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The Beginnings of EDS in EPMA

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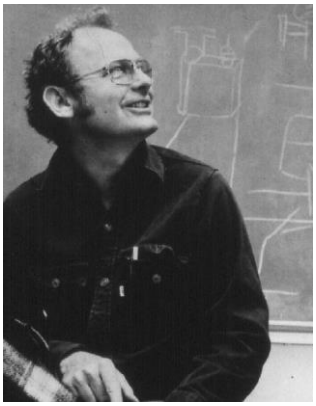
On February 2, 1968, Fitzgerald, Keil and Heinrich [1] described, in a seminal paper in *Science*, a solid-state Si(Li) energy dispersive spectrometer (EDS) for electron probe microanalysis (EPMA) with an initial resolution of 600 eV. This tool, for the first time, allowed energy dispersion of X-rays of ~ 3-30 keV and separation of characteristic X-ray peaks of elements adjacent in the Periodic Chart with atomic numbers 20 and higher in complex X-ray spectra. This spectrometer ushered in a new era not only in EPMA, but also in SEM, ATEM, XRD and XRF.

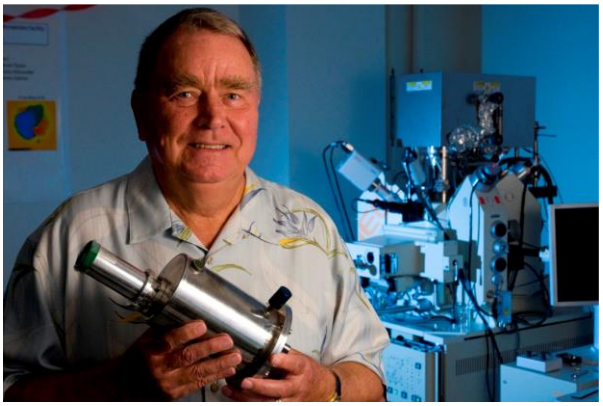
Theirs was not the first attempt in using energy dispersive spectroscopy to detect X-Rays. Earlier attempts were mostly made using the rather limited energy resolution of ~1.3-1.8 keV for CuK_α radiation of gas-filled proportional counters [2]. For example, Dolby [3] used a flow-proportional counter to obtain signals for the K-bands of boron, carbon, nitrogen, and oxygen; Duncumb [4] built an electron microscope microanalyzer (EMMA) that combined a TEM with an EPMA and featured a gas-filled proportional counter to detect X-rays; and, similarly, Birks and Batt [5] also used gas-filled proportional counters in conjunction with a 400 channel pulse height analyzer in an EPMA. However, while these results were discouraging, [5] made a visionary statement: "The possible applications of EDS to X-ray spectro-chemical analyses are unlimited." Finally, Bowman et al. [6] used what they refer to as a "high-resolution" solid-state semiconductor Si(Li) detector for the detection of X-rays in an XRF apparatus with a resolution of 1.1 keV, still insufficient to resolve the K_α X-ray lines of neighboring elements in the Periodic Chart. However, [6] noted that such devices had a great future in all fields where X-rays were to be detected and, specifically, pointed to the EPMA, noting that "the semiconductor X-ray spectrometer would be an excellent device for analysis of this radiation."

What inspired [1] to develop their solid-state Si(Li) EDS for EPMA? Fitzgerald (Fig. 1) attended a talk at Stanford University in 1965 on the use of a solid-state ionization chamber used in conjunction with a multichannel analyzer for energy dispersive analysis. That prompted him to work with F.J. Walter and R.C. Trammel of ORTEC to develop an EDS (Fig. 2) that had sufficient energy resolution of 600 eV in the X-ray range to be of practical analytical use. The spectrometer consisted of a nitrogen-cooled lithium-drifted silicon diode, a low-noise preamplifier (ORTEC 116), a linear amplifier (ORTEC 440), a 1024 multi-channel analyzer (Nuclear Data 2200), and a read-out device such as a high-speed printer. The detector was mounted inside a separate vacuum chamber, isolated from the main vacuum chamber of the ARL EPMA by a 0.125 mm Be window.

Fig. 3 shows a composite of pure element K and L X-ray spectra obtained with the original solid-state Si(Li) energy dispersive spectrometer (EDS) with a resolution of 600 eV of [1], mounted in an existing X-ray port in an ARL EPMA. By comparison to the performance of modern solid-state EDS devices, the performance of the spectrometer by [1] seems archaic, but it was an exciting and seminal step forward in the detection of x-rays in a host of analytical devices, including the EPMA.

References:
[1] Fitzgerald, R., Keil, K., and Heinrich, H., Science 159 (1968), 528-530.
[2] Arndt, U.W. et al., Proc. Phys. Soc. (1954), B 67, 357-359.
[3] Dolby, R.M. Proc. Phys. Soc. (1959), 73, 81–94.
[4] Duncumb, P. in "X-ray Optics and X-ray Microanalysis," ed. Pattee, H. et al., New York: Academic Press (1963), pp. 431–439.
[5] Birks, L.S. and Batt, A.P., Anal. Chem. 35 (1963), 778–782.
[6] Bowman, H.R., Hyde, E.K., Thompson, S.G., and Jared, R.C., Science 151 (1966), 562–565.





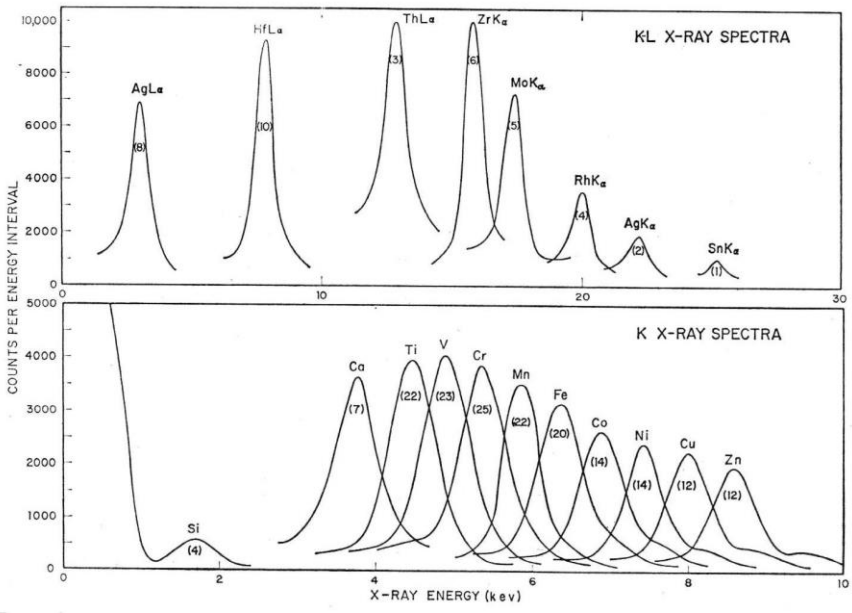


Figure 1 (upper left). This talk and paper is dedicated to my friend, Ray Fitzgerald (Fig. 1), who really was the brains behind our 1968 Science paper [1]. Image ca. 1970. **Figure 2 (upper right).** Keil in December 2008, with the original solid-state Si(Li) energy dispersive spectrometer (EDS) of [1]. **Figure 3 (bottom).** Composite of pure element K and L X-ray spectra obtained with an ARL EPMA with the solid-state Si(Li) energy dispersive spectrometer (EDS) with a resolution of 600 eV of [1]. Peak to background ratios in parentheses, integration time 100 s. The characteristic X-ray lines of elements adjacent in the Periodic Chart are clearly separated. Lower panel: accelerating potential 20 keV, target current 1 nA; upper panel 30 keV, 1 and 5 nA for L_α and K_α, respectively. Reprinted with permission from Science.

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