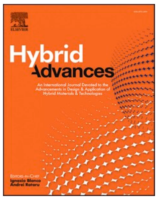
Hybrid Advances 5 (2024) 100157

Contents lists available at ScienceDirect

Hybrid Advances

journal homepage: www.journals.elsevier.com/hybrid-advances



Research Article

New method for collecting XPS and other spectra: A thought (Gedanken) experiment

Samira Jafari [a], Gregory Snow [b], Jeff Terry [c], Matthew R. Linford [a,*]

[a] Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT, 84602, USA
[b] Department of Statistics, Brigham Young University, Provo, UT, 84602, USA
[c] Illinois Institute of Technology, 3101 S. Dearborn St., Chicago, IL, 60616, USA

ABSTRACT

We suggest a new approach for collecting data, with accompanying statistical analysis, that could be useful for assessing sample damage in X-ray Photoelectron Spectroscopy (XPS) and for target detection in XPS imagining. It is based on the concept of the 'constant signal, variable time' (CSVT) spectrum that is in many ways the opposite of the traditional approach of collecting 'variable signal, constant time' spectra. In many cases, CSVT spectra should allow better visual comparisons of spectra and also for more rigorous statistical analyses based on paired t-tests and sums-of-squares of errors. We discuss the possibility of taking both survey and narrow CSVT spectra and provide a statistical discussion of how the resulting data might be treated. As we have no ability to collect CSVT spectra with our XPS instrument, this paper is a thought (Gedanken) experiment. The ideas presented herein may also be transferable to other spectroscopies.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is a powerful surface analytical technique that is widely used for probing the chemical compositions of materials [1–6]. Conventional XPS uses soft X-rays to generate photoelectrons, which are characteristic of the atoms and chemical environments they come from. Conventional XPS is surface sensitive because the photoelectrons it generates can only travel 5–10 nm in materials without suffering inelastic losses. Practically speaking, XPS detects all the elements except hydrogen and helium [7]. In this paper, we propose a new way to collect XPS data. We believe it will be helpful in various ways, including in damage and hyperspectral imaging studies. We believe that this approach will also be applicable to other spectroscopies.

Unfortunately, sample damage occurs in some XPS analyses [2,8–13] This can be understood by comparing the dissociation energy of a typical covalent bond (ca. 3–5 eV) to the energies of the X-rays and photoelectrons involved in conventional XPS (ca. 100–1500 eV) [14]. Nevertheless, different materials experience sample damage to different degrees [1,15–17]. Many inorganic materials are essentially undamaged in conventional XPS analyses [18,19], and some organic materials, especially those with aromatic character, similarly undergo little damage. However, organic materials that can generate a stable small molecule through an available chemical pathway, e.g., a polymer like polyvinylchloride [10] that can produce HCl [20], are sometimes damaged to a substantial extent in conventional XPS analyses. Specific examples of materials that are damaged in XPS analysis include a PVC–PMMA polymer blend [21,22], films of poly (2-chloroethylmethylacrylate) [23], fluorinated acrylate homopolymers [24], butyl methacrylate polymers [25], and nitrocellulose [26]. Sample damage in XPS manifests itself as shifts in peak positions and/or a changes in peak intensities [12]. Many biological materials are damaged by X-rays [27].

A common method for identifying sample damage in XPS has been to acquire a survey or narrow scan at the beginning of an analysis, take whatever other scans are necessary for that analysis, and then to reacquire the original spectrum. These first and last spectra are then ratioed [28]. If no sample damage has occurred, their ratio should be unity everywhere with, of course, some noise on the results. Another method for identifying sample damage is to simply overlay/compare spectra taken at different analysis times [29]. Whitesides and coworkers introduced a somewhat unconventional method for identifying XPS sample damage to self-assembled monolayers [30,31]. After an XPS analysis, they might induce condensation on the sample, e.g., by deliberately breathing on it. If the sample had been damaged or changed in some way, including in its adventitious carbon layer, these condensation or breath figures would identify the spot where the X-ray beam had irradiated the sample. That is, damage could be identified because of the different wetting properties of the illuminated spot compared to the rest of the sample. Of course, an analysis using breath figures should

---

* Corresponding author.
E-mail address: mrlinford@chem.byu.edu (M.R. Linford).

https://doi.org/10.1016/j.hybadv.2024.100157
Received 16 January 2024; Received in revised form 16 February 2024; Accepted 18 February 2024
Available online 27 February 2024
2773-207X/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC license (http://creativecommons.org/licenses/by-nc/4.0/).