

Energy-dispersive X-ray Spectroscopy

Introduction

1. Surface/near-surface technique (about 1 μm deep)
2. Useful for getting the elemental composition of a selected spot on a solid
 - a. Can scan across surface for a 1- or 2- dimensional map of element concentrations

Physical Basis

1. Electronic energy “shells” defined by primary quantum number.
 - a. Core shells $n = 1, 2, 3$ represented by K, L, M, respectively
 - b. Transitions to higher or lower energy levels can be achieved via absorption or emission of EM radiation, respectively.
 - i. Frequency of radiation dependent on spacing of energy levels
 1. Spacing of core levels corresponds to X-rays
 2. Emission spectra from atomic cores characteristic, but difficult to observe since K, L tend to already be filled
2. Bombardment of sample with electron beam leads to emission of X-rays
 - a. Continuous spectrum from electrons grazing past nucleus – useless background noise
 - b. If beam electrons knock out core electrons, higher-level electrons fall back to fill the gap => characteristic X-rays emitted

Instrumentation and Sample Preparation

1. Instrument – basically an SEM with an X-ray detector.
 - a. Detector generally a wafer of ultrapure Si or Si doped with Li
 - i. X-ray impacts move electrons into conducting band => signal
 - ii. Cooled by liquid nitrogen to control thermal noise
2. Sample should be stable under moderate vacuum
 - a. For qualitative analysis, it otherwise just needs to fit in the instrument
 - b. Accurate quantitative analysis needs thin sample (several hundred angstroms) with minimal self-absorption/fluorescence
 - i. Spatial resolution improves in all cases if the sample is not overly sensitive to the beam.

Data Interpretation

1. Qualitative analysis – which elements are present?
 - a. Each element has a characteristic set of Gaussian X-ray emission peaks
 - i. Presence of characteristic peaks provides strong evidence that the element is present.
2. Quantitative analysis – relative abundances of each element
 - a. Older Be windows to detector make seeing elements lighter than Na impossible
 - i. Newer thin/ultrathin polymer windows allow detection down to Be
 - ii. Abundance of an element given as percent of the number of atoms the detector can see in the sample.
 1. For example, water would register as 100% O.
 - b. Requires standard of known atomic concentration for each element being analyzed.
 - i. Ratio of sample concentration to standard = ratio of sample X-ray emission to standard
 1. Need 40,000 counts to get 2σ precision at $\pm 1\%$

Limitations

1. Requires a larger volume of sample than XPS or Auger
 - a. Larger sampling volume also leads to less depth info
 - i. Can't see interfaces distinctly, if at all, while the other two surface techniques can.
2. Can't see Be or lighter (at best)
 - a. Can see Li and Be with XPS and Auger
3. Quantification relies on high-quality standards
4. Some combinations of elements produce noticeable differences in absorption or fluorescence from the pure standards => throws off quantification

Sources

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