Improving the Sensitivity of Electron Beam Microanalytical Techniques by Enhanced X-ray Spectrometry: X-ray Microcalorimetry, Silicon Drift Detector Energy Dispersive X-ray Spectrometry, and Polycapillary X-ray Optics

Dale E. Newbury†
National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
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The microcalorimeter energy dispersive x-ray spectrometer, the silicon drift detector (SDD), and polycapillary x-ray optics are recent developments that have significantly advanced analytical x-ray spectrometry for electron beam instruments. The microcalorimeter EDS is capable of high resolution operation (∼5 eV wide peaks) over a wide range of photon energies (250 eV ~ 10 keV). The microcalorimeter EDS can be successfully applied to peak interference problems that are not accessible with the conventional semiconductor EDS such as TiN and BaTiO₃. Polycapillary x-ray optics can augment the collection angle of the microcalorimeter EDS to increase its sensitivity. The SDD is capable of extremely high count rates, up to 1 MHz, and is especially useful for high speed x-ray mapping. [DOI: 10.1380/ejssnt.2003.130]

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I. INTRODUCTION

Chemical characterization by electron-excited x-ray microanalysis frequently involves challenging problems that require determination of trace level constituents under measurement conditions that approach the limit of detection [1]. For a spectral situation in which peak interference is not an issue and only the variance in the background sets a limit on the determination of the peak intensity, the classic formula for the instrumental limit of detection, \( C_{MMF} \), contains two critical spectrometry terms: \( P \), the peak counting rate (characteristic x-ray peak, counts/second) and \( P/B \), the spectral peak-to-background [2]:

\[
C_{MMF} = \frac{3.29a}{\left[n\tau P(P/B)\right]^{0.5}} \tag{1}
\]

In equation (1), \( n \) is the number of measurements and \( \tau \) is the integration time in seconds for a single measurement. The term ‘\( a \)’ is the factor in the hyperbolic relation [3] between the concentration, \( C \), and the experimentally-measured ‘k-value’ (defined as \( k = \frac{I_{UNK}}{I_{STD}} \), where ‘UNK’ is the unknown, ‘STD’ is the standard, and I is the peak intensity for the same x-ray peak measured under the same beam and spectrometer conditions [4]):

\[
1 - \frac{C}{C} = a - \frac{k}{k} \tag{2}
\]

Extraordinary advances have recently been made in instrumentation for x-ray spectrometry suitable for exploitation in the electron probe microanalyzer (EPMA)/analytical scanning electron microscope (ASEM) and the analytical electron microscope (AEM). The microcalorimeter energy dispersive x-ray spectrometer, the silicon drift detector (SDD), and polycapillary x-ray optics are recent developments that have significantly advanced analytical x-ray spectrometry for electron beam instruments. These advances directly impact the sensitivity, spectral specificity, and spatial resolution of these methods, leading to improved limits-of-detection both in the fractional concentration and in the minimum mass that can be effectively measured. These advances are particularly important for the newly emerging area of interest in low beam energy microanalysis (incident beam}

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†Corresponding author: dale.newbury@nist.gov

FIG. 1: Spectrometer energy resolution versus photon energy for various spectrometers: (1) solid lines = Si-EDS, upper = 50 mm² detector and lower = 10 mm² optimum resolution; (2) dashed lines = WDS with various crystal diffractors; (3) open circles, open squares = WDS with various synthetic layered material diffractors; (4) x = first generation microcalorimeter EDS with Ag absorber and Al-Ag transition edge sensor; (5) + = second generation microcalorimeter EDS with Bi absorber and Cu-Mo transition edge sensor; (6) filled triangle = third generation microcalorimeter EDS with Bi absorber, thinned to limit photon energies to approximately 2.5 keV and Cu-Mo transition edge sensor; (7) boxes with internal crosses: natural peak FWHM of Kα₁ peaks for various elements.
The NIST microcalorimeter EDS operates by measuring the temperature rise of a metal target (normal conducting state) when it absorbs an x-ray photon [5]. The electro-thermal thermometry circuit, illustrated in Figure 2, is cooled externally (with liquefied N$_2$ and He gases and an adiabatic demagnetization refrigerator) until it reaches an equilibrium established when the input Joule heating from the internal current source is balanced by the heat losses. This operating point is sharply defined at the superconducting transition temperature of a transition edge sensor (TES, a thin film bilayer of Al-Ag or Cu-Mo) through which heat is exhausted to a low temperature reservoir. After equilibrium is established at approximately 100 mK, the absorption of an x-ray in the target of the quiescent circuit deposits extra heat in the electrothermal circuit, which responds by lowering the internal current. This changing current induces a changing magnetic field in the inductor, which is detected by the SQUID. The measure of the x-ray energy is thus the time integral of the magnetic field history. This process can respond to any x-ray energy and is thus energy dispersive in character. The resolution response over a wide photon range is shown in Figure 1. The first generation microcalorimeter EDS used an Ag absorber and Al-Ag TES which achieved a resolution of 8.9 eV at MnK$_\alpha$ (5890 eV) [5]. The best resolution performance of the NIST microcalorimeter EDS to date has been 4.5 eV at MnK$_\alpha$ (5890 eV) for a second-generation broad energy range spectrometer (Bi absorber, Cu-Mo TES, 250 eV to 10 keV [6]) and 2.0 eV at AlK$_\alpha$ (1487 eV) for a third-generation narrow range spectrometer (thin Bi absorber,
TABLE I: Comparison of WDS and Semiconductor EDS.

|                      | EDS                        | WDS                        |
|----------------------|----------------------------|----------------------------|
| Photon Energy Range  | 0.1~25 keV (Si-EDS)        | 0.1~15 keV with 6 diffractors |
|                      | 0.1~100 keV (Ge-EDS)       |                            |
| Instantaneous Energy Coverage | Full spectrum             | FWHM, ~10 eV              |
| Resolution           | 129 eV (Si-EDS, 10mm²)    | 13 eV (LiF)                |
| (at MnKα, 5890 eV, 1.3 eV FWHM) | 125 eV (Ge-EDS, 10mm²)  |                            |
| Deadtime             | 50 µs (optimum resolution) | 500 ns                     |
| Solid angle (Ω/4π)   | 0.2~5%                     | <0.2%                      |
| Overall efficiency   | 100% (3~15 keV Si-EDS)     | <30%, variable             |
| Maximum Count rate   | 5 kHz (whole spectrum, optimum resolution) | 100 kHz (at one E)        |
| Spectral collection time for major (C>0.1) and minor (0.01≤C≤0.1) constituents | 10 s ~ 200 s | Tens of minutes |
| Strengths            | Qualitative analysis, Low beam current operation | Resolving peak interferences |

FIG. 3: Spectra of BaTiO₃ under 'conventional' microanalysis conditions, E₀ = 10 keV, comparing the Si-EDS (129 eV resolution at MnKα) shown in dashed line and the first generation microcalorimeter EDS (8.9 eV resolution at MnKα) in the region of 4500 eV where the Ti K-family and the Ba L-family peaks mutually interfere.

The maximum count rate (full spectrum) is approximately 500~1000 cps, limited by the long time constant necessary to accurately measure the pulse history to achieve high spectral resolution.

The range of problems that can be solved with the NIST microcalorimeter EDS is demonstrated in the examples presented in Figures 3~7 [8–10].

A. Resolution of classic Si-EDS spectral interferences

There exist a number of technologically interesting materials for which the x-ray spectra measured with Si(EDS) contain such severe peak interferences that peak stripping, such as the multiple linear least squares method, is inadequate to separate the components, especially when the spectral quality is limited by poor counting statistics. Figure 3 shows an example for the optoelectronic material BaTiO₃ analyzed under conventional beam energy conditions (E₀ ≥10 keV). The interferences of TiKα and TiKβ with the Ba L-family peaks are unresolved by Si-EDS, whereas the same spectral region is completely resolved with the microcalorimeter EDS. Figure 4 shows a similar problem for the compound WSi₂, used in semiconductor manufacturing, where the Si-K family peaks suffer severe interference from the W M-family peaks in Si-EDS spectra, while the NIST microcalorimeter EDS completely resolves the major peaks.

FIG. 4: Spectrum of a film of WSi₂ on an SiO₂ substrate as excited at E₀ = 5 keV (low beam energy microanalysis conditions) and measured with the first generation microcalorimeter EDS (8.9 eV resolution at MnKα).

B. Low beam energy microanalysis

Low beam energy microanalysis, where the incident beam energy E₀ ≤5 keV, is hampered by the low fluorescence yield of the low ionization energy shells, especially for L- and M-family shells compared to K-shell x-rays of similar photon energy. This situation is illustrated...
EDS (2.0 eV resolution at AlKα and F, for which there is no alternative x-ray family of K-shell x-rays of the light elements, Be, B, C, N, O, the reference relative peak abundances. To observe a suite of Ba-M family members, several at the same weight fraction), and there is sufficient resolution to observe a suite of Ba-M family members, several of which appear with much higher relative weight than the reference relative peak abundances.

C. Low photon energy microanalysis

Low photon energy microanalysis is encountered with the K-shell x-rays of the light elements, Be, B, C, N, O, and F, for which there is no alternative x-ray family of higher photon energy available. Frequently L- and M-shell x-rays from heavier elements that are also present will interfere with the low atomic number element K-peaks, requiring high spectral resolution for separation. The layered synthetic materials (e.g., W-C, Mo-C, etc.) that have become the preferred diffraction techniques for WDS in the low energy photon region (E_p < 1 keV) are noted for their high efficiency but limited resolution (FWHM 10 to 20 eV), as shown in Figure 1. A further complication occurs because of the chemical effects in which the peak position and shape are dependent on the chemical state of the element, since the electron transitions involved in the emission of the x-ray are modified by the chemical bonding states. It is thus necessary to view the entire peak and adjacent background to make an accurate measurement of the x-ray intensity, which requires WDS scanning at a considerable time penalty. The usual WDS practice of measuring the intensity at the peak and background positions determined on a pure element standard may be subject to serious errors if the peak shape and position shift due to variations in the local chemical state, which itself may depend upon position within the specimen if the cation is multivalent and the composition is heterogeneous. Figure 6(a) shows a comparison between Si-EDS and microcalorimeter EDS spectra of the N-K region in TiN excited with E_0 = 2 keV. The full complexity can only be appreciated with the high resolution of the microcalorimeter EDS, but even with a spectrometer resolution performance of 2 eV at AlKα, the N-K peak suffers interference from the TiL_α and TiL_β peaks, as seen in Figure 6(b). To correct the N-K peak for the Ti-L contribution, a reasonable strategy might be to use the TiL_1α and TiL_β peaks from a Ti-metal spectrum (obtained by scraping under inert gas before insertion in the vacuum) to scale the TiL_α and TiL_β peaks. However, close examination of the TiL_1α,2 and TiL_β1 in TiN and Ti shows a dramatic change in the peak shape which would introduce a severe error in such a peak scaling procedure on N-K. Interestingly, this chemical effect is not seen in TiO_2 compared to Ti metal in Figure 6(c), where the peak shapes are virtually identical for the TiL_α and TiL_β peaks as well as the TiL_1α,2 and TiL_β1 peaks.

III. POLYCAPILLARY X-RAY OPTICS

Because the resolution of the microcalorimeter EDS depends inversely upon the mass of the detector, to achieve the best possible resolution the detector area is minimized. The detector heavy metal (Bi) absorber dimensions are typically 0.5 mm x 0.5 mm. This small detector area (0.25 mm²) and the large specimen-to-detector distance needed to accommodate the extended detector snout, needed to shield the detector so that it can operate at 100 mK, result in an extremely small detector solid angle. The small solid angle places the microcalorimeter EDS at a distinct disadvantage when absolute efficiency is important. A case in point is low beam energy microanalysis where the beam current is limited to 1 nA or less by the diminished brightness of the electron source and the desire to focus a small diameter probe to take advantage of the much reduced range of low energy electrons. Polycapillary x-ray optics have been used to increase...
FIG. 6: (a) TiN under low beam energy microanalysis conditions with $E_0 = 2$ keV showing the region of C K, O K, N K, and Ti L, as measured with the Si-EDS (129 eV resolution at MnK$_\alpha$, red dashed line) and with a third generation microcalorimeter EDS (2.0 eV resolution at AlK$_\alpha$, blue solid line); (b) comparison of spectra as measured with the microcalorimeter EDS of Ti metal (dashed red line), obtained by scraping under inert gas to reveal a fresh surface prior to immediate insertion into the SEM, and TiN (solid blue line); (c) comparison of spectra as measured with the microcalorimeter EDS of Ti metal (dashed red line) and TiO$_2$ (solid blue line).

the solid angle of the microcalorimeter EDS. The principle of the polycapillary or Kumakhov x-ray optic is total external x-ray reflection at the inside surface of a tube, shown schematically in Figure 7(a) [11]. X-rays that approach a surface at an angle below a critical angle are efficiently reflected, while x-rays above the critical angle penetrate into the wall material and are absorbed. Multiple shallow angle reflections along the length of the tube can conduct x-rays over centimeter or greater distances. To maximize the efficiency, the available surface area for reflection must be maximized, which can be accomplished by combining many thin-walled, fine diameter capillaries into a bundle. By gradually tapering this bundle, a converging optic is created. The converging optic has the effect of focusing a parallel source of x-rays that is incident on the untapered end of the optic. Alternatively, if a point source of x-rays, such as that effectively produced by the focused electron beam, is placed at the focus of the tapered end of the polycapillary optic, then a large solid angle is collected and rendered into a nearly parallel beam of x-rays. Finally, if the other end of the optic is also tapered, that near-parallel beam can be converged to a small area crossover.

A double-tapered polycapillary optic is used to more efficiently couple the electron-excited source of x-rays at the specimen to the detector of the microcalorimeter EDS, Figure 7(b) [12]. The performance of this optic is demonstrated in Figure 8, which shows the effective increase in detector solid angle for TiL$_\alpha$ and TiK$_\alpha$ as a function of the lateral position of the x-ray source. For a centrally located source, the improvement is nearly a factor of 300 for the low energy TiL$_\alpha$ radiation at 452 eV. Because the critical angle for x-ray reflection varies inversely with x-ray energy, the improvement in efficiency is reduced by
approx 30% for the more energetic TiK\(\alpha\) radiation at 4510 eV.

With the double-tapered polycapillary x-ray optic in place, the NIST microcalorimeter EDS becomes a practical device for analytical spectrometry even with the reduced excitation encountered in low beam energy microanalysis.

**IV. LIMITS OF DETECTION COMPARISON: SI-EDS, WDS, AND MICROCALORIMETER EDS**

**A. Limits of detection with no peak interference**

It is illuminating to compare the concentration minimum mass fraction, \(C_{MMF}\), that can be detected under low beam energy conditions with the Si-EDS, WDS, and microcalorimeter EDS. Using equation (1) for the calculation of \(C_{MMF}\), consider the problem of measuring low levels of aluminum in a matrix of SiO\(_2\) with the Si-EDS, WDS, and the microcalorimeter EDS. This is a case in which the characteristic x-ray peaks are sufficiently well resolved with conventional semiconductor-EDS to permit easy separation with multiple linear least squares fitting, so that only P and P/B are being compared among the three spectrometry methods. Moreover, for elements like Al and Si with similar atomic numbers, critical ionization energies, and x-ray energies, the \(\alpha\) factor in equation (1) is close to unity, especially for low beam energy analysis conditions that limit beam penetration and reduce x-ray absorption. For typical low measurement conditions (\(E_0 = 5\) keV; \(I_B = 1\) nA; \(\tau = 100\) s; \(n = 1\)). Table 2 compares the performance characteristics as implemented on an SEM platform of the first generation NIST microcalorimeter EDS augmented with polycapillary optics compared with WDS and Si-EDS. Typical values of detector solid angle, efficiency, and other performance characteristics have been used in preparing this table. The
TABLE II: Comparison of Analytical Sensitivity for Various X-ray Spectrometries.

| Parameter                              | WDS                | Si-EDS             | Microcalorimeter-EDS |
|----------------------------------------|--------------------|--------------------|----------------------|
| Resolution (at AlK)                    | 3.8 eV (TAP)       | 78 eV              | 8.5 eV               |
| Al peak count rate at 5 keV            | 260 c/s/nA         | 5200 c/s/nA        | 540 c/s/nA (optic)   |
| Limiting count rate                    | 10^3 c/s (peak Channel) | 3,000 c/s (whole spectrum) | 800 c/s (whole spectrum) |
| P/B on Al (5 keV)                      | 272/1 (TAP)        | 14.5/1             | 79.2/1               |
| C_{MMF} (5 keV, 1nA, 100s)            | 0.0012             | 0.0018             | 0.0016               |

C_{MMF} calculated for Al in SiO₂ for the WDS (TAP crystal) considers the WDS measurement sequence of on-peak and off-peak background measurements needed to extract the peak intensity.

Surprisingly, the values of C_{MMF} span a range of only 1.5 for the three very different types of spectrometers. This unexpected behavior can be understood by considering the relative contributions of the key factors, P and (P/B), in equation (1). Note that both the peak counting rate, P, and the spectral peak-to-background, P/B, enter equation (1) with equal weight. The WDS is a high resolution spectrometer with very high P/B but with poor absolute efficiency, so when the beam current limited to 1 nA, the resulting peak counting rate, P, is low, yielding a P^{*}(P/B) product that limits C_{MMF} to the value listed. For the Si-EDS, the P/B is low compared to WDS, but the geometric efficiency is very high, so that the peak count rate for a 1 nA beam current is high compared to WDS, resulting in a similar product P^{*}(P/B) that yields a similar value of C_{MMF}. Finally, the microcalorimeter EDS equipped with a polycapillary optic has a P/B approaching the WDS while having a better geometric efficiency than the WDS, giving a higher P for a 1 nA beam current. However, P is not as good as that of the Si-EDS because of geometric factors, so that again the C_{MMF} is comparable. The results in Table 2 reveal that both P and P/B must be optimized if the lowest possible values of C_{MMF} are to be obtained under practical measurement conditions.

B. Limits of detection with peak interference

Another approach to estimating the minimum mass fraction, C_{MMF}, can be applied when a constituent is present as a known minor constituent (0.01 ≤ C ≤ 0.1 mass fraction) or a trace constituent (C < 0.01 mass fraction) or has been determined as a result of a quantitative analysis procedure. C_{MMF} can then be estimated from the assumption that the working curve of x-ray counts versus concentration is linear. That is, the slope of the working curve N vs C is controlled by the interelement effects due to the major constituents of the matrix with no significant change as the concentration of the minor or trace constituent varies. With these assumptions and the usual convention that the limit of detection is defined when N - N_B = 3N_B^{1/2}, the concentration limit of detection C_{MMF} (minimum mass fraction) is given by Ref. (Goldstein et al., 2003):

\[ C_{MMF} = \frac{3N_B^{1/2}C_s}{n^{1/2}[N_s - N_B]}, \] (3)

where C_s is the known (or measured) concentration of the dilute constituent, N_s is the gross peak count, N_B is the background under the peak, and n is the number of replicate measurements.

Figure 9 shows a comparison of various spectra of Al-GaAs, where the Al peak suffers some interference from the As L-family x-rays. Applying equation (3) to determine the limit of detection for Al in AlGaAs gives a value of C_{MMF} = 0.000870 (870 parts per million) with Si-EDS spectrometry for a specific set of primary electron dose and detector solid angle. The improved spectral quality achieved with the microcalorimeter EDS (8.6 eV at MnKα, augmented with polycapillary x-ray optics) for the same electron beam dose at 5 keV gives C_{MMF} =
FIG. 11: Schematic diagram of the back surface of a silicon drift detector showing the nested ring electrodes, the biasing bridge of resistors, and the central anode. Cross section showing the charge collection channel formed with the silicon wafer by the applied field.

FIG. 12: Performance of a prototype SDD showing constant resolution as a function of beam current (equivalent to input count rate) for two different time constants.

FIG. 13: Measured SDD output count rate vs. beam current (equivalent to input count rate) demonstrating throughputs as high as 450 kHz.

The AlGaAs example provides a simple demonstration of the improved trace performance of the microcalorimeter EDS compared to Si-EDS where limited interference occurs. A much more challenging example is shown in Figure 10, where the interference occurs between two trace constituents, SiK (0.00126 mass fraction) and TaM (0.00803 mass fraction). In the Si-EDS spectrum in Figure 10(a), these peaks are completely unresolved (resolution 129 eV at MnKα) and cannot be distinguished as peaks above the background. These trace constituents are effectively lost to the analyst if there is no prior knowledge suggesting their presence. With the microcalorimeter EDS, Figure 10(b), the resolution of the peaks is complete, and the limit of detection is at least a factor of 10 lower than the trace concentration level analyzed in the material, e.g., \( C_{MMF} = 0.00013 \) mass fraction for Si and 0.00080 mass fraction for Ta.

V. INCREASING SENSITIVITY BY IMPROVING P: HIGH COUNT RATE SPECTROMETRY WITH THE SILICON DRIFT DETECTOR

The conventional Si-EDS is based on a large Si crystal, ranging in area from 10 mm\(^2\) for a ‘high resolution’ (129 eV at MnKα) version to 60 mm\(^2\) or larger for a large solid angle detector (145 eV at MnKα). The crystal has a thickness of 3 mm and thin (∼10 nm) uniform gold electrodes on both the entrance and exit surfaces. To minimize thermal noise, the Si-EDS operates at a temperature of ∼80 K, achieved with a liquid nitrogen reservoir. The limiting throughput is typically 25 kHz with reduced resolution, and 5 kHz at optimum resolution.

The silicon drift detector (SDD) represents an important advancement on the classic Si-EDS design [13, 14]. The physical principle of x-ray photon detection is the same as in the familiar semiconductor EDS: photoelectric absorption and subsequent inelastic scattering of the photoelectron to create electron-hole pairs that are separated by an applied bias field and collected at the respective electrodes. The nature of this applied bias field is the key distinction of the SDD operation. The SDD is based upon a thin Si crystal wafer (0.3 mm) with an area of 10 mm\(^2\) to 100 mm\(^2\). The entrance surface electrode is uniform, but the back surface electrode is applied lithographically in the form of a concentric set of electrode rings separated by a series of resistors that permit application of a graded potential, as shown schematically in Figure 11. This graded potential has the effect of placing a lateral displacement on the free electrons, focusing their collection onto a central anode only 100 micrometers in diameter, or about 1/10,000 of the area of the anode on a
conventional Si-EDS. This design significantly reduces one of the major noise sources of the Si-EDS detector. The SDD is also operated at much higher temperature, about 250 K, achieved with a Peltier cooler, so that the drift velocities of the electrons and holes are substantially higher than at liquid nitrogen temperature. The combination of detector thickness, the focusing effect of the graded potential, and the higher drift velocities enable the SDD to operate at much higher count rate for a given resolution, e.g., 250 kHz (measured throughput count rate at 59% deadtime) at 220 eV FWHM (MnKα) for a 50 mm² detector, as shown in Figure 12, which also shows the constancy of the resolution with input count rate (proportional to beam current). Equally interesting is the capability of the SDD, when operating with a long time constant comparable to the conventional Si-EDS, to achieve a resolution of 127 eV (MnKα) for a 10 mm² detector, comparable to the best performance of the Si-EDS despite the much higher operating temperature of the SDD.

The SDD offers the prospect for EDS operation with count rates of 500 kHz or higher, as shown in Figure 13. Thus, the possibility exists for recording very short duration ‘flash’ EDS spectra with much higher integrated counts in the peaks than has ever been possible with the conventional Si-EDS. Through equation (1) this will lead to improved limits of detection by increasing P for equivalent values of the P/B. However, the major contribution of the SDD is that it enables a previously unobtainable level of speed for x-ray mapping, including mapping by spectrum imaging, where a complete x-ray spectrum is recorded at each picture element (pixel). Even with a dwell as short as 10 ms, which gives a total mapping time of 650 seconds for 256×256 pixels, each pixel spectrum will contain about 5,000 x-ray counts for an throughput count rate of 500 kHz. Figure 14 shows mapping results obtained with 10 milliseconds spent per pixel, giving a complete map in 164 seconds at a spectrum throughput count rate of 200 kHz. The backscattered electron image of the mapped field of Raney nickel alloy is shown in Figure 14(a) with maps for the major constituents Al in Figure 14 (b) and Ni in Figure 14 (c). Single pixel spectra for the three distinct phases recognizable in Figure 14(a) are shown in Figures 15(a), 15(b), and 15(c). These figures show that the spectrum quality at such very high count rates is still reasonable.

The high count rates achievable with the silicon drift detector make possible the recording of very short duration spectra, 10 seconds or less, that can still provide useful limits of detection. Figure 16 (a) shows a spectrum of copper integrated over 10 seconds at an output count
FIG. 15: Single pixel (dwell time = 10 millisecond) x-ray spectra obtained from (a) the high nickel; (b) intermediate nickel; and (c) low nickel, high aluminum phases seen in the SEM BSE image of Figure 14 (a).

FIG. 16: SDD spectrum of copper recorded at $E_0 = 20$ keV for 10 s at an output count rate of 164 kHz. (a) Plot showing the major K- and L-family peaks for copper; (b) expansion of the vertical axis showing detection of iron at $C = 0.0040$ mass fraction and establishment of a limit of detection for manganese at $C_{MMF} = 0.00092$ mass fraction.

VI. MAXIMIZING BOTH P/B AND P

From the comparison of trace measurement performance listed in Table 1, it is clear that the best possible x-ray spectrometry for trace level characterization would be EDS operation with both the peak counting rate, P, and the peak-to-background, P/B, optimized. While SDD offers pure element peak counting rates of 250 kHz or higher (and total spectrum counting rates approaching 1 MHz), the peak-to-background is limited by the considerable peak degradation imposed by the SDD resolution function as a consequence of the extremely short pulse processing times that must be employed (500 ns or less). Given that EDS operation is desired, advanced development of the microcalorimeter EDS is the most promising route to a truly advanced x-ray spectrometry system. Recent microcalorimeter EDS detector research has indicated that it will be possible to create an $n \times n$ array of microcalorimeter detectors, each of which has an area of approximately 0.25 mm$^2$ [15, 16]. A $16 \times 16$ array would therefore have a total area of 64 mm$^2$ which would provide a large solid angle of collection even without the use of polycapillary optics, thus raising the limiting value of the peak counting rate. (If desired, a single-taper polycapillary bundle could be used to more efficiently couple the array detector to the specimen x-ray source.) Since each independent detector in the array should be capa-
ble of processing at a count rate of 500 to 1,000 Hz, the overall detector array count rate would be in excess of 100 kHz. The individual detectors should be capable of a resolution of 5 eV at MnKα (wide photon energy range). Multiplexing the signals from the independent detectors will likely result in a degradation of resolution in the composite spectrum, but it is hoped the resolution will be in the range 10–15 eV. Thus, it should be possible with a microcalorimeter array to realize high values for both P and P/B in a full EDS operational mode so as to achieve trace level performance at the limits of performance: low beam energy analysis, low photon energy analysis, etc.

Another possible route for future development of analytical x-ray spectrometry is to extend the work that has already been demonstrated on augmenting the solid angle of collection of the WDS by using single-taper polycapillary optics. A single-taper polycapillary collects x-rays over a large solid angle and the low angle reflection through the straight portion of the polycapillary acts to present a nearly parallel x-ray beam to a large flat diffractor. As in the conventional WDS, to view the peak and its immediate spectral background, the diffractor must be scanned. A more efficient measurement schedule could be accomplished if the diffracted peak could be imaged, including a section of background on either side of the peak. This can be done in principle by using a curved focusing diffractor and placing an imaging detector nearer to the diffractor than the focus crossover on the Rowland circle [17]. Such an imaging WDS would be especially useful for peaks that shift and change shape due to chemical effects, such as the situation for TiN shown in Figure 6.

VII. SUMMARY

Trace sensitivity with analytical x-ray spectrometry performed in electron beam instruments depends on both the peak counting rate, P, and the peak-to-background, P/B. Recent advances in analytical electron spectrometry with the microcalorimeter EDS and the silicon drift detector have increased the number of effective tools available to the analyst. In its current form, the microcalorimeter EDS augmented with polycapillary x-ray optics can effectively attack problems involving peak interferences which arise in low beam energy microanalysis and low photon energy microanalysis that the conventional Si-EDS cannot solve. Under low beam energy microanalysis conditions, the microcalorimeter EDS, Si-EDS, and conventional WDS show very similar limits of detection because of the interplay of P and P/B. The silicon drift detector can operate at extremely high count rates, 10^6 to 10^8 Hz (full spectrum), which can achieve extraordinary improvements in x-ray mapping. Future developments to produce arrays of microcalorimeter detectors may achieve optimization of both P and P/B in full EDS operation. A polycapillary optic augmented WDS with imaging of the diffracted peak may also significantly advance analytical x-ray spectrometry.

[1] J. I. Goldstein, D.E. Newbury, D.C. Joy, C. E. Lyman, P. Echlin, L. Lifshin, L. Sawyer, and J.R. Michael, Scanning Electron Microscopy and X-ray Microanalysis, 3rd ed. (Kluwer Academic Plenum, New York, 2003)
[2] T. O. Ziebold, 'Precision and sensitivity in electron microprobe analysis', Anal. Chem., 39, 858 (1967).
[3] T. O. Ziebold, and R. E. Ogilvie, 'An empirical method for electron microanalysis', Anal. Chem., 36, 322 (1964).
[4] R. Castaing, Thesis, University of Paris (1951).
[5] D. A. Wollman, C. Jezewski, G.C. Hilton, Qi-Fan, K.D. Irwin, J.M. Martinis, 'Use of Polycapillary Optics to Increase the Effective Area of Microcalorimeter Spectrometers', Proc., Microscopy and Microanalysis Conf., Cleveland, OH: pp. 1075-1076 (August, 1997).
[6] K. D. Irwin, G. C. Hilton, J. M. Martinis, S. Deiker, N. F. Bergren, S. W. Nam, D. A. Rudman, D. A. Wollman, 'A Mo-Cu Superconducting Transition-Edge Microcalorimeter with 4.5 eV Energy Resolution at 6 keV', Nuclear Instruments and Methods in Physics Research A 444, 184 (2000).
[7] D. A. Wollman, S. W. Nam, D. E. Newbury, G. C. Hilton, K. D. Irwin, N. F. Bergren, S. Deiker, D. A. Rudman, J. M. Martinis, 'Superconducting Transition-Edge Microcalorimeter X-ray Spectrometer with 2 eV Energy Resolution at 1.5 keV', Nucl. Instrum. and Methods in Phys. Res. A 444, 145(2000).
[8] D. A. Wollman, G.C. Hilton, K.D. Irwin, K.D., L.L. Dulcie, N.F. Bergren, D.E. Newbury, K-S. Woo, B.Y.H. Liu, A.C. Diebold, J.M. Martinis, 'High-Resolution Microcalorimeter Energy-Dispersive Spectrometer for X-Ray Microanalysis and Particle Analysis', Proc., AIP Conf. on Characterization and Metrology for ULSI Technology, Gaithersburg, MD, pp. 799-804 (1998).
[9] D. E. Newbury, D.A. Wollman, K.D. Irwin, G.C. Hilton, and J.M. Martinis, 'Lowering the Limit of Detection in High Spatial Resolution Electron Beam Microanalysis with the Microcalorimeter Energy-Dispersive X-ray Spectrometer', Ultramicroscopy 78, 73 (1999).
[10] D. E. Newbury, D.A. Wollman, G. C. Hilton, K. D. Irwin, N. F. Bergren, D. A. Rudman, J. M. Martinis, 'The Approaching Revolution in X-ray Microanalysis: The Microcalorimeter Energy Dispersive Spectrometer', J. Radioanalytical and Nucl. Chem. 244, 627 (2000).
[11] M. A. Kumakhov, and F. F. Komarov, 'Multiple reflection from surface x-ray optics', Phys. Rep. 191, 289 (1990).
[12] D. A. Wollman, K. D. Irwin, G. C. Hilton, L. L. Dulcie, D. E. Newbury, J. M. Martinis, 'High-Resolution, Energy-Dispersive Microcalorimeter Spectrometer for X-Ray Microanalysis', J. Microscopy 188, 196 (1997b).
[13] L. Struder, C. Fiorini, E. Gatti, R. Hartmann, P. Holl, N. Krause, P. Lechner, A. Longoni, G. Lutz, J. Kemmer, N. Meidinger, M. Popp, H. Soltan, and C. von Zanthier, 'High Resolution Non Dispersive X-ray Spectroscopy with State of the Art Silicon Detectors', Mikrochim. Acta. Suppl. 15, 11 (1998).
[14] J. S. Ivanczyk, B. E. Patt, C. R. Tull, and S. Barkan, 'High-Throughput, Large Area Silicon X-ray Detectors for High-Resolution Spectroscopy Applications', Micros. Microanal. 7 (Suppl. 2: Proc.), 1052 (2001).
[15] C. W. Nam, D. A. Wollman, D. E. Newbury, G. C. Hilton, K. D. Irwin, D. A. Rudman, S. Deiker, S. N. F. Bergren, J. M. Martinis, 'Progress Towards Arrays of Microcalorimeter X-ray Detectors', Microscop. Microanal. 7 (Suppl. 2: Proc.), 1050 (2001).
[16] K. D. Irwin, J. A. Beall, S. Deiker, G. C. Hilton, L. King, S. W. Nam, D. E. Newbury, C. D. Reintsema, J. A. Small, L. R. Vale, 'The Development of Microcalorimeter EDS Arrays', Microsc. Microanal., 8, (Suppl. 2: Proc.), 78 (2002).

[17] C. E. Fiori, S. A. Wight, and A. D. Romig, Jr., 'A Controlled-Dispersion Parallel-Wavelength Dispersive X-ray Spectrometer for Electron Microscopy', in Microbeam Analysis (1991, San Francisco Press), pp. 327-328.