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HIGH RESOLUTION X-RAY SPECTROSCOPY WITH A MICROCALORIMETER

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ABSTRACT

Energy-dispersive spectrometry (EDS) is often the preferred choice for X-ray microanalysis, but there are still many disadvantages associated with EDS, the most significant of which is the relatively poor energy resolution, which limits detection sensitivity and the ability to distinguish among closely spaced spectral features, limiting even qualitative analysis. A new type of EDS detector that operates on the principle of microcalorimetry has the potential to eliminate this shortcoming, reaching resolutions an order of magnitude better. The detector consists of an absorber in thermal contact with a transition edge sensor (TES). An X-ray from the specimen hits the absorber and manifests itself as a change in temperature. Because the system is kept at 80 mK, the heat capacity is low and the temperature spike is observable. The TES responds to the increase in temperature by transitioning from its superconducting to its normal conducting state, thus sharply raising the overall resistance of the circuit. The circuit is kept at a constant voltage, so the increase in resistance is manifested as a decrease in current flow. This decrease in current is measured by a superconducting quantum interference device (SQUID), and by integrating the current over time, the energy of the incident X-ray is determined. The prototype microcalorimeter was developed by NIST, and this technology is now available commercially through a partnership between Vericold Technologies and EDAX International. ORNL has received the first of these commercial microcalorimeters in the United States. The absorber in this detector is gold, and the TES consists of a gold-iridium bilayer. It is designed to offer spectral resolution of 10-15 eV at a count rate of $\sim 150 \text{ s}^{-1}$. The goal of this project was to analyze and document the performance of the detector, with particular attention given to the effects of an X-ray optic used to improve collection efficiency, the multiple window system and any other sources of spectral artifacts. It was found that the detector is capable of distinguishing many $L\alpha$ and $L\beta$ spectral lines, with a resolution between 13 and 17 eV. It was also observed that the background has an unusual shape, and this is largely being attributed to the variable transmission coefficient of the X-ray optic. These preliminary results suggest that the microcalorimeter has a high potential for use in microanalysis, but more work to quantify its capabilities must still be done.

INTRODUCTION

Energy-dispersive X-ray spectroscopy (EDS) is often preferred over wavelength-dispersive X-ray spectroscopy (WDS) because it is possible to collect the entire spectrum at once, with consequently shorter acquisition times and more uniform sensitivity to spectral features across a wide range of photon energies. However, there are many disadvantages associated with EDS, the most significant of

which is the relatively poor energy resolution, which limits detection sensitivity and the ability to distinguish among closely spaced spectral features, limiting even qualitative analysis. A new type of EDS detector that operates on the principle of microcalorimetry has the potential to eliminate this shortcoming, reaching resolutions comparable to, and perhaps even superior to, WDS detectors. The prototype microcalorimeter was developed by the National Institute of Standards and Technology (NIST) [1], and this technology is

now available commercially through a partnership between Vericold Technologies and EDAX International. ORNL has received the first of these commercial microcalorimeters in the United States. It has been installed within the past two months, so the results presented here are preliminary, but timely.

MATERIALS AND METHODS

Operating Principles

The microcalorimeter is designed for X-ray microanalysis with conventional scanning electron microscopy (SEM) techniques. The detector consists of an absorber in thermal contact with a transition edge sensor (TES) thermometer. The TES is a metallic bilayer consisting of a superconductor and a normal conductor. By varying the thickness of the layers, one can “tune” the transition temperature of the TES between its normal and superconducting states. When an X-ray from the specimen hits the absorber, the energy of the photon is deposited as heat and manifests itself as a change in temperature. The heat sink quickly returns the absorber to its initial temperature. Because the system is kept at a very low temperature (< 0.1 K), the heat capacity is small ($C \propto T^3$), allowing for a more sensitive response. The TES responds to the increase in temperature by transitioning from its superconducting to its normal conducting state, thus sharply raising the overall resistance of the circuit of which it is a part. The circuit is kept at a constant voltage, so the increase in resistance is manifested as a decrease in current flow. This decrease in current is measured by a superconducting quantum interference device (SQUID), and by integrating the current as a function of time, the energy of the incident X-ray is determined [1,2,3].

Establishing the Baseline Temperature

As mentioned before, it is important that the heat capacity of the absorber be small so that the temperature change will be more noticeable. This also allows the system to return to the baseline temperature more quickly, thereby improving the count rate capability. The small heat capacity is obtained by operating at a very low temperature, approximately 80 mK. The cryogenic system used to achieve this temperature is comprised of three stages. The first, outermost stage is a nitrogen refrigerator that will drop the temperature of the system to below 77 K. A second stage helium refrigerator in series with the first stage will drop the temperature to below 4 K. The third stage uses an adiabatic demagnetization

Line	Energy	Resolution (eV)
C	282	16
O	523	14
Mg	1254	15
Al	1487	17
Si	1740	19

Table 1. Resolution data determined from the NIST glass standard spectrum.

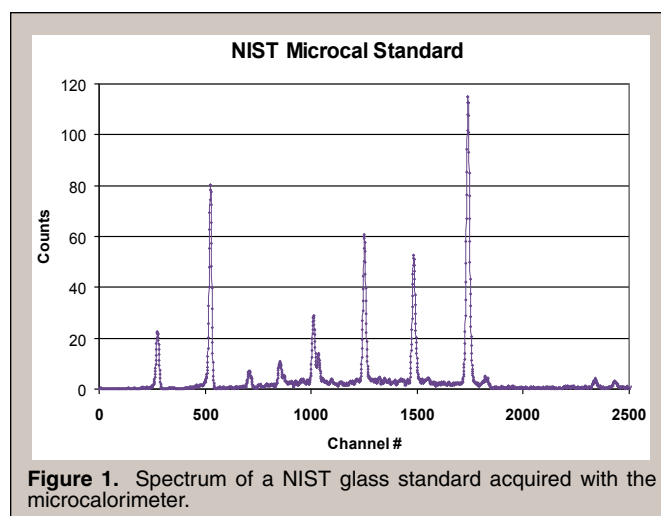


Figure 1. Spectrum of a NIST glass standard acquired with the microcalorimeter.

refrigerator (ADR), which uses a paramagnetic salt pill capable of reaching temperatures below 100 mK. The salt is in thermal contact with the second heat sink ($T < 4$ K). The spins of the paramagnetic atoms within the salt are randomly oriented. A magnetic field is applied, aligning the spins along the field direction. The increase in energy necessary to align the spins (drawn from the field) generates heat that flows to the heat sink. The salt is then isolated from the heat sink and the magnetic field is removed. The spins will randomize to increase entropy, and this change of polarity requires energy. Because the salt is now thermally isolated from the heat sink (i.e., adiabatic), the energy used must come from the internal energy of the particles, thus reducing the temperature from ~ 4 K to less than 100 mK. The ADR in the ORNL microcalorimeter operates at 70 mK, but perfect thermal equilibrium is difficult to achieve, so the absorber itself has a baseline temperature of 80 mK.

The Absorber

The absorber in the ORNL microcalorimeter is made of gold. It has lateral dimensions of $250 \mu\text{m} \times 250 \mu\text{m}$ and a thickness of $1 \mu\text{m}$. Because the lateral dimensions of the absorber are small in comparison to the distance between the absorber and the specimen, which is approximately 45 mm, the solid angle subtended by the detector is extremely small, on the order of 10^{-3} steradians. Because characteristic X-ray emission occurs isotropically, the small solid angle results in a proportionately small X-ray collection efficiency, and a poor count rate [4]. This is one of the primary limitations of the microcalorimeter.

The TES Thermometer

The TES in the ORNL microcalorimeter is made of a gold-iridium bilayer. At very low temperatures, gold is a normal conductor and iridium is a superconductor. The TES has lateral dimensions of $300 \times 500 \mu\text{m}$ and a thickness of $1 \mu\text{m}$. The thickness ratio of gold to iridium is adjusted so that the TES will transition between its normal conducting state to its superconducting state at a temperature of 94 mK, 14 mK above the baseline temperature. The TES never goes fully normal conducting as energy sensitivity would be lost. The temperature increases stay within the temperature range of the

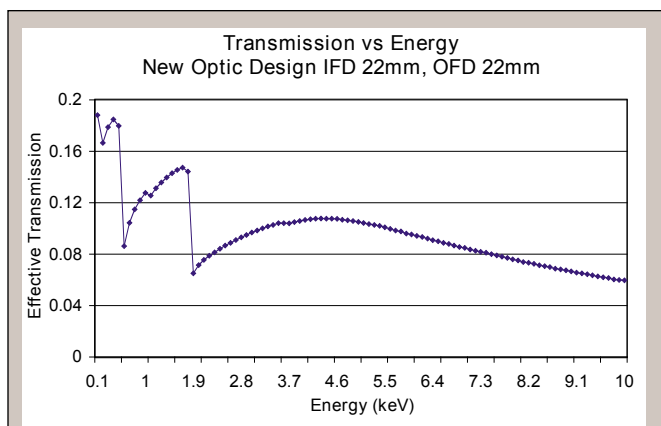


Figure 2. Transmission coefficient of the X-ray optic.

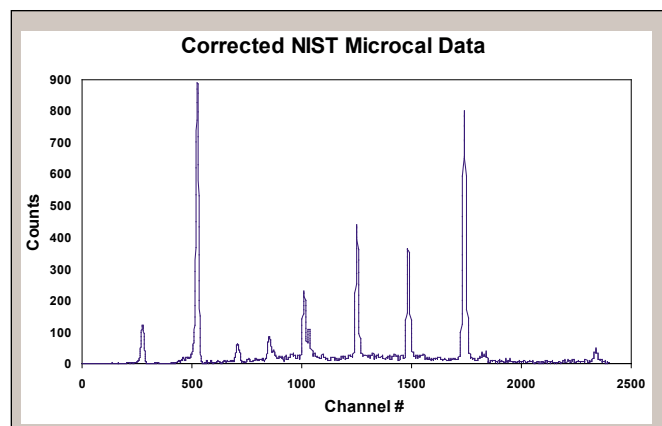


Figure 3. NIST glass standard spectrum corrected for X-ray optic transmission effects.

normal-to-superconducting transition. After an X-ray increases its temperature, the TES returns to its baseline temperature of 80 mK in less than 2 ms. To unambiguously identify the energies of detected X-rays, i.e. to avoid pulse pile-up, if two pulses are detected within 2 ms of one another, both are discarded. Under these operating conditions, the detector achieves a maximum theoretical output count rate of 500 s^{-1} , although the maximum practical count rate is considerably smaller, $\sim 150 \text{ s}^{-1}$. The rejection of overlapping pulses creates an effect somewhat analogous to dead time in a conventional EDS detector.

The X-Ray Optic

To improve collection efficiency, a polycapillary X-ray optic has been inserted between the specimen and the absorber. While the optic does increase the collection efficiency by a factor of 100, it also introduces a nonlinear transmission coefficient that can obscure the interpretation of the data. The prototype microcalorimeter developed by NIST initially had an X-ray optic [2], but because of the nonlinearity it was eventually removed. The ORNL microcalorimeter continues to take advantage of the focusing effects of the optic, and the nonlinear transmission is accounted for mathematically.

The Multiple Window System

The ORNL microcalorimeter has a series of six windows, a noticeable difference from both a conventional EDS detector, which has one window, and the NIST microcalorimeter, which has four. The multiple window system is necessary to screen the background of room temperature infrared (IR) radiation as well as to protect the vacuum. The first (outermost) window is a Moxtek film on a silicon membrane at room temperature. The remaining five windows are made of parylene. The second and third windows are kept at the temperature of the first cooling stage, $< 77 \text{ K}$; the fourth and fifth are kept at the temperature of the second cooling stage, $< 4 \text{ K}$; the sixth (innermost) window is kept at the temperature of the detector, $\sim 80 \text{ mK}$. All six windows have a thickness of approximately 100 nm, and all are reinforced with aluminum to mitigate electrostatic charging and to reflect light and heat. The second and fourth windows have a copper grid reinforcement as well.

Research Goals

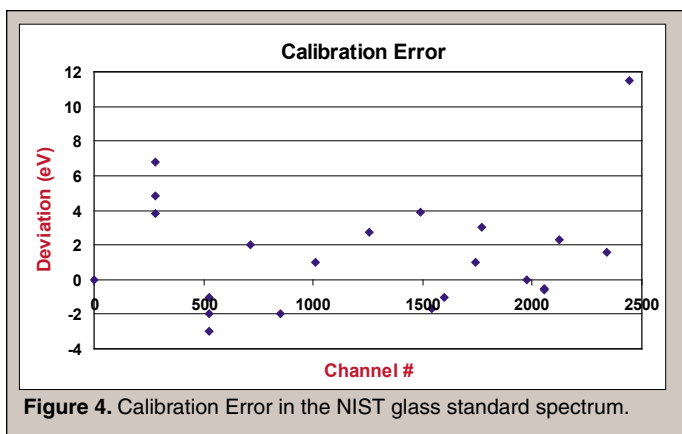
It is the goal of this research to analyze and document the performance of the microcalorimeter, with particular attention given to the effects of the X-ray optic used to improve collection efficiency, the multiple window system used to safeguard the cryogenic temperature of the detector, and any other sources of spectral artifacts. The eventual goal is to obtain a thorough understanding of the detector, its electronics and software, to optimize energy resolution and thereby achieve high detection sensitivity, to distinguish low-intensity M and N-shell X-ray spectral lines for high-Z elements, to resolve low-Z elements, and potentially to observe chemical shifts. We are also interested in raising the count rate for improved collection efficiency. This is still a work in progress, but much has already been learned from the preliminary data presented below. The spectra presented in this paper were collected using a glass standard prepared by NIST and an iridium alloy.

RESULTS

Figure 1 presents a spectrum acquired from a NIST glass standard with the ORNL microcalorimeter. It is immediately evident upon inspection that the count rate is very low; this is described in more detail in the discussion section. As desired, the energy resolution of this spectrum is significantly better than that of conventional EDS. However, before the resolution can be accurately quantified, the transmission effects of the X-ray optic must be addressed. The transmission data were determined experimentally by Vericold Technologies and are presented in figure 2. Because of the obvious dependence on X-ray energy, it is important to account for this variation. The relevant relationship is

$$\text{Counts (observed)} = \text{Counts (real)} \times \text{Transmission Coefficient}$$

Thus, calculating the real counts is as simple as multiplying the observed counts by the reciprocal of the transmission coefficient. The result of this correction is presented in figure 3, the corrected spectrum of the NIST glass standard. Energy resolution is defined as the FWHM of the spectral lines; the resolution of the peaks in this spectrum were determined with a fitting program and are presented in table 1. The resolution range of 14 to 19 eV is close to the 15 eV provided by Vericold Technologies. To corroborate this result, one can examine the peak separations that would not be distinguishable



with conventional EDS. The $L\alpha$ peak for nickel occurs at 849 eV, and the $L\beta$ peak occurs at 866 eV, a difference of 17 eV. It is possible to discriminate between these two peaks, thus suggesting that the microcalorimeter is resolving at least 17 eV. The $L\alpha$ peak for iron occurs at 704 eV, and the $L\beta$ peak occurs at 717 eV, a difference of 13 eV. Because these two peaks are not distinguishable on the spectrum, this suggests that the microcalorimeter is not currently resolving at 13 eV. These findings are consistent with the FWHM measurements.

In addition to quantifying the energy resolution, it is important to determine how accurately the experimental spectral lines reflect the real energies of the characteristic X-rays. Figure 4 presents the deviation of the microcalorimeter peak centers from those documented in the NIST database. The error is less than the resolution of the detector, and the values in the NIST database are not known with absolute certainty, so the deviations are statistically acceptable. However, it might still be desirable to try to enhance the accuracy of the measurements, and it will be necessary to do so if the resolution of the microcalorimeter can be improved to 10 eV or better. This can be done by using a fifth order polynomial calibration of the X-ray energy.

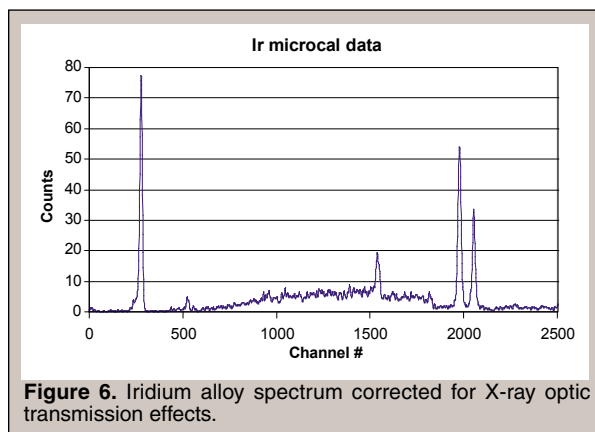
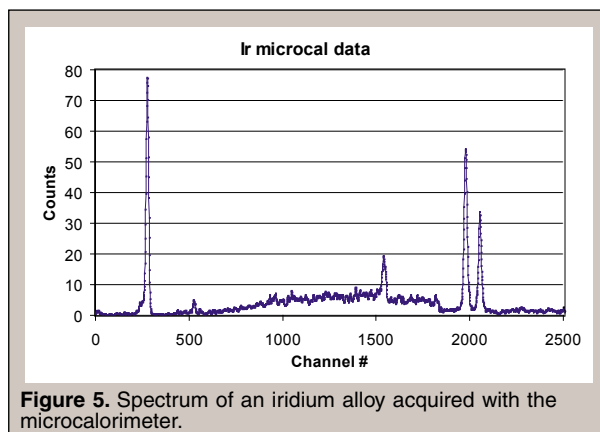
Another feature of the corrected spectrum (figure 3) is the more expected shape of the background over the initial spectrum (figure 1). In the initial spectrum, there is a clear discontinuity in the background at the silicon absorption edge, ~ 1.8 keV. Beyond this point, it simply flattens out rather than falling inversely with energy as expected. Examining the X-ray optic data, there is a large drop in transmission at this point, beyond which the transmission

is significantly less efficient. The corrected spectrum is much smoother and exhibits a background shape more like the expected bremsstrahlung background. To further investigate the effects of the X-ray optic on the background, a spectrum of an iridium alloy was taken. Figure 5 presents the initial spectrum collected by the microcalorimeter, and figure 6 presents the same spectrum after the transmission correction. While the drop at the silicon edge is not completely eliminated by the correction, it is noticeably reduced. Furthermore, the overall shape of the background is dramatically improved. This indicates that future work with the microcalorimeter/X-ray optic system will require that this kind of correction be made for quantitative analysis.

DISCUSSION AND CONCLUSIONS

The preliminary results are promising: the microcalorimeter generates spectra with a resolution almost an order of magnitude better than conventional EDS, which generally gives an optimum resolution of 135 eV. However, there are still many issues to be addressed. Perhaps the most apparent shortcoming of the microcalorimeter is the extremely low collection efficiency. Even with the X-ray optic, count rates typically have not exceeded 70 counts per second, twenty to fifty times lower than conventional EDS. If it takes a long time to collect a statistically quantifiable spectrum, the potential uses for microanalysis may be limited. Operating at high beam currents will help increase the count rate, but depending on how sensitive the specimen is to contamination or beam damage, this may create other problems. Another problem that must be addressed is that the transmission effects of the multiple window system are as of yet unknown. The windows could have as significant an impact as the X-ray optic, although whereas the X-ray optic transmits most efficiently at low energy due to its polycapillary structure, the windows will likely transmit most efficiently at higher energies. The transmission of the windows must be quantified for the microcalorimeter to be used for microanalysis.

Also of interest is the manner in which the spectra are constructed from the raw data. The spectra presented in this paper were not binned in the traditional manner. Instead, each data point was given an artificial line width, a Gaussian curve with a spread of 1 eV and unit area. This is the technique preferred by Vericold Technologies, but it gives rise to some concerns about the interpretation of the spectra where counts are few. Because each



count is represented by a curve of unit area distributed over several channels instead of a count of unit height assigned to a single channel, the final spectrum contains a fractional number of counts within each channel. Also, it is currently unknown how much of the background can be attributed to the spread of the artificial curves. If this technique continues to be used, more investigation into the statistical implications will be necessary. Alternatively, if conventional step-function binning is used, it will be necessary to determine what size bins are most appropriate.

Finally, there is some concern regarding the shape of the X-ray lines: the statistical intensity distribution within the characteristic peaks is such that they appear to be noticeably sharper than a Gaussian distribution. Although the peaks in the microcalorimeter spectra are better than expected, it is unknown why this is so. Further investigation will be necessary to explain this result before microcalorimetry can be used for quantitative compositional analysis. The natural intrinsic line-width of an X-ray is determined by the lifetime of the ionization event which created the X-ray. A long-lived event will create a sharper peak, whereas a short-lived event will create a peak with more spread. Typical values range between 2 and 8 eV. Because the detector resolution is still significantly larger than the natural line-widths, the sharper distribution observed is characteristic of either the detector response or the method of data rendering.

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