WDXRF as an Investigative and Analytical Tool using Small Spot/Mapping and Thermo Scientific UniQuant

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Process control, failure troubleshooting, in-situ identification is all now possible using a standard laboratory wavelength dispersive X-ray fluorescence (WDXRF) spectrometer with the advent of small spot/mapping capability. To narrow a sample surface analysis area down to 0.5 mm and obtain chemistry of an inclusion or irregularity has helped many a scientist solve problems once only possible through other, more complex techniques. An analysis at 0.5 mm by WDXRF is in no way a challenge to these other methods such as SEM but still offers the ability to produce answers which could help resolve a process situation rapidly and easily. The test results provided in this article were performed using the Thermo Scientific ARL PERFORM'X WDXRF.

A surface stain or inclusion on a material can quickly be targeted and elementally defined showing where it originated in the process. This answer can define the breakdown or wearing of a particular step in the process which requires attention, servicing, or replacement. Identification of larger minerals from field exploration can be both defined and chemically imaged in 2 and 3 dimension displays. Homogeneity testing of a coating over a large or small area, forensics testing on minute samples or scattered residue, the list goes on and on.

Elemental distribution for the examples mentioned above are easily displayed in an intensity format and normally this would provide the required answer to the common question 'what is it?', but if concentration resolution is required the operator may run into some trouble – how do you calibrate for a stain? What reference materials are readily available for a metal inclusion in a wire? How do you quantify components on a circuit board
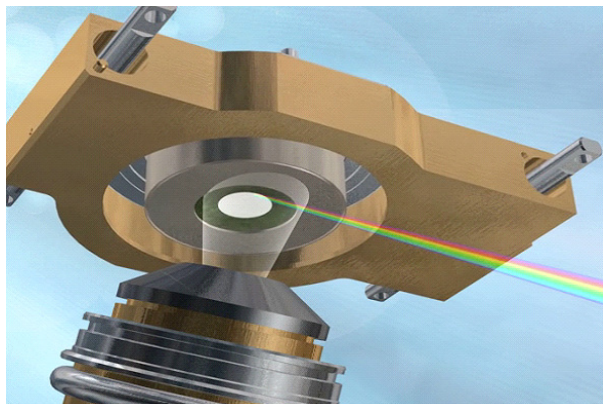
without removing them? This is where the second step to total small spot analysis comes into play – UniQuant™.

There are a number of examples presented next showing the results of small spot mapping, what needs to follow is the ability to put a concentration to those findings. Before proceeding further it is necessary to define both small spot workings and the UniQuant calibration.

Small Spot/Mapping Description

Small spot analysis is a rather easy concept to describe. The first step is for the XRF unit to image the sample surface. From this image it is possible, using the mouse, to click on areas of interest to designate analysis areas; for mapping the operator would select one of a number of 'shapes' and enlarge or contract it to a size which best contains the area of interest. The sample is excited through the use of a primary X-ray beam. The secondary X-rays emitted are collimated through an aperture which allows only the 0.5 mm area of interest excitation to continue on through the beam path to the detector (see Figure 1). Obviously the collimator and sample surface are tightly aligned. Small spot analysis is a selection of one or more unique and individual points on a sample surface, each one producing a singular analysis result whereas mapping is the joining of adjacent individual points into a unified pattern to produce a 2 or 3 dimensional presentation along with intensity/concentration results for the selected area.

Figure 1: Small spot analysis

UniQuant Description

UniQuant uses the original factory calibration to determine concentrations for completely unknown samples by subjecting the intensities acquired from the samples to comprehensive mathematical algorithms. These algorithms correct for matrix effects as well as inter-elemental effects to provide results. UniQuant is also unique in its method of intensity measurements. Unlike other semi-quantitative software programs, UniQuant uses a method known as peak hopping instead of a continuous scan technique to acquire the intensities for all measurable elements. The procedure of peak hopping allows for faster analysis by not wasting measurement time on any location where an element peak will not be found or the time to climb and descend existing peak shoulders. UniQuant will measure the theoretical 2-theta angle for each element, including alternative lines for some heavier elements and background positions. By focusing the elemental counting times to only peak locations, UniQuant is able to provide more accurate results and lower detection limits compared to other scan based semi-quantitative methods. UniQuant uses a Primary Beam Filter device to remove spectral interference from Rhodium Tube lines. An interesting feature is that the counting time for each analytical line can be defined separately depending on the main interest of the analyst. This last point makes this analysis routine extremely useful for small spot analysis since the obtained intensities will be far lower than the standard 29 mm aperture and therefore require longer count times.

Small Spot Examples

Combining both Small spot and UniQuant provides a powerful tool to solve many application problems.

Problem:
- Glass sample shows a shiny spot
- Traditional UniQuant analysis only provides the global composition over a 29mm diameter area

Oxide/ Element	Conc. %	StdErr %
SiO2	69.77	0.23
Na2O	12.16	0.16
CaO	7.57	0.13
MgO	3.54	0.09
Al2O3	1.09	0.05
K2O	0.330	0.016
SO3	0.215	0.011
Fe2O3	0.200	0.010
TiO2	0.0704	0.0035
BaO	0.0239	0.0052
Cl	0.0228	0.0011
CuO	0.0175	0.0009
MnO	0.0118	0.0007
ZrO2	0.0091	0.0005
P	0.0073	0.0006
Cr2O3	0.0069	0.0006
SrO	0.0066	0.0003
SnO2	0.0018	0.0009
ZnO	0.0016	0.0004
StdErr = error due to counting statistics		

Table 1: Glass Sample - 29 mm Analysis

Example 1: Small Spot for Glass inclusion

In this example a glass disk shows a small inclusion (see Tables 1 and 2). Analyzing the full surface would lead to no definitive answer and traditional methods for analysis require the removal of the inclusion to determine exact composition. With small spot analysis a 0.5 mm spot is analyzed on the inclusion and using UniQuant the shiny spot is found to be a copper alloy which means that the copper content in Table 1 does not belong to the glass.

Solution:
- Using 0.5 mm spot on 'clean' area and inclusion area

Major differences in spots

| Element	Shiny Spot %	Glass Surface %
Al	0.74	0.50
Cu	24.34	0.02
Fe	1.57	0.16
Sn	1.19	0.50
SiO2	34.84	70.46

Spot analyses (all values in %)

Table 2: Shiny Inclusion - 0.5 mm Analysis

Example 2: Small Spot Quantitative Analysis using Empirical Calibrations

Small spot analysis is not limited to UniQuant as the Quantification routine. In this example Empirical Calibrations based on 0.5 mm spots are used to determine statistics on a metal program (Table 3). Rick Conrey from Washington State University has done some extensive testing on small spot analysis for geological materials – some of his findings are also included here (see Figures 2 and 3).

- **V Regression**
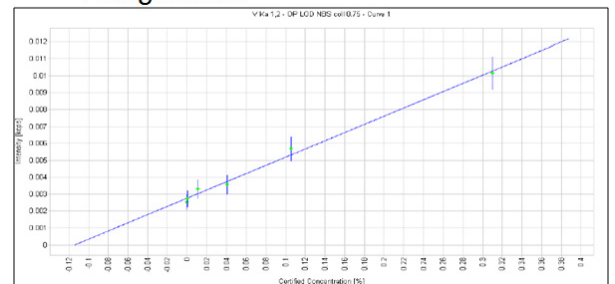
- **Si Regression**
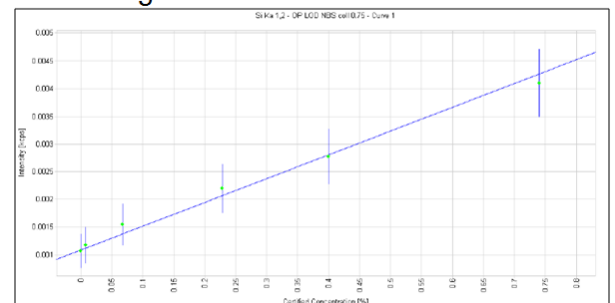
Element	Line	Cert. Conc. (%)	Analyzed Conc. (%)	RSD
Al	Ka	0.24	0.21	0.047
Co	Ka	0.05	NA	0.010
Cr	Ka	1.31	1.32	0.015
Cu	Ka	0.1	0.10	0.010
Mn	Ka	1.5	1.47	0.026
Mo	Ka	0.03	0.03	0.002
Nb	Ka	0.05	0.06	0.003
Ni	Ka	0.32	0.32	0.017
P	Ka	0.03	0.02	0.008
Si	Ka	0.74	0.63	0.041
Sn	Ka	0.1	0.10	0.009
Ta	Lb	N.A.	0.07	0.015
Ti	Ka	0.05	0.04	0.012
V	Ka	0.31	0.29	0.012
Zr	Ka	0.05	0.07	0.003

Table 3: Accuracy and precision data in ferrous base for 0.5 mm spots

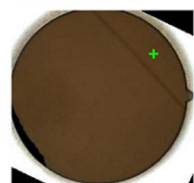## Example 3: Homogeneity Testing on Ceramics with Small Spot

The simplest application for small spot eliminates the need for quantification. Elements of interest are collected as intensity only (see Table 4). With this method the answer to the homogeneity of a sample can be arrived at rapidly and easily.
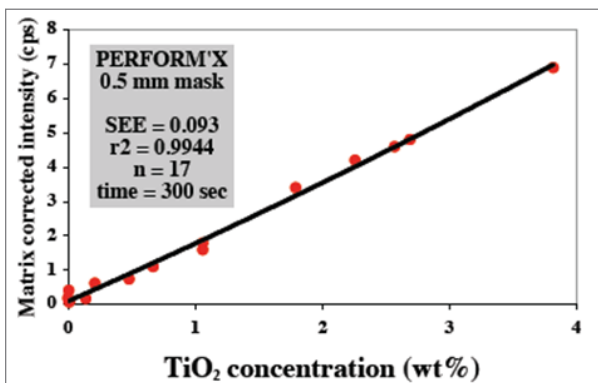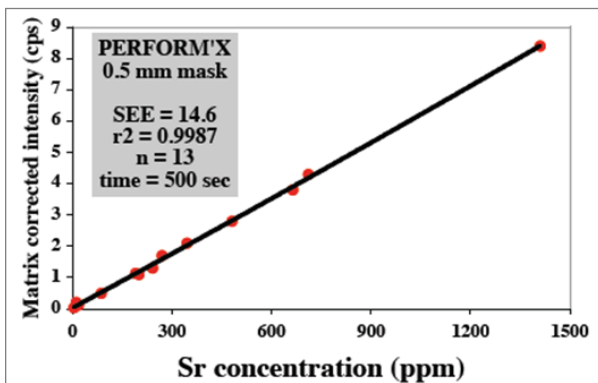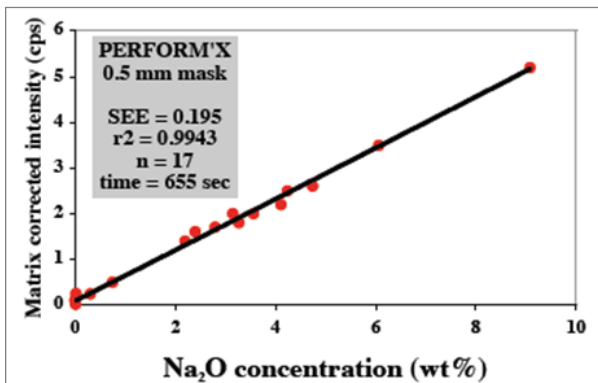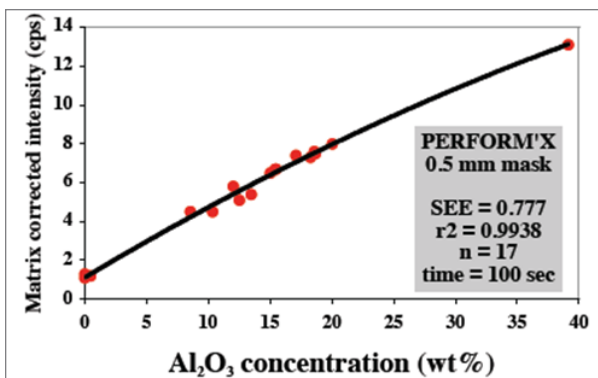
Intensity Results #1

Samples	Al (kcps)	Fe (kcps)	Mg (kcps)	Na (kcps)	Si (kcps)	Y (kcps)
Ceramic Pt1 - Run1	80.1142	0.2252	2.7922	0.3756	0.3212	13.6216
Ceramic Pt1 - Run 2	80.4153	0.2296	2.781	0.3692	0.3186	13.6475
Ceramic Pt2 - Run 1	80.8061	0.2219	2.8113	0.3708	0.3296	13.4829
Ceramic Pt2 - Run 2	80.9326	0.2241	2.788	0.3757	0.3347	13.4752
Ceramic Pt3 - Run 1	82.2972	0.2277	2.8514	0.377	0.3343	13.6661
Ceramic Pt3 - Run 2	82.3316	0.2298	2.8601	0.3833	0.336	13.6724
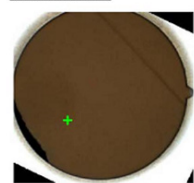
- Varying element intensities at different locations in the sample

- Most notably for Al

- Analysis performed using 0.5 mm aperture

Table 4: Heterogeneity Testing on Ceramic Material

Mapping Examples

All examples so far have dealt with small spot analysis as a solution to everyday analytical problems. This next section highlights the use of mapping as an investigative tool.

Mapping presents the analyst with 2 and 3 dimensional imaging. This is a very helpful way of better understanding a problem. The 2D images can be viewed as individual element distributions or overlaid to give a more comprehensive correlation of the elements as a group. The 3D images are single element display and can be rotated for a full 360 degree visualization or even a birds-eye view. While most maps are collected as intensity only images, empirical calibrations can also be used to fully quantify the result.
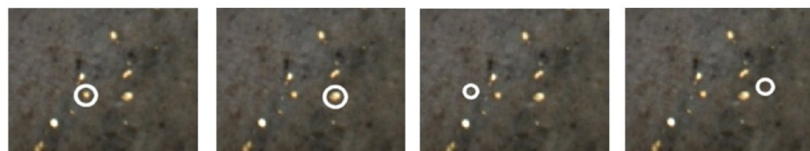
Figure 2: Al, Na, Sr, Ti Calibrations, 0.5 mm

Figure 3: Pyrite in Sandstone

Example 1: Mapped Elements in a Geological Sample

Geological samples can offer the most interesting and informative mapping images. In the Figure 4, one can see the base material being Mn due to its uniform base and strong intensity response but also note the other elements present with a large formation of Si to one side and the presence of possibly a Ca-P vein running through the center of the sampled area.
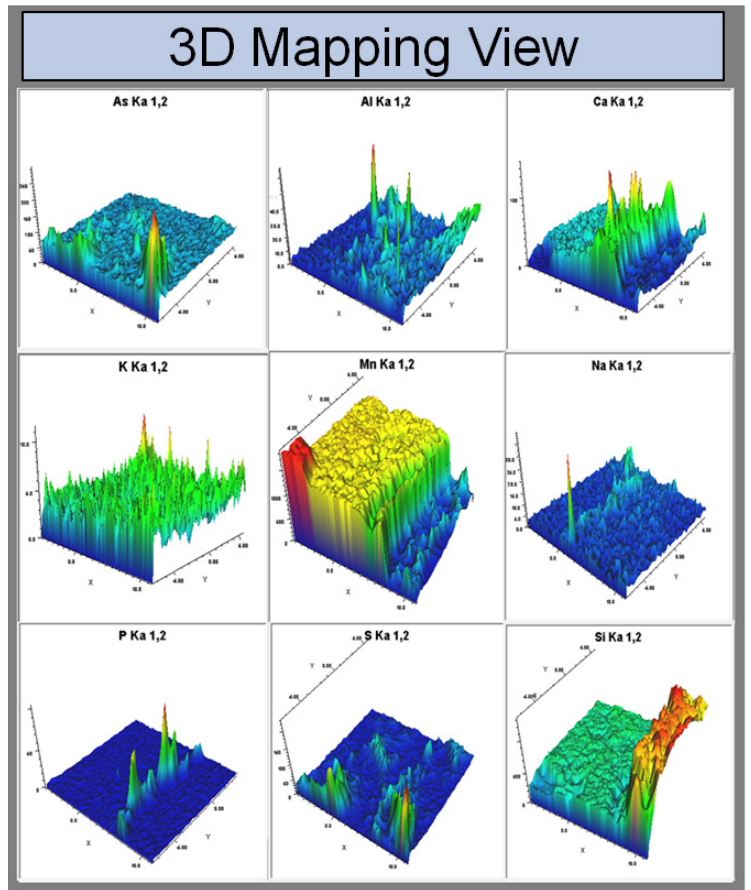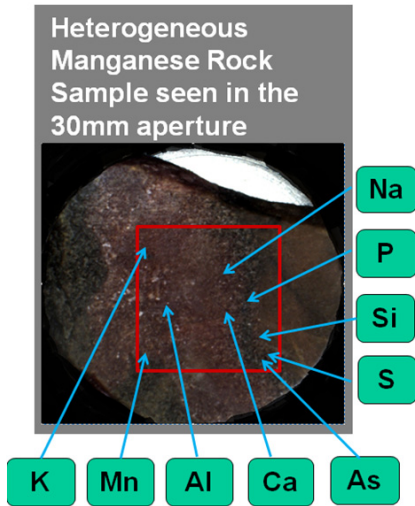

Figure 4: Mapping of a Mn Rock

Example 2: Mapped inclusion in Glass

In the Figure 5, UniQuant did not pick up any anomalies for the inclusion other than standard glass material when a 29 mm analysis was performed. A map of the strongest intensity responses was performed. Interestingly the inclusion was Si itself but in a metallic form. The maps of the additional elements also show a marked intensity decrease where the Si metal is found (see Figure 6).
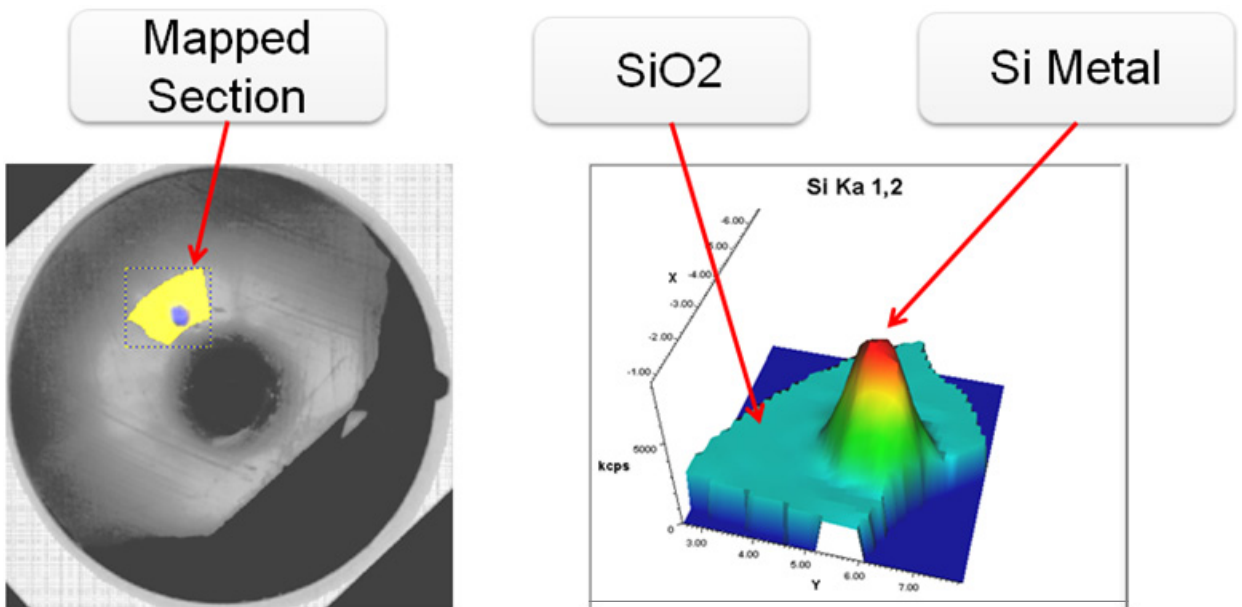
Figure 5: Si Metal in Glass
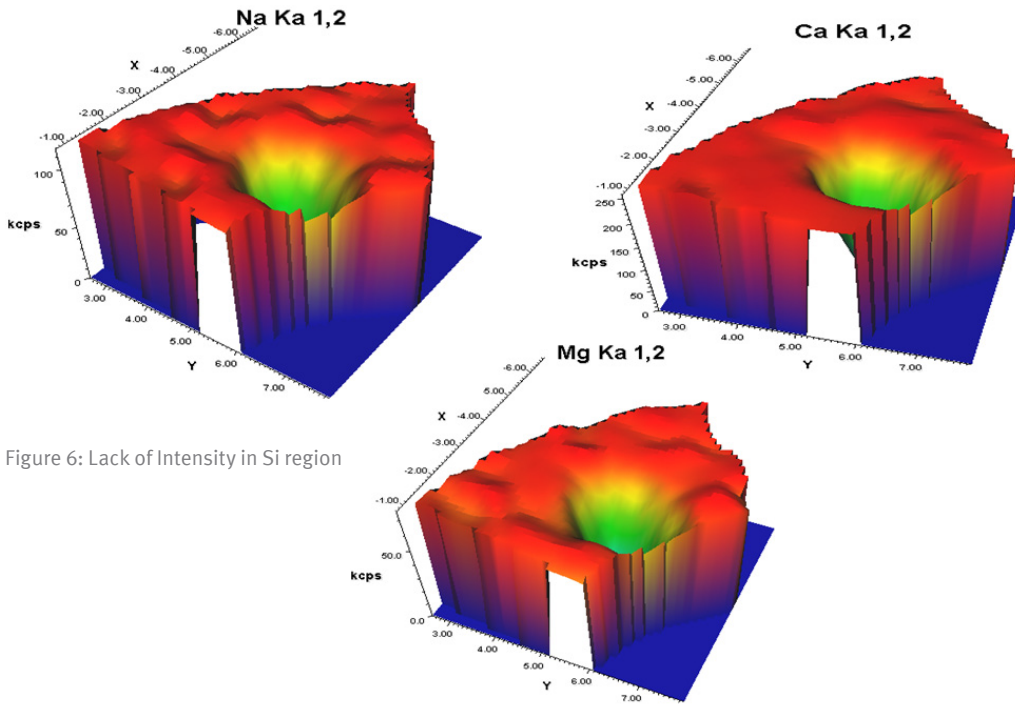
Figure 6: Lack of Intensity in Si region

Example 3: Mapped Electronic Chip

This final example shows the image detail which can be obtained from a sample. A metro pass chip was first analyzed via a line map and then a large area was mapped for specific elements in a test to determine elemental distribution. The patterns that were collected show intricate details of the components within the chip.

Figure 7 shows the results of a profile map across the chip detailing the individual element relationship across that line. The 2D images have been displayed individually in Figure 8 to better see intensity pattern responses. The actual sample image from the system camera is shown on the left with all elements overlaid.
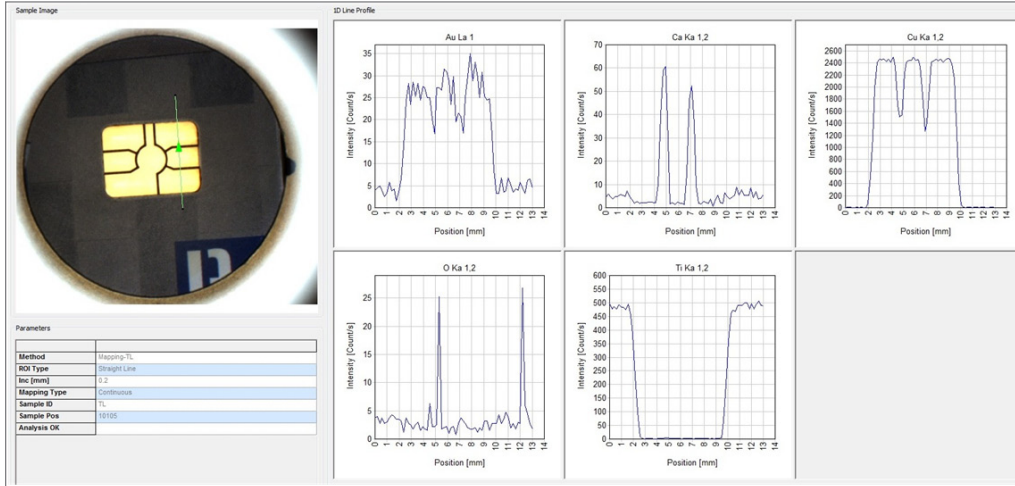
Figure 7: Line Map
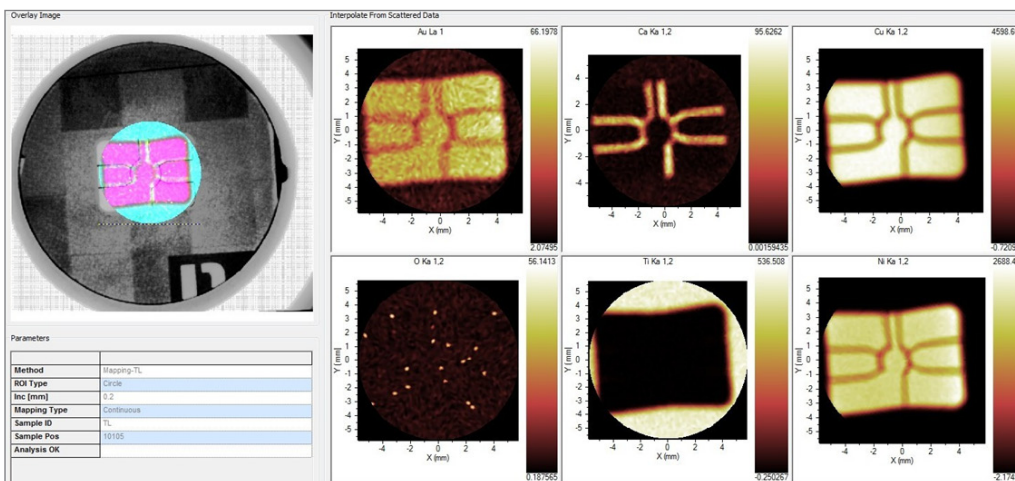
Figure 8: 2D Map Images

Finally the 3D images are displayed in Figure 9. Here it is evident that there is a sharp division between the elements in their separate components with Ti not present in the chip but as a major component in the surrounding material. The individual O spikes may be in relation to connections between components or oxidization spots on the card surface.

Conclusion

The examples presented here are only a fraction of the applications that many analysts are using today. Investigative abilities using WDXRF have been shown to save thousands of dollars in process monitoring.

With UniQuant, small samples are no longer a hindrance due to size and lack of calibrating materials. Coating thickness across a surface is now possible to review without the need of specialized instrumentation. Quantification using empirical calibrations on undersized or irregular shaped or inhomogeneous materials is possible through the use of a standard laboratory WDXRF, even in-situ.

Mapping/small spot analysis brings many benefits to the analyst which simply was not available in the past, especially when combined with a standardless routine such as UniQuant. All tests results provided in this article were performed using the ARL PERFORM'X WDXRF.
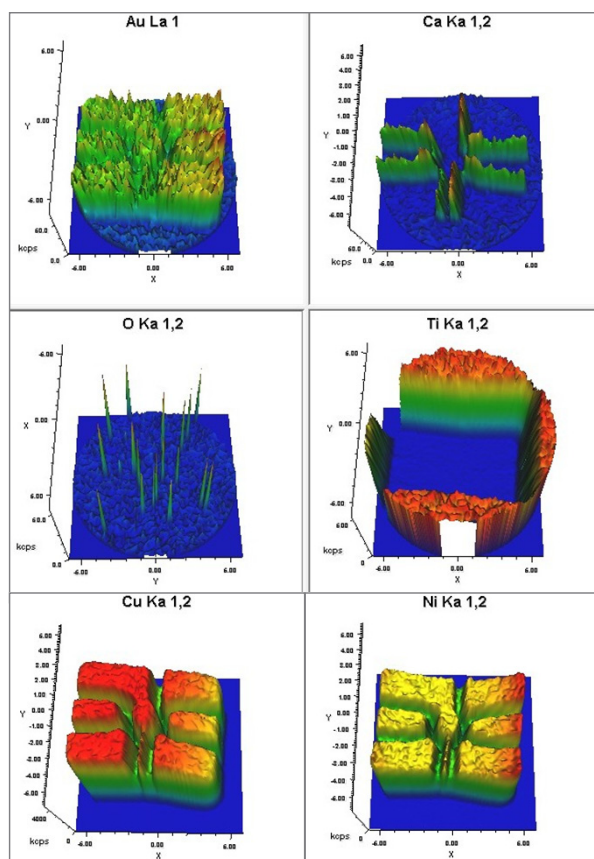

Figure 9: 3D Images

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