QUANTITATIVE ANALYSIS WITH THE TRANSITION EDGE SENSOR MICROCALORIMETER X-RAY DETECTOR

Terrence Jach¹, Nicholas Ritchie¹, Joel Ullom², and James A. Beall²

¹Surface and Microanalysis Science Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, Maryland 20899
²Quantum Electronics Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305

ABSTRACT

The use of a microcalorimeter X-ray detector with a transition edge sensor in an electron probe to perform quantitative analysis is reported. Two bulk samples of multielement glasses that have been previously characterized by chemical methods for use as standard reference materials were analyzed. The spectra were analyzed against standards using three different correction schemes. In one of the standards, the reference line was easily resolved despite its proximity within 45 eV of another line. With the exception of direct measurements of oxygen (a particularly challenging element), the results are in agreement with the certified characterization to better than 1% absolute or 8% relative. This demonstrates the potential of microcalorimeter detectors as replacements for conventional energy dispersive detectors in applications requiring high energy resolution.

INTRODUCTION

Microcalorimeter X-ray detectors represent a new technology that achieves high energy resolution over a large energy range [1,2]. They make it possible to resolve individual lines of a broad range of elements that would have interfered in earlier detectors. Previous studies have concentrated on the resolution [3] and stability [4] of the microcalorimeter detectors as a precondition for use in actual analyses. There are further questions regarding the counting rates, the times required to obtain statistically significant spectra, and the suitability of the detector for use with electron microscopes and microprobes [5,6]. We address these concerns by reporting on quantitative analyses that we have carried on non-stoichiometric materials with a microcalorimeter detector employing a transition edge sensor (TES) as the thermally sensitive element [7]. The analyses were performed on an electron beam probe. The samples consisted of bulk glasses that were previously characterized by chemical analysis and certified as NIST Standard Reference Materials.

DESCRIPTION OF THE EXPERIMENTAL PROCEDURE

The NIST-designed microcalorimeter detector that we used in this investigation is similar to one that has been previously described [4]. It consists of an X-ray absorbing element that is isolated except for contact with a thermal reservoir held at 70 mK. Sudden temperature increases caused by the absorption of individual X-ray photons are registered by the TES, a thin film of superconductor maintained in the middle of its superconducting-normal transition by a dc current. The changes in the resistance of the film in response to the temperature pulses determine
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the sensitivity, resolution, and linearity of the instrument. The detector that we used in these measurements had an energy range greater than 7 keV and a best measured resolution of 4.4 eV. The thermal stability of the spectra was better than 1 eV over a period of hours. The thermal reservoir was maintained at low operating temperature for periods of at least 6 h by an adiabatic demagnetization refrigerator (ADR).

The detector was located near the end of a horizontal probe that projects into the electron microscope. The samples were mounted with an orientation of 45° with respect to both the vertical electron beam and the detector. The detector was positioned approximately 35 mm from the sample behind an aluminized vacuum window and additional aluminized radiation shields. These windows determined the lower limit of the detector response, ~400 eV.

The sample height was optimized for a collimator on the front of the detector. Thereafter, all samples were measured at the same height and distance from the detector. The response of the detector to sample height was very broad, so that a variation of 0.5 mm at the optimum position might cause a 2% change in the count rate, but the samples were easily repositioned to within 0.1 mm.

Pulse processing consisted of analog pseudo-Gaussian shaping of the pulses and analog pulse pileup circuitry modified for the relatively long microcalorimeter pulses (~260 μs). This supplied the dead time corrections and largely limited the maximum count rate to 300 counts/s. The resulting pulses were then recorded by a 14 bit ADC in a 16K channel spectrum with an average width of 0.5 eV. This method resulted in instrumental resolution which was somewhat less than the best observed using digital pulse processing on the same spectrometer but which made for real-time observation of entire spectra and rapid calibration.

The microcalorimeter spectra from the sample and comparison standards were all obtained in a single cooldown period when both the thermal (slow) feedback stabilization and the electrothermal (fast) feedback stabilization were unchanged [2]. Under these circumstances, the sample and standard spectra are remarkably stable. Energy calibration was carried out by fitting the line energies to the values currently assigned from the tables of Deslattes et al. [8]. The spectrometer generally requires a linear correction to the bin size and a small quadratic correction for nonlinearity of the detector (approximately $1 \times 10^{-5}$) over the entire energy range.

The analyses were carried out at an electron beam energy of 12 keV, and a beam current of approximately 10 nA. This resulted in count rates for different spectra between 80 counts/s and 200 counts/s. Each spectrum was accumulated for 1000 s live time. Total sample counts were normalized to the beam current.

RESULTS

Spectra were obtained from two samples. The first is a glass designated K411 [9]. This glass is a NIST Standard Reference Material containing Si, Ca, Mg, Fe, and O. The bulk analysis for the certified content has been carried out using wet chemical methods, with a collective uncertainty of 0.2% (2σ). Spectra were obtained from the comparison standards Ca$_5$(PO$_4$)$_3$Cl (chloroapatite), MgO, K412 (another reference glass for Si) and Fe. Fig. 1 shows the entire K411 spectrum.
Figure 1. Spectrum of K411 glass, 1000 s live time.

Given the high resolution of the detector, all of the major lines are observable from 400 eV to 7 keV. Fig. 2 shows an expanded comparison of two of the lines used for the analysis: the Ca Kα line in the K411 spectrum (black) and the same line in an apatite standard (green).

The second sample is a glass designated K458 [10]. This glass is a Standard Reference Material containing Si, Ba, Zn, and O with 2σ uncertainties assigned by a method described in the reference. Spectra were obtained from standards Zn and BaTiSi3O9 (benitoite). An expanded view of the benitoite standard is shown in Fig. 3. The spectrum shows the resolution of the Ba Lα_{1,2} line, which is used for the Ba reference. On a conventional EDS detector, this line would
interfere with the Ti Kα₁,₂ line, which is only 45 eV away. The entire K458 spectrum is shown in Fig. 4.

![Figure 4. Spectrum of K458, 1000 s live time.](image)

**ANALYSIS**

Peak intensities were extracted from reference and unknown spectra by counting the X-ray events in a range-of-channels encompassing the peak and then subtracting a trapezoidal estimate of the bremsstrahlung background. The peak intensity ratios were corrected for atomic number, absorption and secondary fluorescence effects using three different correction algorithms, each of which is capable of handling non-normal beam incidence—Proza96 [11,12], XPP [13], and NISTMonte [14]. The three correction algorithms gave similar results. The K411 measurement was repeated four times with similar results in the course of assessing the reliability of sample and reference measurements. The Kα lines of the elements, including O, were used for the analysis of the K411 glass. The results are shown in Table I. All percentages are stated in weight percent. We report the XPP results in Col. 2. The uncertainties in the results have been divided into two categories. The uncertainties (1σ) obtained from Poisson statistics applied to both the peak and background estimates are shown in Col. 3. Additionally, we report the standard deviation from the mean weight concentrations by the three different correction algorithms as the “estimation uncertainty,” shown in Col. 4. Col. 5 contains the values and uncertainties (2σ) that are certified for the standard reference material. Col. 6 lists the relative difference between the measured and certified compositions.

The results of the K458 analysis are shown in Table II. The elements were analyzed using the O K, the Si Kα, the Zn Lα₁,₂, and the Ba Lα₁,₂ lines. The results are displayed in the same manner as Table I.
Table I. K411.

<table>
<thead>
<tr>
<th>Element</th>
<th>Measured Composition (%)</th>
<th>Statistical Count Uncertainty (%)</th>
<th>Correction Variation (%)</th>
<th>Certified Value with 2σ Uncertainty (%)</th>
<th>Relative Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>10.92</td>
<td>0.13</td>
<td>0.03</td>
<td>11.06 ±0.14</td>
<td>-1.3</td>
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<tr>
<td>Fe</td>
<td>12.09</td>
<td>0.33</td>
<td>0.05</td>
<td>11.21 ± 0.15</td>
<td>7.9</td>
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<tr>
<td>Mg</td>
<td>8.77</td>
<td>0.09</td>
<td>0.36</td>
<td>8.85 ± 0.12</td>
<td>-0.9</td>
</tr>
<tr>
<td>Si</td>
<td>25.39</td>
<td>0.22</td>
<td>0.08</td>
<td>25.38 ± 0.09</td>
<td>0.0</td>
</tr>
<tr>
<td>O</td>
<td>40.02</td>
<td>0.83</td>
<td>2.30</td>
<td>42.37 ± 0.20</td>
<td>-5.6</td>
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<tr>
<td>Total</td>
<td>97.15</td>
<td>2.33</td>
<td></td>
<td>98.87</td>
<td></td>
</tr>
</tbody>
</table>

Table II. K458.

<table>
<thead>
<tr>
<th>Element</th>
<th>Measured Composition (%)</th>
<th>Statistical Count Uncertainty (%)</th>
<th>Correction Variation (%)</th>
<th>Certified Value with 2σ Uncertainty (%)</th>
<th>Relative Difference (%)</th>
</tr>
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<tbody>
<tr>
<td>Ba</td>
<td>40.45</td>
<td>0.82</td>
<td>0.07</td>
<td>41.79±0.20</td>
<td>-3.2</td>
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<td>Si</td>
<td>22.47</td>
<td>0.22</td>
<td>0.16</td>
<td>23.05±0.34</td>
<td>-2.5</td>
</tr>
<tr>
<td>Zn</td>
<td>2.92</td>
<td>0.11</td>
<td>0.40</td>
<td>3.01±0.06</td>
<td>-3.0</td>
</tr>
<tr>
<td>O</td>
<td>33.38</td>
<td>0.66</td>
<td>1.66</td>
<td>31.86</td>
<td>4.8</td>
</tr>
<tr>
<td>Total</td>
<td>99.21</td>
<td>1.71</td>
<td></td>
<td>99.71</td>
<td></td>
</tr>
</tbody>
</table>

**DISCUSSION**

The uncertainties in the measured composition which we have estimated in the analysis include the uncertainties due to counting statistics and the uncertainties among various nonlinear correction algorithms. These uncertainties are smaller than 1% absolute (except O) or 8% relative. The largest absolute errors are in the measurement of O. The relatively large errors in the oxygen measurement can be attributed to two factors—relatively poor count statistics due to reduced X-ray production of the O Kα and large corrections resulting from strong absorption of the O Kα by the matrix. This is compounded by the fact that correcting microanalytical spectra collected at non-normal incidence is less well understood than correcting spectra collected at the classical normal incident beam geometry.

Somewhat surprisingly, two factors which can be attributed to the high resolution of the detector also limit the statistical accuracy. The resolution of various satellite peaks and Compton scattering in the vicinity of the lines make it more difficult to establish clean background regions around these lines. In addition, the count rates which are obtainable from our single pixel detector integrated over practical counting times provide relatively low statistics per channel in bremsstrahlung backgrounds.
CONCLUSIONS

The spectra obtained from the samples and the comparison standards in 1000 s live time yielded results that were in agreement with the other analyses to generally better than 1% absolute or 8% relative. The absolute error in the direct measurement of O were somewhat larger. The TES microcalorimeter X-ray detector is demonstrated to be capable of quantitative analyses over its entire energy range. The excellent energy resolution makes it possible to analyze lines at very low energies and where different elements were previously regarded as conflicting. The current limitations in the accuracy are the counting statistics, given the count rates of single-pixel detectors. Improved electronics and multi-pixel detectors currently being developed should offset these limitations [15].

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REFERENCES