

# A New Technique For Electron Microprobe Trace Element Analysis: The Multipoint Background Method



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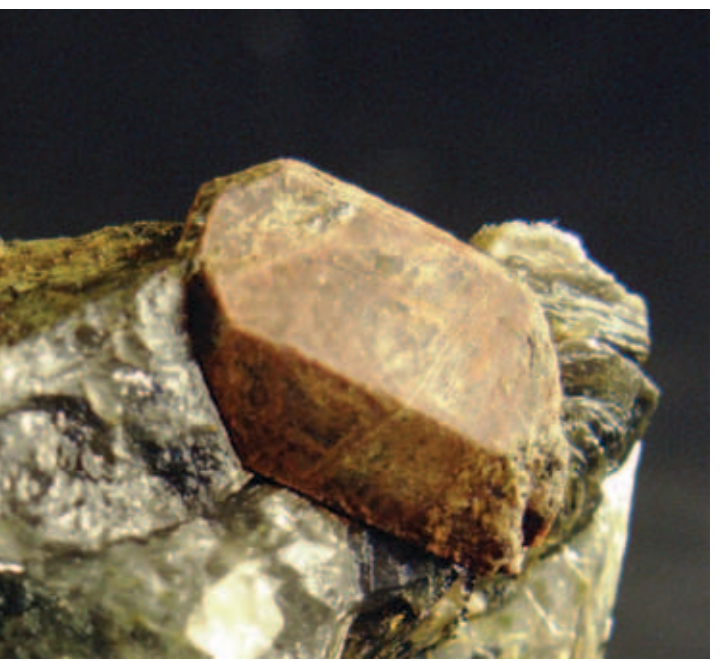


Julien ALLAZ, Michael L. WILLIAMS, Michael J. JERCINOVIC

Department of Geosciences, University of Massachusetts, Amherst (MA), USA.

& John DONOVAN

CAMCOR, University of Oregon, Eugene (OR), USA.



Typical large (1 cm) Ce-monazite found in a pegmatite from Tveit, Ireland, Aust-Agder, Norway (source: mindat.org)

**INTRODUCTION:** Electron microprobe trace element analysis is a significant challenge. Due to the low net intensity of peak measurements, the accuracy of trace element analyses relies critically on background measurements, and on the accuracy of any pertinent peak interference corrections (see Jercinovic et al., 2008; this meeting). Background measurement for major element analysis is usually constrained by the acquisition of counts at two points selected at appropriate off-peak positions. The intensity at the peak position is calculated by interpolation. Unfortunately, the background spectrum may not be linear, and

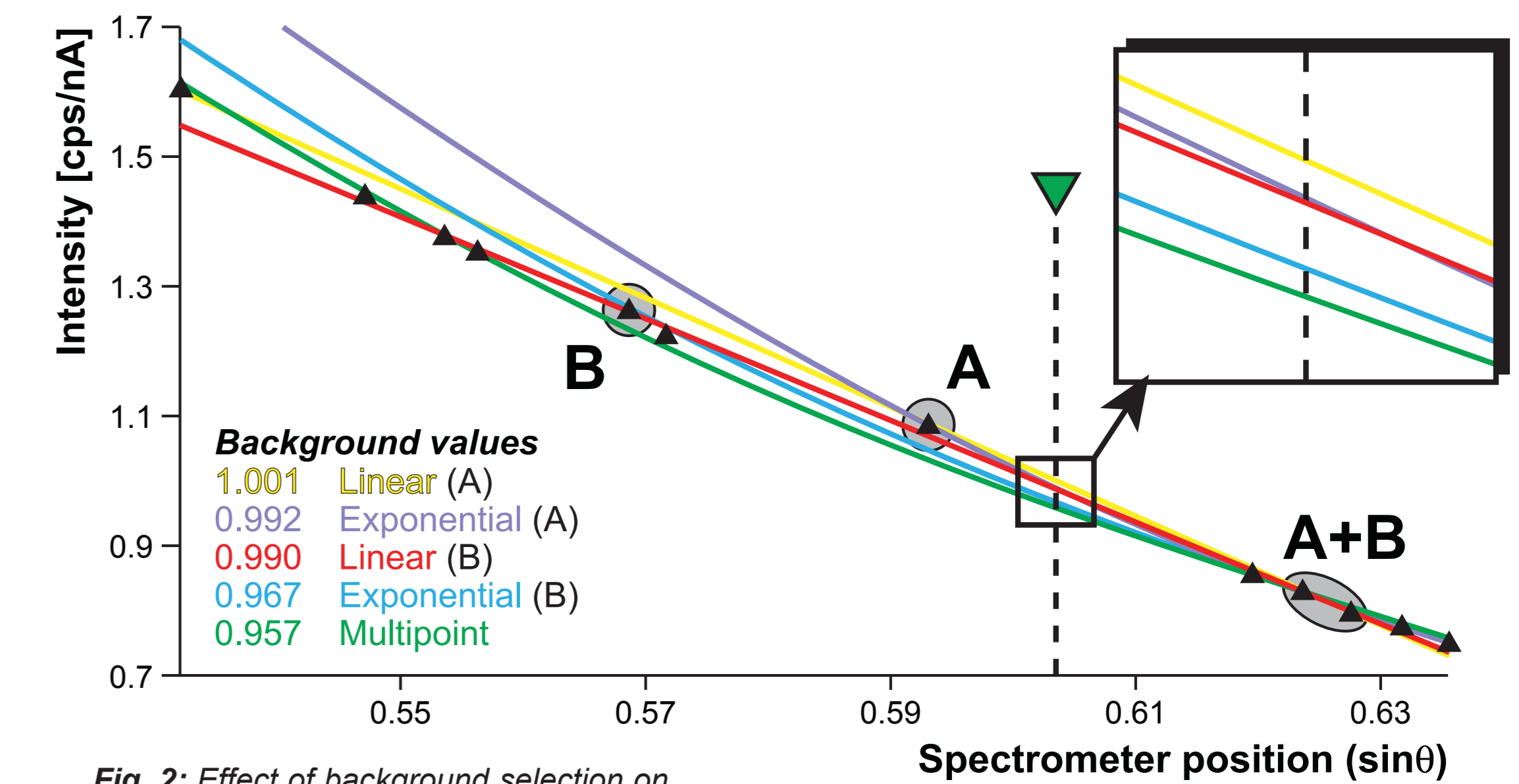
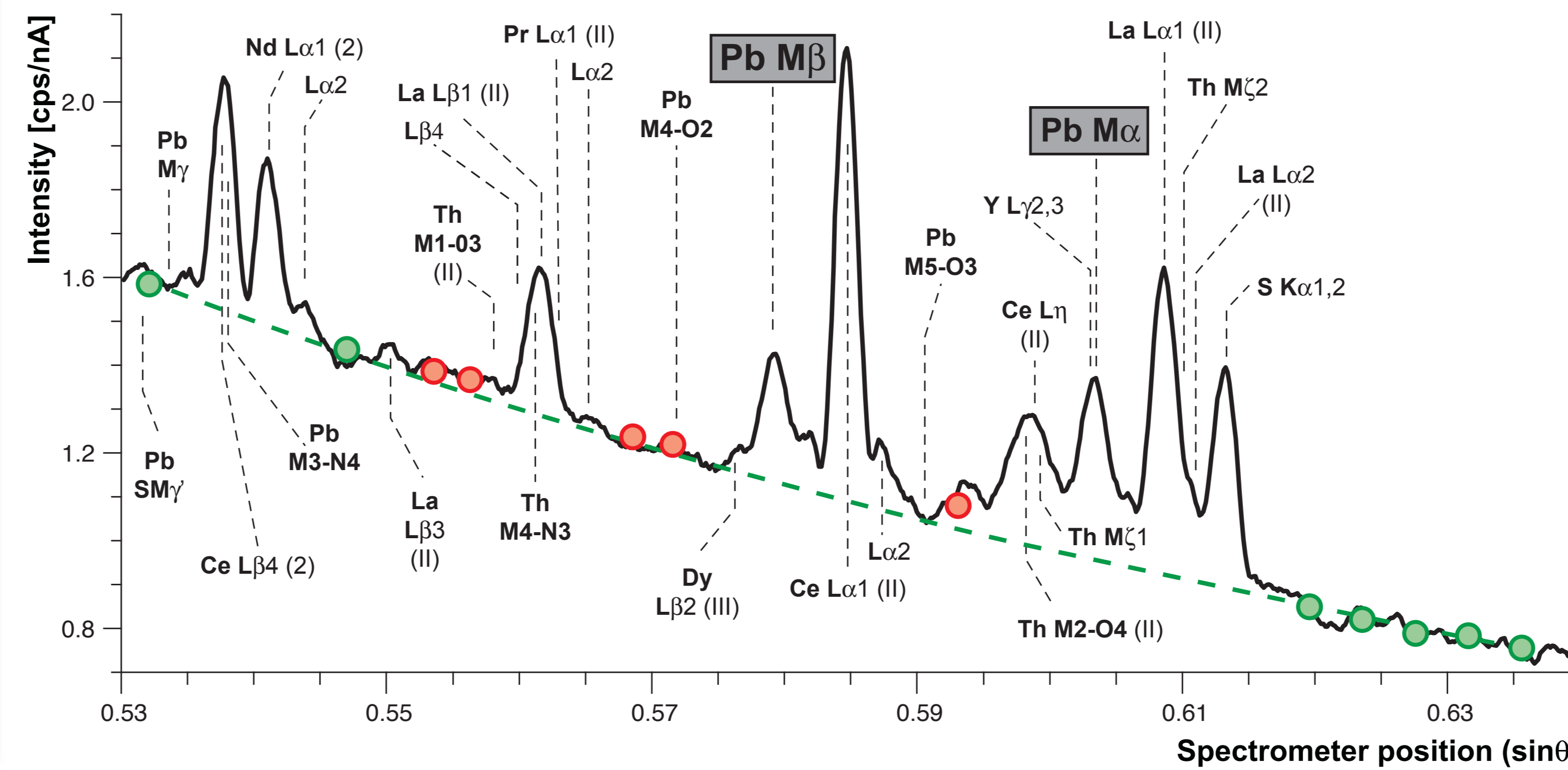
when an exponential or polynomial regression is applied, two points are insufficient to constrain the true curvature. Moreover, background interferences can be present, and can dramatically affect the results if underestimated. To constrain the curvature, a quantitative WDS scan should always be acquired over the spectral region of interest. Background intensity values can be obtained from regression of the background portions of the scan. However, this technique retains an element of subjectivity because the analyst has to select those areas in the scan that represent background.

We propose here a new method of multipoint background acquisition to raise the precision, accuracy, and objectivity of background measurements for trace elements, notably Pb measurement in monazite (REE-phosphate). This method also improves the overall efficiency, as no WDS scan needs to be acquired in order to check for the presence of possible background interferences. This idea originated from efforts to refine EPMA monazite U-Th-Pb dating, where it was recognised that background errors can result in errors of several tens of million years (or more) on the absolute age.

**TECHNIQUE:** The principle of multipoint background method is to acquire up to 24 off-peak background measurements from wavelength positions around the peaks. Positions are chosen based on the expected ideal background positions (e.g. using Virtual WDS, a theoretical peak position table or a list of possible interferences), or based on a series of WDS scans. The background spectrum is fit to a subset of the analyzed points by regression (preferably an exponential regression, but linear or polynomial are also available). The intensity at the peak position is obtained from the regression. Only the statistically most optimum background measurements are included. We are currently working on a statistical tool to automatically reject points outside a 2σ window, minimizing thus the subjectivity introduced by a user-made selection.

With the help of the multipoint background method, a minimum of 8 backgrounds are collected around U, Th and Pb peaks. This ensures a rigorous background curvature modelling (exponential curve) and an accurate measure of background intensity under the analyzed peaks. **Figure 1** shows an application to Pb measurement in monazite. The spectrum is complex because of numerous interferences present on and around the peak. **Figure 2** illustrates the variability in background depending on the background positions for a “classical” two-points background acquisition and the curvature (linear vs. exponential). It is compared with the multipoint background acquisition, which yields more accurate results.

**Fig. 1:** WDS scan smoothed using a Savitzky-Golay filter and multipoint background (dots) with exponential regression over the Pb M $\alpha$  and M $\beta$  region (PET crystal) of the monazite age standard (“Moacyr”; TIMS Th-Pb age 506.5 ± 2.0 Ma). Green dots are retained to determine background below Pb M $\alpha$  peak, while red one are excluded.

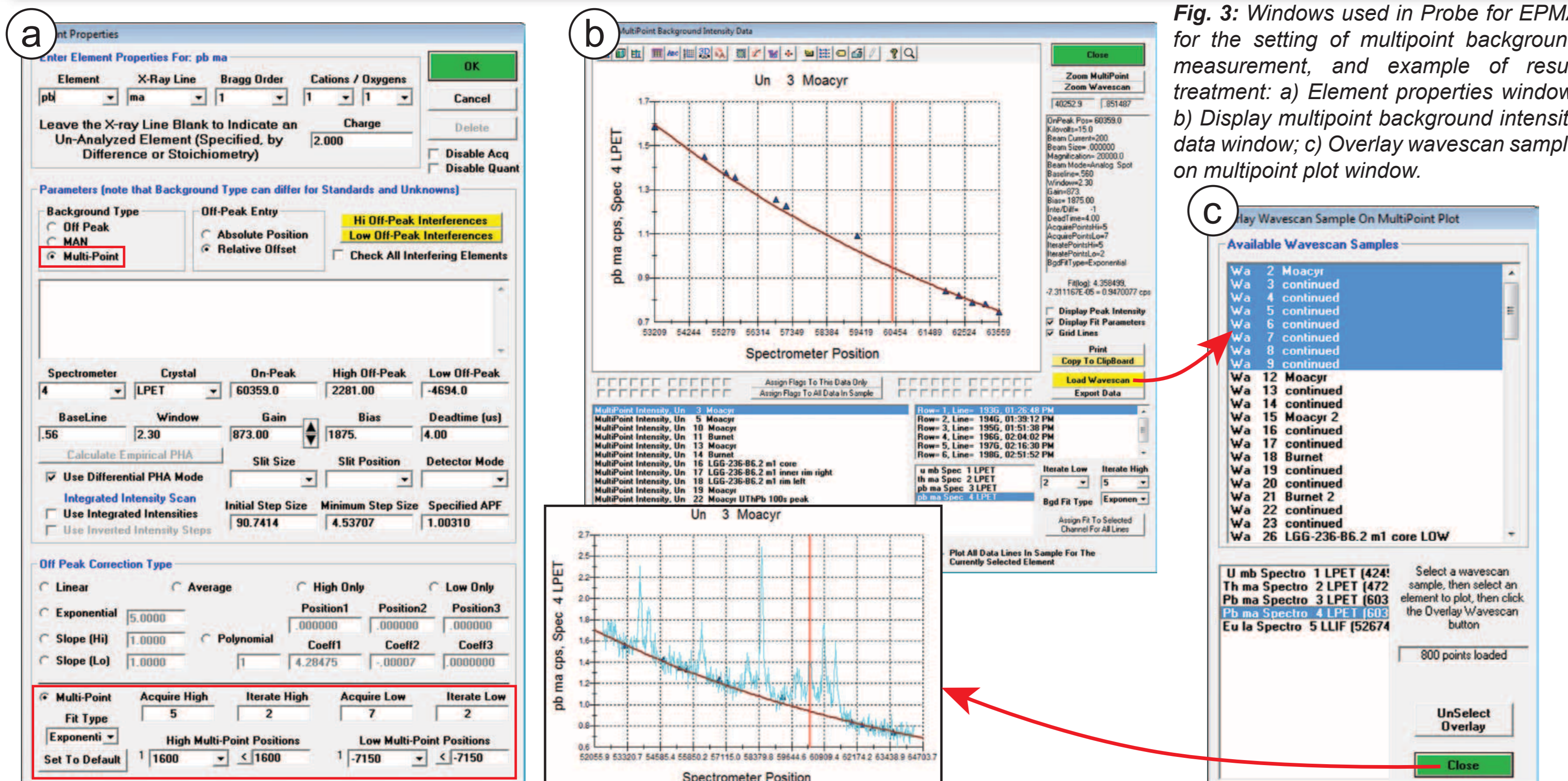


**Fig. 2:** Effect of background selection on U, Th and Pb measurement, and resulting age. Points (A) and (B) are common two-point background positions used for Pb measurement. The multipoint background results perfectly match the expected age for the “Moacyr” monazite age standard (TIMS Th-Pb age 506.5 ± 2.0 Ma), closely followed by the exponential regression using points (B).

	Age [Ma]	U [ppm]	Pb [ppm]	Th [%]
Multipoint bkg	509 ±5	743	1523	6.419
Exponential (B)	500 ±5	764	1496	6.419
Linear (B)	471 ±5	727	1405	6.415
Exp. (A)	472 ±5	764	1413	6.418
Linear (A)	463 ±5	727	1381	6.415

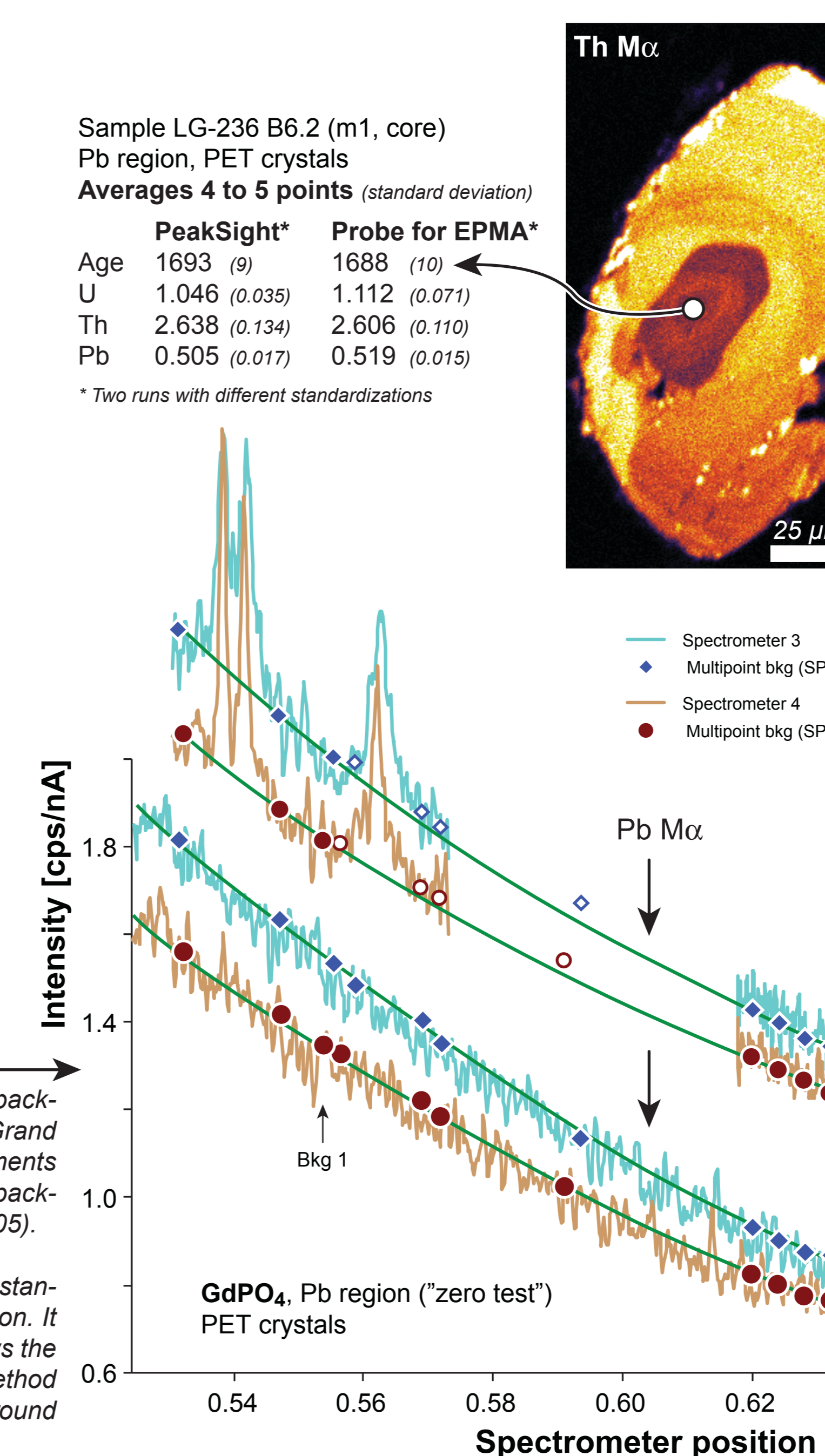
**SOFTWARE:** The multipoint background method is exclusively available within the software “Probe for EPMA” from John Donovan (ProbeSoftware, Inc.). The setup is easily configured (**Fig. 3**):

- The analyst selects the appropriate background positions (up to 12 on each side of the peak)
- Once the analysis is done, results of multipoint background acquisition are displayed. The software currently automatically selects optimum backgrounds iteratively excluding high intensities relative to the chosen fit, but these selections can be overridden by the user. The regression can be either linear, exponential or polynomial.
- If a WDS scan has been acquired, it can be plotted over the multipoint results. This is helpful for testing purposes (i.e. before applying it to any unknown), to ensure the background positions are adequate.



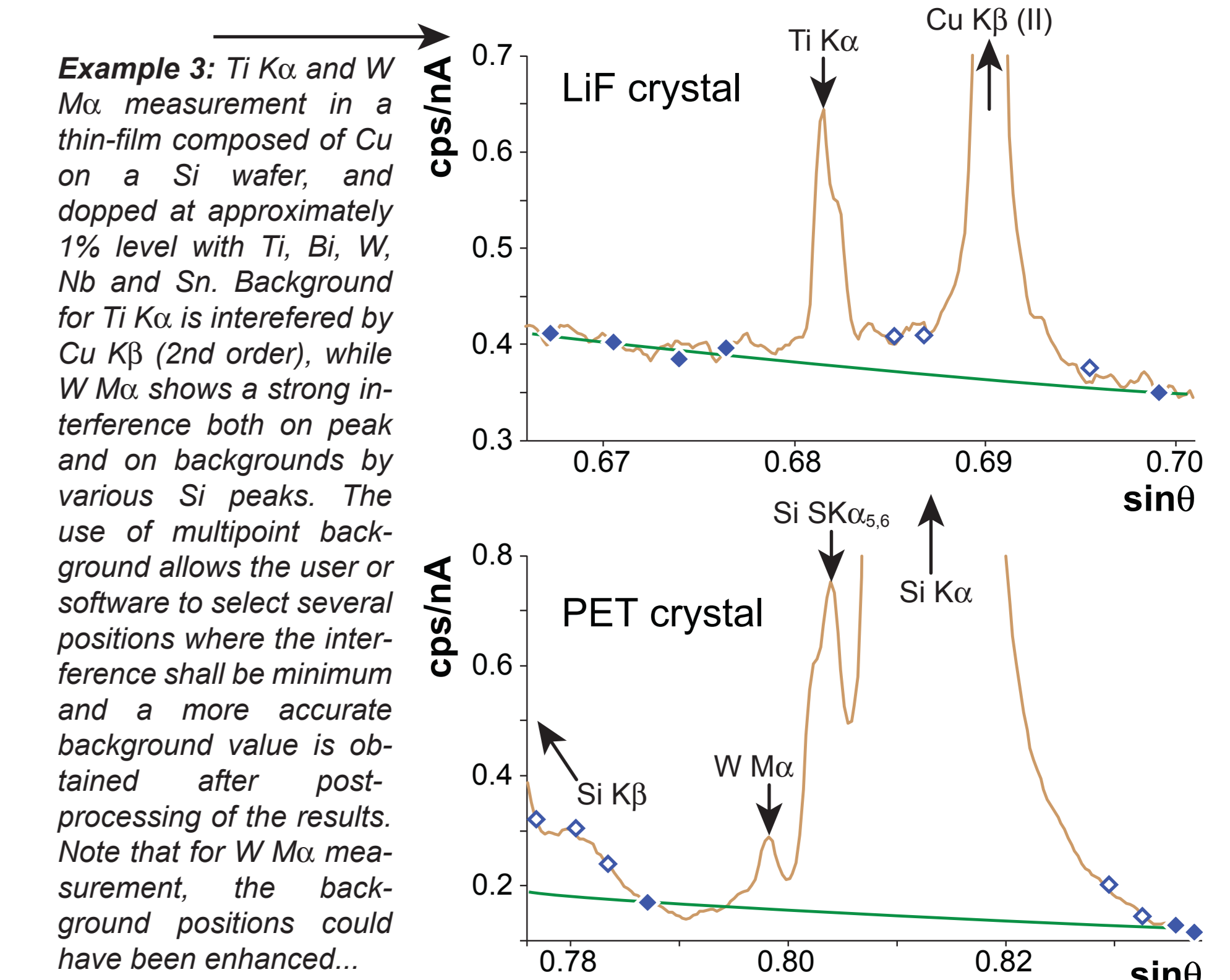
**Fig. 3:** Windows used in Probe for EPMA for the setting of multipoint background measurement, and example of result treatment: a) Element properties window; b) Display multipoint background intensity data window; c) Overlay wavescan intensity on multipoint plot window.

**APPLICATIONS:** Results obtained on a CAMECA SX-100 “Ultra-Chron” using monazite standards and well characterized unknowns yield excellent agreement with ages obtained either by TIMS or by other microprobe analysis, using a background determined by regressing a WDS scan (**example 1**). In addition, successful quantitative analysis of trace elements in thin-films on Si-wafer have been acquired on another CAMECA SX-100. This latter application illustrates the case where the analyst is unaware of potential background interferences. The multipoint method saves time by acquiring directly several possible adequate backgrounds without the need of a WDS scan (**example 3**).



**Example 1 (top):** Example 1 (top): WDS scans and multipoint background acquisitions in a monazite from the Lower Gorge (Grand Canyon, USA). Results are consistent with the previous measurements acquired with our previous dating method using PeakSight and a background model from a WDS scan (see Jercinovic and Williams, 2005).

**Example 2 (bottom):** Similar acquisition in GdPO $_4$  standard. This standard is Pb-free and has no significant lines near the Pb M $\alpha$  position. It is used as a “zero test” for Pb M $\alpha$  measurement, and clearly shows the background curvature. Results using the multipoint background method yield -0.0004 versus -0.0225 wt-% for a classical two-point background (at “bkg 1” and “bkg 2”) and an exponential regression.



**CONCLUSION:** Multipoint background allows...  
- Precise and accurate background acquisition.  
- Saving your time, no obligation of acquiring long and detailed WDS scans from your unknown.  
- No more risk of picking a wrong background.

**REFERENCES:**  
Jercinovic & Williams (2005) American Mineralogist 90; 526-546.  
Jercinovic et al. (2008) Chemical Geology 254; 197-215.