter profile. The regularization parameter $\alpha$ balances the relative importance of the two norms, and must be selected so as to produce the best combination of fitting the data and smoothing the profile.

Progress in this field has arisen from methods and techniques borrowed from the inverse theory literature and subsequently adapted to the details of the inversion of ARXPS data. A case in point is regularization itself, using both Tikhonov regulators (mathematical functions for the solution norm) [5], and the Maximum Entropy [6,7] regulators employed successfully in astronomy. Other examples include the L-Curve criterion for choosing the value of regularization parameter [8–10], as well as variants of the Backus–Gilbert method [2,11].

More recently, Babanov et al. [12] have demonstrated the applicability of the matrix-based Tikhonov solution [13,14] to the inversion of ARXPS data. Many studies [8–10,15–17] focus on the numerical minimization of the joint function, with the residual norm defined in terms of peak intensity ratios or apparent concentrations in at.% and with a positivity constraint imposed on the possible concentration values in the profile. However, if peak intensities are used rather than ratios, and if constraints are removed, the Tikhonov solution allows the minimization problem to be solved analytically using a matrix-based approach.

In this paper, the characteristics of a Tikhonov solution will be explored using a novel matrix-based model, and will be compared to the characteristics of a well-established numerical method. Special attention will be given to the effects of using intensities rather than intensity ratios, as well as to the removal of positivity constraints on the concentration values. Noisy ARXPS data from four different profiles (two curved exponential decay profiles and two sharper step profiles) will be simulated and analyzed. These simulations will be repeated 50 times in order to observe trends and compute averages. Finally, the benefits and drawbacks of this matrix approach will be discussed, as well as the implications for ARXPS profile reconstruction in general.

## 2. Methodology

### 2.1. Intensity model

The purpose of this paper is to investigate the mathematical aspects of inversion and regularization, rather than the physics of a real measurement. Therefore, certain simplifications were made: elastic scattering, which may play a significant role in the analysis of a real sample at photoemission angles in excess of $60°$, was ignored, and the starting point for the calculations was the Beer–Lambert equation (i.e. the straight-line approximation [18]), given by

$$I(\theta) = sK(\theta)F\eta \left[1 + \frac{1}{2}\beta\left(\frac{3}{2}\sin^2 \gamma - 1\right)\right] \int_0^\infty c(z)\exp\left(\frac{-z}{\lambda \cos \theta}\right) dz \tag{2}$$

in which $I(\theta)$ is the peak intensity at a photoemission angle $\theta$. The concentration depth profile of the element giving rise to the peak is denoted by $c(z)$, with $z$ representing the depth into the sample perpendicular to the surface. The counting time, which serves to increase the intensity, is quantified by the scale factor $s$, while $K(\theta)$ represents a set of instrumental and geometric factors and $F$ is the analyzer transmission/detector efficiency function. Other terms include the photoionization cross-section ($\eta$), the photoelectron inelastic mean free path ($\lambda$), the asymmetry parameter of the angular distribution of photoelectrons excited from a given atomic orbital ($\beta$) and the angle between the X-ray source and the detector ($\gamma$).

A number of additional assumptions are made. The solid angle of collection of photoelectrons is taken to be negligibly small, and the transmission function $F$ is assumed to be flat with respect to energy and equal to unity. It was also assumed that the instrumental/geometric factor $K(\theta)$ can be fully accounted for (as supported by the recent work of Herrera-Gomez et al. [19]), and was therefore set to unity for simplicity. Finally, the value of $\beta$ was 2 for all peaks and $\gamma$ was set to $\theta + 15°$ in this simplified simulation of a "parallel collection" geometry.

Using the concentration gradient model [20], which assumes constant concentration gradients between $n$ discrete concentration-depth data points ($c_i$, $z_i$), with $z_1$ at the surface and a constant concentration in the bulk, the intensity can be calculated as follows:

$$I(\theta) = s\eta\frac{3}{2}\sin^2(\theta + 15)\left\{c_1\lambda \cos\theta + \lambda^2 \cos^2\theta \sum_{i=1}^{i=n-1}\left(\frac{c_{i+1} - c_i}{z_{i+1} - z_i}\right)\right.$$
$$\left.\left[\exp\left(\frac{-z_i}{\lambda \cos\theta}\right) - \exp\left(\frac{-z_{i+1}}{\lambda \cos\theta}\right)\right]\right\} \tag{3}$$

### 2.2. Numerical approach

A typical approach [8–10,15–17] is to use the "apparent" concentration as a function of photoemission angle at.% ($\theta$). For instance, for the case of oxygen in a sample containing only oxygen and carbon, and with $F$ set to unity, the apparent concentration is

$$\text{at.\%}(\theta)_{\text{oxygen}} = \frac{100(I(\theta)_{\text{oxygen}}/\eta_{\text{oxygen}})}{(I(\theta)_{\text{oxygen}}/\eta_{\text{oxygen}}) + (I(\theta)_{\text{carbon}}/\eta_{\text{carbon}})} \tag{4}$$

The residual norm is then defined as the sum of the squared differences between the input and calculated apparent concentrations, while the solution norm is some function of the proposed concentration profile.

By combining intensities in such a way, certain factors, such as the scale factor $s$ and the instrumental and geometrical factor $K$, are eliminated by cancellation. However, the minimization of the joint function must be performed numerically. In this study, a numerical global minimization algorithm written in *Mathematica 8* (Wolfram) was used. It will be shown, however, that by redefining the problem in terms of peak intensities, the minimization can be performed analytically.

### 2.3. Matrix-based approach

If the concentration values in the profile and the peak intensities are given by the vectors $c = [c_1, \ldots, c_n]$ and $I = [I(\theta_1), \ldots, I(\theta_m)]$, there exists a matrix $A$, referred to as the coefficient matrix, such that

$$I = A \cdot c \tag{5}$$

If the depth spacing ($t$) between concentration values is kept constant, the elements of the coefficient matrix $A$ (an $m \times n$ matrix, where $m$ is the number of emission angles and $n$ is the number of points in the concentration profile) corresponding to a matrix form of the linear segment model [20] are given by

$$A_{i,j} = \begin{cases} f_i\left(\frac{t}{\lambda \cos\theta_i} + \exp\frac{-z_2}{\lambda \cos\theta_i} - \exp\frac{-z_1}{\lambda \cos\theta_i}\right), & j = 1 \\ f_i\left(\exp\frac{-z_{j-1}}{\lambda \cos\theta_i} - 2\exp\frac{-z_j}{\lambda \cos\theta_i} + \exp\frac{-z_{j+1}}{\lambda \cos\theta_i}\right), & 1 < j < n \\ f_i\left(\exp\frac{-z_{n-1}}{\lambda \cos\theta_i} - \exp\frac{-z_n}{\lambda \cos\theta_i}\right), & j = n \end{cases} \tag{6}$$

in which the term $f_i$ is given by the following expression:

$$f_i = \eta\frac{3}{2}\sin^2(\theta_i + 15)\frac{\lambda^2 \cos^2\theta_i}{t} \tag{7}$$

This $A$ matrix, which depends predominantly on the photoelectron peaks involved (through $\lambda$ and $\eta$), quantifies the relative importance of each profile point (i.e. how much it contributes to the calculated peak intensity) as a function of the angle $\theta$, independently of the concentration profile. This relative importance arises primarily from the exponential decay of sensitivity with depth of XPS, but also depends on the model used. For instance, using the concentration gradient model, the first point contributes solely to one gradient rather than two, and the concentration at the last point extends to infinite depth. As such, these points will be less and more important, respectively, to the calculated intensity than the exponential decay of sensitivity would otherwise dictate.

The residual norm can be calculated by taking the sum of the squared differences between the noisy input intensities as a function of $\theta$ and the values calculated from the $A$ matrix (Eq. (5)), which is equivalent to the square of the Euclidean norm. Since each elemental profile has its own residual norm, the total residual norm, equal to the sum of the individual residual norms, will be used in this study.

$$\text{residual norm} = \sum_{i=1}^{i=m}(I_i - A_i \cdot c)^2 = \|I - A \cdot c\|^2 \tag{8}$$