

Standards-Based Quantification in DTSA-II—Part I

Nicholas W.M. Ritchie

National Institute of Standards and Technology, Gaithersburg, MD 20899-8371

nicholas.ritchie@nist.gov

Introduction

Quantifying an X-ray spectrum is the process of converting a measured spectrum into an estimate of the *composition* of the material from which the spectrum was collected. In a certain sense, interpreting X-ray spectra is very simple. A spectrum from even the most complex material can be thought of as a sum of spectra from the constituent elements (see Figure 1). To first approximation, if you know the spectrum for the constituent pure elements, you can estimate the spectrum for the complex material. Regardless of the software vendor or the name of the algorithm, this is the basis for quantification of all X-ray spectra.

Typically, the result from a quantification is a *composition*: a measure of the relative amount of the elemental constituents. A common way to report the composition is in terms of *mass fraction*: the fraction by mass of each element in the material. Sometimes, compositions are reported in *atomic fraction*: the fraction by number of atoms per volume of each element.

This article is part of a series describing DTSA-II, a new software application that simulates and quantifies X-ray spectra. There have been two previous articles in the series [1, 2].

Three Types of Spectra

Spectra from materials of known composition are called *standard spectra*. The quantification scheme implemented by DTSA-II, standards-based quantification, compares the unknown spectrum to spectra measured from known standards materials. For accurate quantification, the standard spectra should be collected under very similar conditions to the unknown spectrum. In practical terms, this means the standard should be collected with the same beam energy (keV), at the same working distance, and with the same detector configured in exactly same way (distance, take-off angle, and

pulse process time). At a minimum, you must know the probe current, the number of electrons striking the sample per unit time. It is generally a good idea for the standard's probe current to be similar to that of the unknown.

Standard spectra serve to provide characteristic X-ray intensity information. Characteristic X rays are the peaks in the spectrum and are associated with specific elements. On an element-by-element basis, the number of X-ray counts in the associated characteristic peak is compared to the number of X-ray counts in the equivalent peak in a standard spectrum. This ratio (called the *k-ratio*), when appropriately scaled through the ZAF correction factors [3] to account for effects from other elements, equals the mass fraction.

You must know the following information about the conditions under which the standard spectrum was collected: the beam energy, the probe current, the live time, and the composition of the standard material. This information is best recorded in the file representing the standard spectrum (see the first Helpful Suggestion at the end).

Sometimes a second kind of spectrum, called a *reference spectrum*, is also required. Standard spectra are often collected from materials with many elements. The characteristic X-ray lines from one element may be similar in energy to characteristic lines from another element resulting in an overlap or interference. Interferences make it difficult or impossible to determine the peak intensities on an element-by-element basis. An interference can be resolved using spectra in which the element X-ray line shape is clearly resolved. These spectra in which the peak shapes are clearly resolved are called *reference spectra*. Typically reference spectra are collected from pure elements or carefully chosen simple compounds. Because reference spectra only provide shape information, it is not necessary to know the probe current when collecting

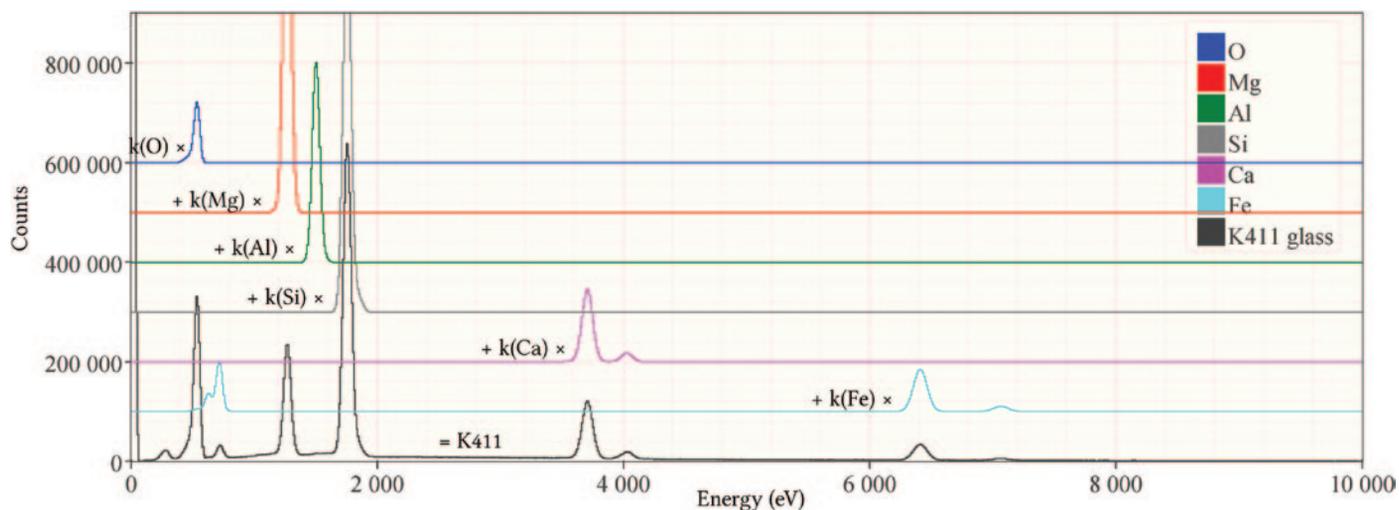


Figure 1: An example showing how the spectrum from a compound (K411 glass) can be expressed as the sum of scaled spectra from the constituent elements. The multipliers have historically been called *k-ratios* and represent the first approximation to the composition.

RENEW YOUR OLD SEM

with Digital Imaging

- Does not interfere with normal microscope operation
- Exact image reproduction
- Complete set of imaging functions



THE MEASURING, ANNOTATING,
PROCESSING, REPORTING, ARCHIVING,
DO EVERYTHING SOLUTION
FOR MICROSCOPY

QUARTZ IMAGING CORPORATION

www.quartzimaging.com • +1-604-488-3911 • inform2@quartzimaging.com

them. Thus, standard spectra provide characteristic X-ray line *intensity* information, and reference spectra provide characteristic X-ray line *shape* information. A more thorough comparison of the differences between standards and references is provided in Table 1.

The final type of spectrum is the *unknown spectrum*: the spectrum you wish to interpret. You must know the beam energy, the probe current, and the live time for the unknown. It is easiest if this information is recorded in the file representing the unknown.

Collecting the Spectra

Before starting the measurement process, you will need:

- Your unknown material
 - Mounted with a flat, polished surface normal to the electron beam
 - Coated with a conductive layer if the sample is an insulator
- A set of standard samples representing all the elements in the unknown with the possible exception of oxygen. Oxygen can be measured directly but is often calculated based on an assumed stoichiometry
- A picoammeter and Faraday cup (see Figure 2) or an in-lens probe current meter to measure the probe current. We need to know the number of electrons per second (usually expressed in nA or pA) *striking the sample*. This is not the same as the emission current, the number of electrons per second leaving the electron gun cathode (usually 10s or 100s of μA).

You will also need:

- Reference spectra for all measured elements. In many cases the standard spectrum can also serve as the reference spectrum. The “Quantification alien” will tell you when additional references are required.

High-accuracy quantitative analysis can only be performed using spectra collected from *flat-polished bulk samples* mounted perpendicular to the electron beam. The definition of bulk is a little loose, but it generally means at least as large as the electron beam interaction volume (on the order of a few micrometers) but potentially as large as the interaction volume of the characteristic X-rays (often tens to thousands of micrometers.)

Using the “Quantification Alien”

Once you have collected the requisite information, you can start the quantification process. Follow along on Figure 3

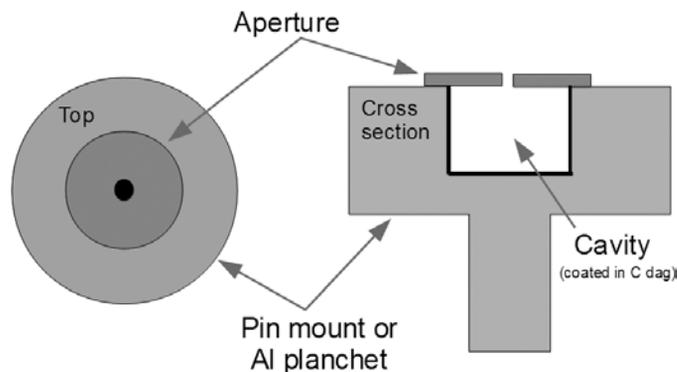


Figure 2: A Faraday cup serves as an electron trap. Electrons enter the small hole, but electrons cannot escape as low-energy secondaries or backscattered electrons.

or on your own computer using DTSA-II, which you can download from <http://www.cstl.nist.gov/div837/837.02/epq/dtsa2/index.html>. Example spectra are available on the DTSA-II “Documentation” page.

1. Load the spectrum you wish to quantify into DTSA-II and select that spectrum in the spectrum list. It will then be displayed in the spectrum display.
2. Identify all the elements present in the spectrum. It is helpful to use the KLM line selector to label all the characteristic peaks in the spectrum. You can use the “copy \rightarrow marked elements” action on the default spectrum display menu to create a list of elements.
3. Select the “Quantification alien” item from the “Tools” menu. The Quantification alien will lead you step-by-step through the quantification process.
4. From page A, select the radio button labeled “Determine the composition of an ‘unknown’ spectrum by MLLSQ fitting to standards” and press “Next” to proceed to the next step.
5. On page B, verify that the instrument, detector, calibration, and beam energy are correct. This information is read from the spectrum selected in Step (1) and should be correct. Press “Next” to proceed to the next step.
6. Use the “File” button on page C to select a standard spectrum for each element identified in step (2). (You may decide to omit oxygen, which can be calculated from assumed stoichiometry.) The “File” button

Table 1: There are three different types of spectra involved in the quantification process: standards, references, and unknowns. Standards provide **intensity** data (characteristic X-ray events per nanoamp per second.) References provide characteristic line **shape** information. References are required because sometimes the characteristic lines present in a standard spectrum are located at similar energies. The difference between standards and references is subtle. Often standards can act as references for one or more characteristic line families, in which case an additional reference is not required. Unknowns represent the spectra we wish to interpret.

Spectrum type	Same beam energy	Known probe current	Known live time	Same element / elements	Same detector	Same detector position	Same detector resolution	Same detector calibration	Unobstructed views of the characteristic lines
Standard	✓	✓	✓	✓	✓	✓	✓	✓	
Reference	*			✓	✓	✓	✓	✓	✓
Unknown	✓	✓	✓	✓	✓	✓	✓	✓	

*It is usually best to collect references at the same beam energy and close to the same probe current, although in many cases it is not strictly necessary.

Select a quantification mode
 First page
 Next: Specify the instrument
 Select the mode which best describes the specimen you wish to perform. The mode you select will determine what information you will be asked to provide and what information will be computed.
 Determine the composition of an "unknown" spectrum by PALSQ fitting to standards
 Determine the composition of an "unknown" spectrum by fitting using a simple method
 Determine measured fractions from comparison

Specify the instrument
 Previous: Select a quantification mode
 Next: Specify standard spectra
 Instrument Acquired on the JOL-SPROOF
 Detector using the Bruker S-av
 with calibration File:Ba(Tm.K)=120.1 eV - Jd 2...
 Setting at a beam energy of 15.0 keV.

Specify standard spectra
 Previous: Specify the instrument
 Next: Specify unmeasured elements

Spectrum	Element	Line Family	Use Time	Probe (nA)	Composition
Std1	Si	Si	2.500	59.4	Si
Ti std	Ti	Ti	2.500	59.4	Ti
Ba22 std	Ba	Ba2	2.500	59.4	Ba2

Specify unmeasured elements
 Previous: Specify standard spectra
 Next: Specify the reference spectra
 No extra element
 Element by difference
 Oxygen by stoichiometry

Element	Carbon	Arsenic	As
Titanium	1	2	NO ₂
Barium	1	1	BaO
Silicon	1	2	SiO ₂

Specify lines to quantify
 Previous: Specify the reference spectra
 Next: Specify unknowns and properties

Element	Line Family	Use Family
Silicon	Si	Si-AL [1.47, 2.00 keV]
Titanium	Ti	Ti-L-CPMUT [0.18, 0.88 keV]
Barium	Auto	Ti-L-Family [0.18, 0.88 keV]
		Ti-K-Family [4.18, 5.18 keV]

Specify unknowns and properties
 Previous: Specify lines to quantify
 Next: The results
 Name: []
 Line Time: 59.4
 Probe (nA): 2.500
 Shape: Bulk
 Add file
 Remove
 Properties
 Sample Shape

The results
 Previous: Specify unknowns and properties
 Fresh
 Normalization: Weight percent Atomic percent

Spectrum	Sum	Weight percent	Normalized weight percent	Atomic percent
Ba22std	99.84 ± 0.15	34.25	19.71 ± 0.03	11.66 ± 0.07
				34.32 ± 0.14

Check the residual
View the report

Figure 3: Shows the path through the "Quantification alien" for quantifying a spectrum containing Ba, Ti, Si, and O.

opens a spectrum file browser. Each time you open a spectrum, you will be asked various questions. If any critical information is missing, you will be asked to provide it. This may include beam energy, probe current, and/or live time. Unless the program can deduce it without operator intervention, you will also be asked which element or elements to associate with each standard spectrum.

7. The spectra will be listed in the table associated with the elements for which they are standards. If the composition of a standard is not available in the spectrum file, then the final column *may not be correct!* Be sure to check that the composition listed in the final column matches the composition of the material from which the standard spectrum was collected. If it does not, highlight the appropriate composition cell and select the correct composition from the drop-down list box. If an appropriate material is not listed, use the “New material” option to define the correct material. (Note: the material editor was described in a previous article in this series [2].)
8. Once you have identified standards for each element in the unknown, review the information in the table. You may use the “Properties” button to edit the probe current or live time. You may replace erroneous standards using the “Remove” button. Make certain all the information is correct. Any mistakes will lead to mistakes in the final result. When you are confident of the information, press “Next” to proceed to the next step.
9. On page D you can specify how to account for unmeasured elements. If you omitted a standard for one element in Step (6), you may specify how to estimate this element. If you specified a standard for all elements, select “No extra element.” If you want to assert that an unmeasured element represents all the remaining unmeasured material, use the “Element by difference.” Most often this mechanism is used to estimate the oxygen or carbon content because these elements are hard to measure directly. Alternatively, you may select “Oxygen by stoichiometry” to calculate the oxygen content based on the quantity of the other elements and an assumed stoichiometry. You may edit the assumed stoichiometry in the table to the right. When you have configured the desired option, use the “Next” button to proceed to the next step.
10. On page E you will select reference spectra. Many times, standard spectra can also be used as references. When this is not the case, there will remain blank entries in the final column of the references table. You must specify spectra to serve as references for each of these vacancies. The quality of the reference is evaluated in the final column. You may select the reference spectrum from a file using the “File” button. You may unassign a reference using the “Remove” button. Note that the “Strip” button allows you to fit, but otherwise ignore, certain elements. If there is an element (like carbon), which is known to coat the sample but does not represent an element present in the unknown material, you may use “Strip” to specify that element that will be fit but otherwise ignored in the final quantification. Select “Next” to proceed to the next step.
11. Usually the program selects which characteristic lines to use for optimal results. However, on page F you may override this behavior for elements for which there is a choice. On an element-by-element basis you may use the drop-down list box in the “Line family” column to select a set of characteristic lines. Select “Next” to proceed to the next step.
12. On page G you get one last chance to select spectra to quantify and to ensure that the data associated with the spectrum are correct. You can use the “Properties” button to edit the probe current and live time. You can select additional spectra to quantify or remove spectra

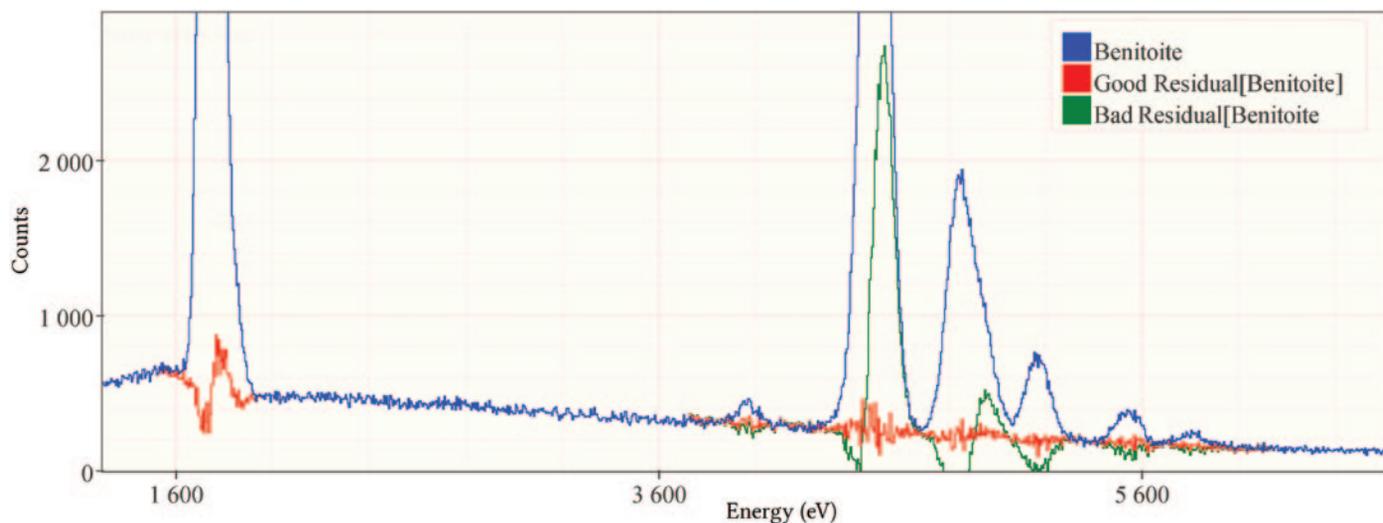


Figure 4: The unknown and good and bad residual spectra. A good residual (in red) shows that all the major characteristic lines have been accounted for in the quantification process. A bad residual (in green) suggests that some element has been omitted. In this example, the peaks between 4 keV and 5 keV are due to Ba and Ti. If we neglect to include Ti (a reasonable omission), we get the bad residual shown in green. The slight S-curve at about 1.8 keV is probably due to slight peak shift possibly due to input count rate shifts and does not suggest a missing element.

Conditions

Item	Value
Instrument	JXA-8500F
Detector	Bruker 5 eV channel width
Beam Energy	20.0 keV
Correction Algorithm	XPP - Pouchou & Pichoir Simplified (Non-normal)
Mass Absorption Coefficient	Superset - Chantler/DTSA

Standards

Element	Material	Spectrum	Ref?	Probe (nA)	Live Time (s)
Si	SiO ₂ = [O(0.5326 mass frac),Si(0.4674 mass frac),5 g/cm ³]	SiO2	Yes	14.962	475.9
Ti	TiO ₂ = [O(0.4007 mass frac),Ti(0.5993 mass frac),5 g/cm ³]	TiO2	Yes	14.981	476.0
Ba	BaCO ₃ = [C(0.0609 mass frac),O(0.2432 mass frac),Ba(0.6959 mass frac),5 g/cm ³]	Barium Carbonate	Yes	14.960	475.9

References

Element/Lines	Spectrum
Ti L-family	\\smsd-s864-files\Users\nritchie\My Documents\My Dropbox\WDS-SDD comparison\WDS-SDD comparison - Ba Ti K glasses (take 2)\Std\Ti.msa

Preferred Characteristic Line Families

Element	Preferred ROI
Titanium	Ti K-family [4.17, 5.19 keV]

Other elements

• Oxygen-by-stoichiometry

Element	Valence	Formula
O	-2	
Si	4	SiO ₂
Ti	4	TiO ₂
Ba	2	BaO

Results

Table: Quantitative results (uncertainties are statistical-only, 1 σ)

Spectrum	Quantity	O		Si			Ti			Ba			Sum
WDS-SDD comparison - Ba Ti K glasses (take 2) Un 11 Benitoite (unk)_606	Line			Si All			Ti K-family			Ba L-family			
	Z · A · F	-	-	1.140	0.715	1.002	1.051	0.954	1.009	0.905	1.013	0.999	
	k-ratios	-	-	0.3304	±	0.0002	0.1913	±	0.0003	0.4557	±	0.0006	
	mass fraction	0.3317		0.1892	±	0.0001	0.1132	±	0.0002	0.3476	±	0.0004	0.9817
I = 15.006 nA	norm(massfraction)	0.3379		0.1927	±	0.0001	0.1153	±	0.0002	0.3541	±	0.0004	-
LT = 59.5 s	atomicfraction	0.6406		0.2081			0.0731			0.0782			
Residual	C:\Documents and Settings\nritchie.SMSD0\My Documents\DTSA-II Reports\2010\November\9-Nov-2010\residual2007372180725530255.msa												

Figure 5: The result table in the final report. This table summarizes the results of the measurement, including the composition as mass fraction and atomic fraction. The k-ratio and ZAF rows provide advanced diagnostic information.

using the “Add file” and “Remove” buttons respectively. (The “Sample Shape” option will be covered in a later article.) Select “Next” to perform the calculations and proceed to review the results.

13. Page H allows you to review the results. The results are tabulated on a spectrum-by-spectrum basis. The first column identifies the spectrum. The second tabulates the *analytical total*: the sum by mass fraction of all elements quantified. The analytical total should be approximately 1.0. With care, a total between 0.95 and 1.05 can be regularly achieved. A total outside this range suggests that there might be a problem worthy of investigation. When you are done reviewing the results, select “Finish.”
14. The quantitative results will be tabulated at the end of the “Report.” The quantified spectrum, the residual spectrum, and a simulated spectrum will be displayed in the spectrum display.
15. Review the residual spectrum (see Figure 4). The residual represents the unknown spectrum minus all the characteristic peaks accounted for in the quantification process. If an element was overlooked in the quantification, the residual will not look “clean,” and the analytical total is likely to be low. There will be intensity in a characteristic peak, which remains in the residual. When this happens, it suggests that you are likely to have omitted an element and that you should collect a standard for this element and repeat the quantification process.
16. The “Report” (see Figure 5) summarizes the standards, references, and other parameters selected to perform the quantification. It also summarizes the results and some other useful pieces of information used during the quantification process.

Helpful Suggestions

- a. It saves time and effort if the standard spectra record all the necessary information within the file. The most important pieces of information are the beam energy, probe current, live time, and composition. It saves time if each time you collect a standard spectrum you open the spectrum and edit the properties to ensure they are correct. Use the “Assign material” item in the “Tools” menu to associate a material with the spectrum. Save the standard spectrum back to disk as an EMSA file. I usually name the edited spectrum after the material and append the letters “std” to indicate that the file contains all the standard-related information.
- b. You can select more than one spectrum to quantify during each pass through the “quantification alien.” All the spectra should contain the same elements and have been collected on the same detector with the same beam energy.
- c. If you control your acquisition conditions and check that your detector’s performance has not changed, you can keep an archive of standard and reference spectra. I usually archive them in directories first organized by detector/process time and then by beam energy. The

results are likely to be slightly less accurate than standards collected on the same day, but the results are still likely to be more accurate than standard-less quantification.

- d. If you don’t have standard samples for the elements you anticipate measuring in your laboratory, you might consider purchasing one or more standard blocks from a suitable vendor. Vendors can provide you with a single 25.4 mm diameter block containing as many as sixty suitable standard materials. The block is typically polished to a sub-micrometer finish and coated with a conductive layer of carbon to eliminate surface charging. A good quality block is not cheap, but the cost represents a small fraction of the cost of your instrument or X-ray detector and will improve the quality of your results more than any other item you can purchase.

Conclusion

The quantification process is complicated. It takes time and an attention to detail. Although I have tried to be concise and complete in this description, a few examples will help to clarify the process. Part II of this article will provide more details and a couple of examples.

References

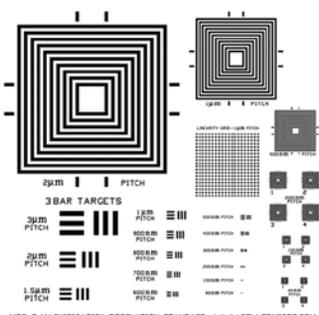
- [1] NWM Ritchie, *Microscopy Today* 19(1) (2011) 26–31.
- [2] NWM Ritchie, *Microscopy Today* 19(3) (2011) 30–34.
- [3] JI Goldstein et al., *Scanning Electron Microscopy and X-ray Microanalysis*, Springer, New York, 2003.

MT

MRS-5

We are ISO-9000 certified and ISO-17025 accredited
Microscopy Calibration Standard
 Now you can calibrate from 1,000X to
 1,000,000X!

This is our fourth generation, traceable, magnification reference standard for all types (SEM, FESEM, Optical, STM, AFM, etc.) of microscopy. The MRS-5 has multiple X and Y pitch patterns ranging from 80nm (± 1 nm) to 2 μ m and 3 bar targets from 80nm to 3 μ m. There is also a STM test pattern.



MRS-5 MAGNIFICATION/RESOLUTION STANDARD - WWW.GELLERMICRO.COM
S/N: MRS-5-1-1 © JAN 2006

Free web resource guide!



GELLER MICROANALYTICAL LABORATORY, Inc.

426e Boston St., Topsfield, Ma 01983
www.gellermicro.com



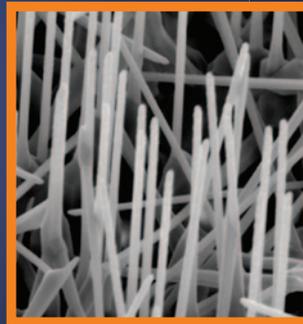
omniprobe®

An Oxford Instruments Company

Create Nanostructures

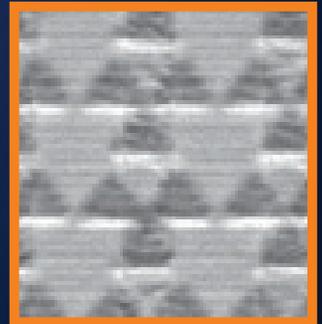


Modify



ALD Surface Alteration

Make



Plasmonic Nanostructures

OmniGIS®

Advanced Gas Injection
for FIB and SEM

Features Include: Multiple Precursors on One Port (Including Gas, Liquid, & Solid) | Single Needle Delivery | Computer Controlled Needle Positioning | Intuitive Software with Three User Levels | Mass Flow Control | Adjustable Precursor Flow | Fast & Easy Precursor Replacement

2011

Upcoming Conferences:

Microscopy Conference 2011 Aug 28 - Sep 2 - Kiel, Germany

AMFA Aug 29 - Boston, MA

ISTFA Nov 15-17 - San Jose, CA

MRS Fall Nov 28-Dec 2 - Boston, MA

P: 214.572.6800 | F: 214.572.6801
<http://www.omniprobe.com>