

STATISTICAL APPROACH TO XPS ANALYSIS: APPLICATION TO NIOBIUM SURFACE TREATMENT

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Abstract

Niobium surface has been studied for more than 20 years and most of these studies have been driven by the demands of high performance SC cavities. Experience has shown that such performances depend critically on the surface treatment applied, be it mechanical, thermal, chemical or any combination of these. The aim of this work is to look whether there is a significant connection among the XPS data acquired on differently treated samples and the cavity performances. To do this, we extract the information out of the spectras using mathematical and statistical concepts rather than chemical knowledge. If this proves successful, we could use the XPS as a very efficient and inexpensive tool to determine the most suitable surface treatment for the next generation SC cavities.

1 INTRODUCTION

Niobium is very commonly used to build RF devices and it is well known that RF superconducting properties of Nb depend critically on a thin layer of material underneath the surface. Indeed, experience has shown that most surface treatments influence considerably the performances of the Nb-made device.

In order to test the effectiveness and goodness of a treatment, one has to design and build several devices (e.g. a RF cavities), carry out the surface treatment and test them.

This procedure is generally time consuming, expensive and requires a non trivial set up to obtain reproducible and reliable results.

On the other hand, Nb surface has been studied by many researchers for several years. Common surface analysis techniques are XPS, AES and, more recently, TOF-SIMS.

Some authors [1] have pointed out that the oxygen distribution both in the form of oxides (Nb_2O_5 , NbO_2 , NbO) and in the form of interstitial oxygen (NbO_x $0 < x < 1$) may be responsible for the observed superconducting RF behaviour.

Among other techniques, XPS is well suited to look for oxidation states. A question arises then: is there a way to infer the goodness of a surface treatment by looking at its XPS spectrum? In other words, does the spectrum contain

the necessary information about the RF superconducting properties and, if it does, can we extract them?

If we can answer to that question, we could use XPS as a very effective tool to test as many surface treatments as we like. This could prove cheap and quick, for the treatments would be performed on small samples rather than on a whole structure and data taking requires only a couple of hours.

With this work, we propose a method to address this problem and, eventually, give an answer.

2 DATA TREATMENT

Generally speaking, XPS data treatment includes smoothing, energy shift adjustments, background subtraction and, most of all, curve fitting. It is through curve fitting that we can tell the various components from a peak or group of peaks, and eventually assign those components to single chemical bond.

Although curve fitting is in most cases appropriate and sometimes even trivial, it becomes a clumsy tool when too many parameters come into play. This is unfortunately the case of Nb peaks group, where we want to identify not only the obvious Nb metallic and Nb_2O_5 doublets but also the more subtle oxide states related to oxygen diffusion in the metal.

Nevertheless, if we deal with a set of sufficiently homogeneous data, we can take advantage of Principal Components Analysis (PCA) [2]. This technique allows us to define a set of orthogonal and normal vectors that represent a geometrical basis (a proper reference frame) for our spectra. Each spectrum is therefore defined through its coordinates (or components) in that reference frame.

Although the basis vectors are not trivially connected to the physical spectra, PCA allow us to determine how many linearly independent components we must use in order to properly fit our data set.

We have taken XPS spectra of 15 different surface treatments (see Table 1); each measure consists of a spectrum taken at 75 degrees (almost perpendicular to the surface) and a spectrum taken at 25 degrees (grazing angle) with respect to the analyser.

The 2 acquisition angles provide us with a structural information about the depth of the various oxides.

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Table 1: Surface treatments applied to our Nb samples

Sample ID	EP (Electro Polishing)	HNO ₃ +HF rinsing	FNP112 (HF+ HNO ₃ + 2xH ₃ PO ₄)	Air (48 h air exposure)	MNF (NH ₄ F+ HNO ₃ + H ₃ PO ₄)	Annealed (1300 °C, 5 days)	Baked (72 h @ 130 °C, 2x10 ⁻⁹ torr)
s0 _A B	X					X	X
s0 _N	X	X					
s1 _N A	X					X	
s3 _N A	X	X		X		X	
s7 _N A					X	X	
s0 _N A	X					X	
s1 _A B	X	X					X
s1 _N B	X						X
s5 _A			X			X	
s7 _N B					X		X
s0 _N B	X	X					X
s1 _A	X	X				X	
s1 _N	X						
s5 _x			X				
s7 _N					X		

2.1 XPS Data Acquisition

In order to apply PCA to our spectra, we need data which are homogeneous with respect to system settings, so that the difference in the spectral shapes must be due to the chemical properties and not to our experimental set-up. Particular care has been taken therefore to use the same acquisition parameters for all the samples.

For each sample, we have considered the following spectral region of interest:

- Nb (B.E. 199 – 219 eV)
- O (B.E. 525 – 545 eV)
- C (B.E. 280 – 300 eV)
- F (B.E. 680 – 700 eV)
- P (B.E. 127 – 149 eV)
- N (B.E. 394 – 414 eV)

Our XPS system is a PHI 5602 CI multitechnique and the acquisition conditions are: Al K α monochromatized source (h ν = 1486.6 eV), analyser pass energy: 5.85 eV, B.E. accuracy: ± 0.1 eV, analysis area 400 mm/diameter, acceptance angle $\pm 7^\circ$, overall acquisition time ≈ 2.5 h / sample.

In Figure 1 and Figure 2, some pre-processed XPS data for Nb and O are shown. As it is easily seen, some spectra almost overlap and some are very different.

We state now a working hypothesis: we assume that each spectrum is a linear combination of a certain number of well defined chemical states and therefore, within experimental errors, we say that the difference in the spectral shape is due to the different weights of these chemical components.

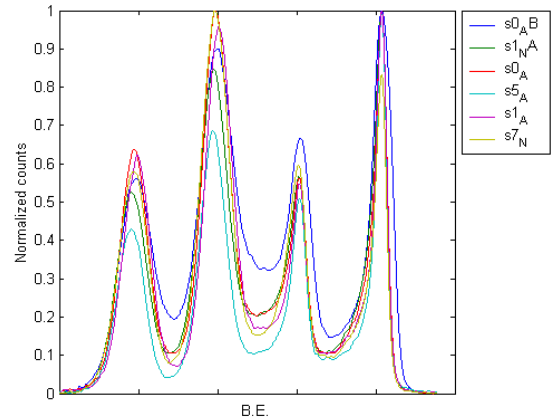


Figure 1: Pre-processed Nb spectra, take-off angle 75°

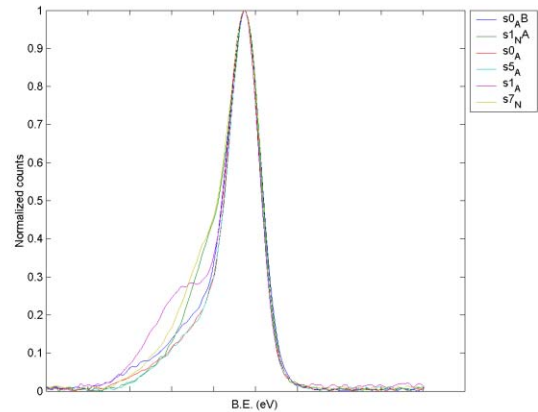


Figure 2: Pre-processed O spectra, take-off angle 75°

2.2 Principal Component Analysis

Instead of looking for the standard chemical states deconvolution, we look for the basis vectors in the space described by our measurements and we use this basis to reconstruct the original spectra.

Each spectrum is then assigned a set of coordinates which describe it uniquely. In other words, the differences in the spectra due to chemical composition are mapped in the PCA coordinates. This approach has the advantage of taking into account the details of our spectrum structure (e.g. the shape of the spectra curve) while being independent from their actual implementation (e.g. from chemical state deconvolution).

PCA shows that 5 components suffices to adequately fit the Nb spectra as well as 5 to fit O (25 deg.), as it is shown in Figure 3 and Figure 4 as an example.

In Figure 5 we show the residues we get when comparing the raw data with the reconstructed ones through the PCA. Clearly, if we took into account all the PCA components and not just a subset, the residue would vanish. We have made the choice about the number of vectors to take into consideration so that the reconstructed spectra differ from the real data within 4 % maximum.

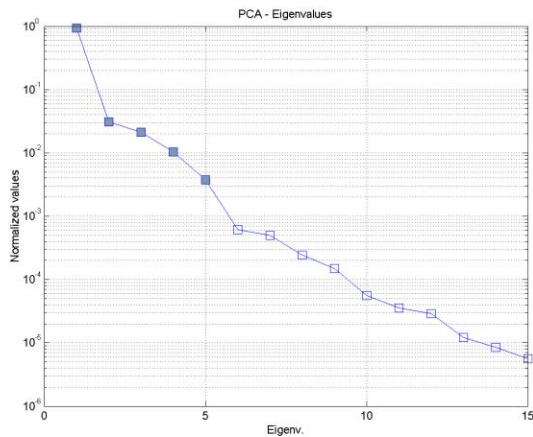


Figure 3: Matrix eigenvalues of the Nb 75 degrees measurements.

3 GROUPING DATA (CLUSTERING)

Once we have transformed the spectra into a set of coordinates, they are treated like points in a n-dimensional space. It is then interesting to see whether these points group together. Grouping data must be such that the points related to different samples which underwent the same surface treatment should be near and the dispersion of such a group of points is then a measure of the reproducibility of the chemical treatment and XPS measurements.

This is accomplished through Cluster Analysis (CA) [3], which enable us to divide our data in classes that share common properties.

There are several ways to form clusters and this freedom allows us to test various hypothesis on the

relevant portions of XPS spectra that contribute to the superconducting properties.

If we admit a relationship between the XPS data and the RF performances, it is conceivable (not granted though) that we look for a continuous, smooth function

$$R = f(X)$$

where X represents the coordinate of the XPS spectrum and R is a set of superconducting properties (that could be, for examples, a cavity Q_0 vs E_{acc} curve).

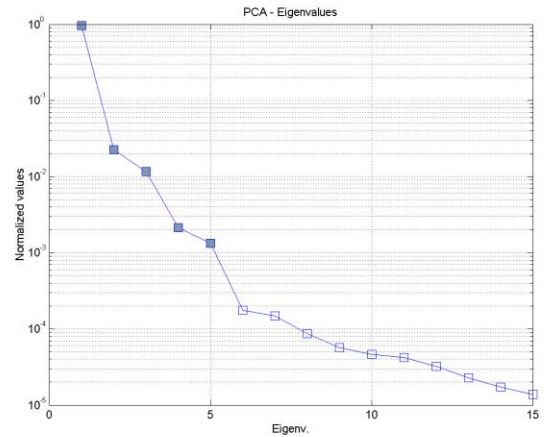


Figure 4: Matrix eigenvalues of the O 25 degrees measurements

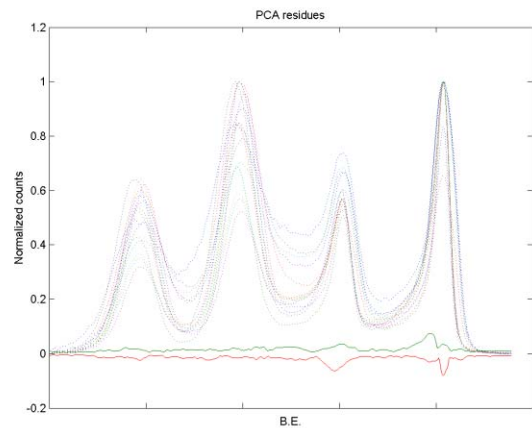


Figure 5: PCA residues. The green and red line mark the maximum deviation of the reconstructed data from the real ones.

Under this hypothesis, if X_1 , X_2 , X_3 represent 3 spectra such that X_1 and X_2 are near each other with respect to X_3 , we should expect the same relationship for R_1 , R_2 and R_3 .

In other words, we are looking for a particular XPS data clustering that shows strong correlation with the RF data clustering.

Experience has shown that a cavity treated with EP + Annealing + Bake gives excellent results; we may be looking therefore to surface treatments that group together with the sample “s0_AB”.

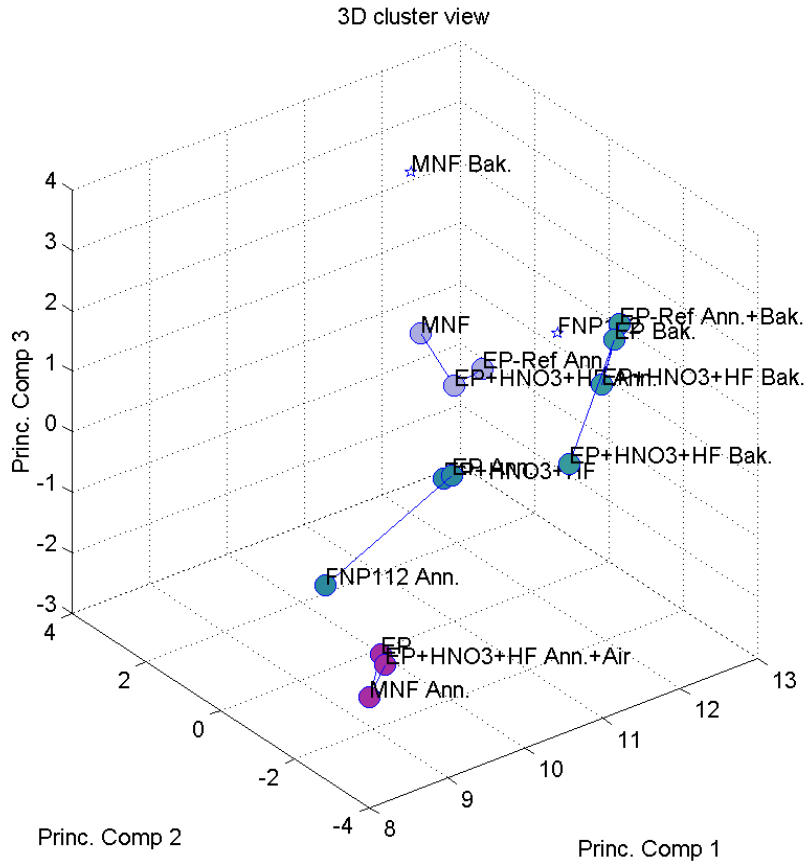


Figure 6: 3D cluster plot

We must not forget though that changes brought to the surface by different treatments might be huge and nevertheless have little influence on the RF properties, while some very subtle changes in the composition and structure might play a role but may be beyond the sensitivity of our instrument. XPS might well be blind as far as RF properties are concerned.

Let then X_1 and X_2 be points representing complete XPS data from 2 samples which underwent 2 different surface treatments, T_1 and T_2 respectively, and be R_1 and R_2 their superconductive properties. If $X_1 = X_2$ (in the sense that they belong to the same cluster, i.e. the XPS data are practically indistinguishable) then we must have $R_1 = R_2$, within the experimental errors. If this statement doesn't prove true then we can't use the XPS technique to discriminate among surface treatments.

Note that the point X should include several B.E. region,

as well as data taken at different take-off angles. In our work, X contains information on Nb, O and C region, each with 2 take-off angles.

In Figure 6, we show a clustering plotted along the first 3 principal components. These classes have been computed according to the Nb region, 75 degrees take-off angle. Points marked with a "★" are not correlated with any cluster, although the clustering correlation coefficient is 0.8, which shows a moderate cluster distribution of the points.

In Figure 7, we show a different clustering, computed using Nb (75 & 25 deg.) and O (75 & 25 deg.) for a total of 18 coordinates (or principal components) per spectrum. This plot is the projection of the points on a plane whose coordinates are the parametric distances from the reference samples. As we can see, there are no treatments sufficiently "near" to the references.

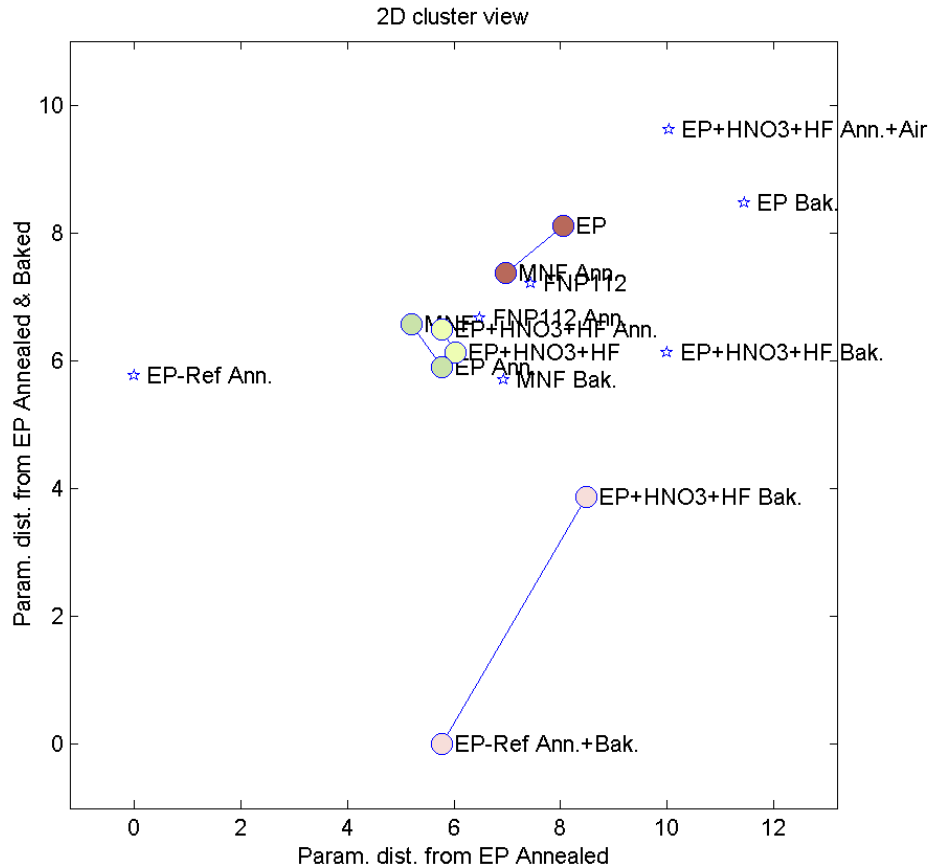


Figure 7: Coordinate distance from the reference samples

We are currently analysing data coming from a set of virtually identical surface treatments, in order to establish the cluster dispersion due to the experimental errors.

4 CONCLUSIONS

We believe that this kind of approach can determine whether XPS is able to help in looking for an affordable, cost-effective surface treatment for RF devices.

Once we get the RF data for the sample we have already measured, it will be possible to continue the analysis and find the function (of the XPS data) which maximizes the correlation between XPS data clustering and RF data clustering. If we do find a correlation, it will be possible to analyse the data backwardly and eventually define the chemical states responsible for the RF behaviour.

We are currently studying also the possibility of actually predicting the RF properties from the "XPS coordinates", rather than merely stating whether a point belongs to a cluster or not. This could be theoretically possible by using other statistical tools (such as response surface fitting and non linear regression) provided we find evidences that XPS is indeed the technique we want.

5 REFERENCES

- [1] C. Antoine, "Surface Studies: Method of analysis and results", this proceedings.
- [2] Jackson, J. E., "A User's Guide to Principal Components", John Wiley and Sons, Inc. 1991
- [3] Brian Everitt, "Cluster Analysis", HEB, 1977. ISBN 0 435 82298 5