

The electronic age: energy-dispersive X-ray analysis and other modern techniques to the present and beyond

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This paper summarizes an oral presentation of the same title presented at the occasion of recognizing the “The 100th Anniversary of X-ray Spectroscopy” at DXC 2013. It gives an overview of the development in electronics with focus on (mainly) energy-dispersive X-ray detectors and related data processing. Naturally this has its origin in the early transistors and the first semiconductor junction detectors of the late 1940s. It was followed by refinement of semiconductor detector technology in general and particularly by the invention of Li-drifting and employment of low-noise field effect transistors until such devices matured sufficiently to be marketed by the late 1960s. Further improvement followed in resolution, speed, operability at room temperature, and development of junction arrays with imaging capabilities. An important aspect is the development of related software requiring affordable laboratory computers, programming languages, and databases of fundamental parameters. Today x-ray fluorescence analysis (and not only the energy-dispersive variant) is widely employed as an analytical tool for the traditional technical and industrial applications but notably also, at an expanding rate as well as variety, in other fields including environmental, medical, archaeological, space, arts, and many more. © 2014 International Centre for Diffraction Data. [doi:10.1017/S0885715614000219]

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I. HISTORICAL REMARKS

The 62th Denver X-ray Conference and the Plenary Session was held under the banner of “The 100th Anniversary of X-ray Spectroscopy” and this paper will focus on the second half of that period. Nevertheless a few words may be in place about the fascinating time following Röntgen’s (1895) discovery of “A New Kind of Rays”, also paying tributes to the scientific achievements by C.G. Barkla, M.T.F. von Laue, N.H. Bohr, H.G.J. Moseley, and many others who laid the foundation of today’s X-ray spectrometry.

Moseley’s (1913) recognition of the mathematical relationship between wavelengths of elements and their atomic numbers was a scientific landmark in general and for X-ray spectrometry in particular – and the publication of N. Bohr’s “Trilogy” (Bohr 1913) about “The Constitution of Atoms” in successive issues of the same volume of the *Philosophical Magazine* was a spectacular coincidence. However, Bohr and Moseley had been in contact before to discuss Bohr’s new theory and Moseley knew about the experiments and theory of von Laue (1913) and P. Ewald; this – together with the findings of the Braggs (senior and son) – allowed him to accurately (and efficiently) determine the numerical wavelength values as required for their mathematical implementation in “Moseley’s law”.

The fact that “secondary X-rays” are emitted by chemical elements and characterized by their atomic weight field effect

translators was originally (1906) described by Barkla as a function of atomic *weight*; its function of atomic *numbers* was established by Moseley’s Law (1913.) (i.e., not by chemical state) was found by Barkla by careful measurement of the absorbability (Barkla, 1905a, 1905b, 1906a, 1906b, 1906c, 1909) of those radiations; their wavelengths and in fact even the nature of X-rays had been still unknown and a matter of dispute. The relationship between energy (in fact, absorbability–no energies/wavelengths were known at that time) was originally (1906) described by Barkla as a function of atomic weight; its function of atomic numbers was established by Moseley’s Law (1913). Consequently he sorted them by atomic weight correctly for example, as Fe–Ni–Co–Cu rather than according to atomic number, Fe–Co–Ni–Cu. Barkla (1912) also showed the polarizability of “Röntgen Rays” as they were still called in English journals at that time.

II. EARLY TIMES OF THE ELECTRONIC AGE

Today’s use of the word “electronics” is – concerning hardware – generally associated with semiconductor devices where transistors are the basic element while vacuum tube technology was already well developed since the 1930s. The earliest technical studies and patents of point-type transistors are perhaps those by J. Lilienfeld in the mid/late 1920s [see IEEE Global History Network (2012)]. His work, however, remained in early prototype state without reasonable perspectives of commercial success, mainly because the required high-purity base material (Ge, Si) was not available at that time in sufficient quantity. This changed during the following

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two decades and was perhaps also stimulated by military developments during WW2 and the cold war thereafter, for example by the frequent employment of Ge-based rectifier diodes in radar technology.

Working point-type junction transistors have been successfully produced by Bell Laboratories by end of 1947 and patents were filed in 1948; manufacturing at the industrial level followed around 1950. For their invention the Nobel Prize in Physics 1956 was awarded to William Shockley, John Bardeen, and Walter Brattain.

The first radiation detector based on semiconductor junction technology was developed by McKay (1949) encouraged and under guidance by W. Shockley; this is further discussed below.

III. SEMICONDUCTOR DETECTORS AND RELATED DEVICES

Naturally electronic consumer products have been among the first to take advantage of the small size and low power consumption of transistors and it must be assumed that this was also the case with certain military devices. The first transistorized car radios were announced in 1954. However, for high-quality/high-reliability devices vacuum tubes were still preferred.

Radiation detectors for X-rays in the 1950s were mainly gas filled counters similar to those employed today. Their disadvantage was low absorption of high-energy radiation by the gas. Attempts instead to use high-purity crystals with electrical area contacts on two opposite faces were made for about a decade after 1945 (Figure 1). The working principle of these “Crystal Detectors” (van Heerden, 1945; Wooldridge *et al.*, 1947; Jentschke, 1948; Hofstadter, 1950) is similar to that of gas-filled detectors: an electrical charge is initially produced proportional to the energy of the absorbed photon or particle (however, with path-length dependent losses of charge carriers on their way to the electrodes), and without the advantage of a (well-defined) equivalent to the “gas amplification factor”. Disadvantages were the high dark current and recombination rate because of impurities and crystal imperfections. The technology went out of use in the mid-1950s.

Semiconductor detectors in today’s sense are **Junction Detectors**. The basic principle is illustrated in Figure 2. When two pieces of a high-purity crystal (e.g., Ge), one doped with p-type atoms (electron acceptors) and the other with n-type (electron donors), are brought into contact, free charge carriers from each side will move into the contact zone and compensate some of the opposite potential. A

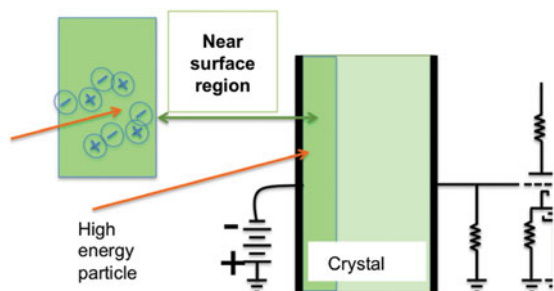


Figure 1. (Color online) Scheme of Crystal Detector as described by Dearnaley (1966).

gradual transition zone builds. If a potential in proper polarity (+ to the n-type, – to the p-type sides) is applied, the free charge carriers are withdrawn from the populated contact zone and a depleted zone (no charge carriers) remains. This is the useful detection volume for absorbed radiation. In the ideal case, the free charge carriers are only built by ionization processes in proportion to the energy of the absorbed photon and particle and led to external amplifiers by an applied potential. Of practical importance are: the size (volume) of the depleted zone; the purity (low concentration of foreign trace elements); the perfectness of the crystal lattice (acting as traps for charge carriers); and the quality (low-noise level) of the amplifier for the collected charge. Today’s Si(Li) detectors (and others) are the result of essential improvements in all mentioned aspects over a period of around 20 years, from the early junction detector by McKay to commercial Si(Li) detectors for X-ray spectrometry and other applications.

McKay’s junction detector (McKay, 1949, Bell Laboratories, under direction of Shockley) is the earliest reported junction detector and consisted of a simple point contact between a phosphor-bronze wire and an n-type Ge-crystal with an area contact at the backside (Figure 3). The configuration corresponds at first view to a metal–semiconductor junction. However, early transistors were “electrically formed” by passing a short but large current pulse in the reverse direction through the collector. This seems to have caused diffusion of Cu atoms into the contact area and formed an increased depletion area. While such procedures were studied and applied at Bell Laboratories and general reports exist (e.g., Pfann, 1950), detailed information specifically related to McKay’s detector is rare; some was reported by Dearnaley (1966, in Figure 1 of that article a “p” denotes the metal side of the junction). Experimental data of the detector have been shown by McKay for detected alpha particles that are slowed down and lose their energy along very short distances in Ge (therefore requiring only a small depletion volume); nevertheless the detected charge varied due to recombination effects. Pulse height analysis was possible and is reported by McKay by showing the relationship between collected charge (extrapolated for correction of losses) and applied detector voltage.

The term “Energy-Dispersive XRF” has its origin probably in the mid-1950s with the advent of (vacuum-tube-based)

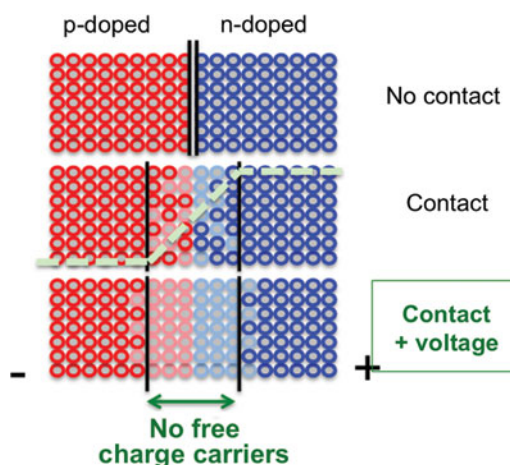


Figure 2. (Color online) Scheme of p-n junction.

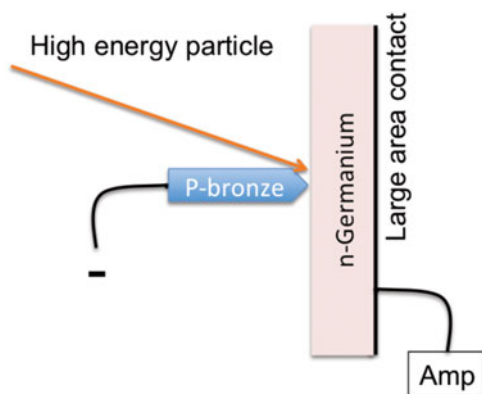


Figure 3. (Color online) Scheme of “Germanium Counter” by K.G. McKay.

multichannel analyzers in combination with gas-filled proportional counters; in 1954 an 8-channel “X-ray Quantometer” was presented at Pittcon (Kemp and Andermann, 1956; Kemp *et al.*, 1955; Lüscher, 1955). Applications by employing a 400 channel MCA and gas proportional counters were described by Birks and Batt (1963) showing Fe–Cr–Ni spectra with a resolution of around 1200 eV; an improved version (but with same energy resolution, Figure 4) for excitation by secondary targets followed 3 years later (Birks *et al.*, 1966). Even for the difficulties with the deconvolution of overlapping peaks arising from the relatively poor energy resolution the technology was seen as advantageous in terms of speed and higher sample throughput.

In the mid-1960s two crucially important prerequisites for practically useful **Si(Li) detectors** [and initially since the early 1960s, **Ge(Li)**] have been finally met: the expansion of the size of the depleted region of the p–n junction (active detector volume) by drifting Li-ions into that area and thereby compensating the effects of impurities and lattice defects; and the development of a low-noise preamplifier stage based on a new generation of cooled field-effect transistors and matching electronics (Pell, 1959; Ryon, 2001; Lechner *et al.*, 2004).

Thereby the Si(Li) detectors presented by Bowman *et al.* (1966) achieved a resolution full width at half maximum comparable to that of gas proportional counters of 1300 eV for Ni–K radiation. The first complete analytical energy dispersive system was probably the “Solid-State Energy-Dispersion

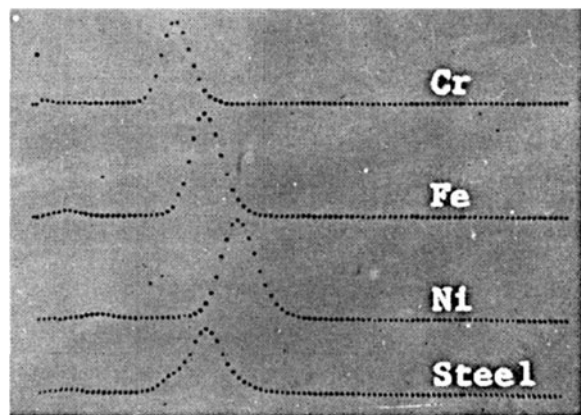


Figure 2. Energy spectra display on multichannel analyzer

Figure 4. Early EDX spectrum of a steel sample. From: Birks *et al.* (1966).

Spectrometer for Electron-Microprobe X-ray Analysis” by R. Fitzgerald, K. Keil, and K. Heinrich (Fitzgerald *et al.*, 1968). The great advantage of the solid-state detector in electron probe microanalysis over dispersion by a crystal in focusing geometry was that the displacement of the source point of fluorescent radiation by the scanning electron beam has only insignificant impact on the measured intensity.

The new technology became quickly popular and developed rapidly in the highly competitive environment of a rising number of high-tech companies. What in 1966 was called a “line-width horse power race” in view of the new 2N3823 low-noise FET and 700 eV resolution for FeK α (Donovan, 1966) was by far exceeded by reality already 2 years later: In 1968, Aitken showed a spectrum illustrating a “best system resolution that has come to the author’s attention to date” of 330 eV for FeK α with a 25 mm² Si(Li) detector; 2 years later Frankel and Aitken reported 170 eV available for the best commercial instruments and 150 eV was in development (Aitken, 1968; Frankel and Aitken, 1970).

In view of the many competent and detailed papers and reports of today’s modern detector technology at the Denver X-Ray Conference (and the presence of manufacturers at the trade show), only a few general comments are given about recent developments. The most significant innovation was the introduction of **Silicon Drift Detectors** by E. Gatti and P. Rehak (Gatti and Rehak, 1984). They consist of a thin Si disc with a generally large sensitive surface area (several mm² up to exceeding 100 mm²) carrying an arrangement of concentric electrodes at the surface and full area back contact. The small size of the center electrode (charge collector and input to the FET amplifier stage) is a key property for low electronic noise even at extremely high count rates (because noise is proportional to capacitance and therefore area). Pahlke (2013) reports the latest progress by models featuring 150 eV resolution at 1 Mio counts s⁻¹ and 150 mm² detector size. A general disadvantage of designs with thin Si discs is that the absorbability for photons with higher energies depends on the direction of incidence. Special models allow application at room temperature (Lechner *et al.*, 2004).

A special design of solid-state detectors are pnCCD detectors consisting of a large array of p–n junction cells (several thousand); during a single exposure cycle the charge created by the absorbed photons is stored in each cell and thereafter shifted through read out electronics to further stages of processing. A typical cycle rate is 200 Hz. If the collected charge comes from a single photon the energy of that photon can be determined from the average ionization energy of the junction: the device is then an array of energy-dispersive detectors and well suited for imaging applications (Send *et al.*, 2013).

Handheld XRF devices have their origin in portable instruments for the analysis of Radon (historical name: Niton, from which a company’s name was derived later) developed around 1990 by L. Grodzins (2012). Extension of the field of analyses (lead in paints of houses, tools, and toys) and more general applications led to cooperation with commercial manufacturers (Pantazis, 2010) and the design of miniaturized instruments known as Handheld XRF. The short air distance between sample and detector entrance window allows also analysis of light elements with reasonable detection limits. The built-in software is often based on libraries of materials (e.g., metals) and matching of spectra.

IV. IMPACT BY COMPUTERS (AND X-RAY ANALYTICAL SOFTWARE)

The first research computer (perhaps more an object of research rather than a tool for research) was probably installed 1953 at the University of Manchester, featuring 92 point contact transistors with an average life time of less than 1 h, and around 500 diodes. No high level programming language was available at that time. Fortran, developed by J. Backus, IBM, became commercially available in 1957 together with the (probably) first commercial “all solid state” computer (IBM 608) followed by DEC PDP-1 (1959), IBM 360 and CDC 6600 (1964), DEC PDP8 (1965), and the IBM PC (1981). The phenomenal success of the IBM PC was not so much because of its technical superiority over others at that time but the fact that the market leader laid open the technical specifications, which guaranteed a high level of stability; this encouraged many smaller enterprises to software and hardware developments as well as implementation of PC’s into industrial instrumentation (such as X-ray analytical equipment).

The historical mathematical attempts to describe the number of X-ray photons from a sample have therefore been quite academic studies (Glocker and Schreiber, 1928; Gillam and Heal, 1953; Beattie and Brisse, 1954; Sherman, 1955) without practical numerical calculations. At the Denver X-ray Conference 1957 J. Sherman presented his equations by proposing also a “method of measured dilution” that “(a) Integration with respect to λ (the polychromatic effect) is avoided by converting the spectrometer into monochromator. (b) The complication of the quadratic and higher terms (...) is avoided by so selecting the wavelength of the monochromator that the element Z is effectively the element of the highest atomic number to be excited” (Sherman, 1957). The first reports of computations obtained by numerical integration of the excitation formula for direct and indirect excitation (including tertiary) was given by Shiraiwa and Fujino (1966), and the first published software for solving fundamental parameter equations in non-trivial cases was probably NRLXRF, developed at the Naval Research Laboratories (NRL) by Criss *et al.* (1978). At that time the required computer readable collections of fundamental parameters including tabulated tube spectra (Gilfrich and Birks, 1968) were available: wavelengths by Bearden and Burr (1967), absorption coefficients by McMaster *et al.* (1969), Auger/Coster Kronig

transition data by Bambynek *et al.* (1972), and various versions of computed tube spectra.

V. CURRENT STATE AND OUTLOOK

Figure 5 shows the graphical representations of statistical data obtained from the SCOPUS database (Elsevier B. V.) by searching for keywords in article titles and abstracts related to energy-dispersive X-ray spectrometry (EDX). The impressive increase of publications during the decade 1970–1980 (Figure 5, left graph) was followed by some stagnation in the 1980s but further increased until present times (Figure 5, center graph). The diversity of applications is shown in Figure 5 (right graph, representing the focus of journals, not individual content of articles), with almost two-thirds related to physics, chemistry, engineering, and materials sciences. The increase of EDX-related publications is, however, at least partially biased by a generally growing number of publications. The data in Figure 6 show the development of “technical” vs. “non-technical” papers therefore relative to the total number of papers in each year. It is interesting that the non-technical fraction greatly increased in the first decade (breaking even with the technical) but was continuously reduced until year 2000; it appears to be stable since then. If a relationship exists between the stagnation in the 1980s and the trend reversal at the same time is unknown. It is, however, frequently observed that authors of papers cooperate with others having a quite different background (often technical vs. non-technical) and then choose the more technical journals (Figure 7).

The obvious trend toward multidisciplinary application of XRF in general and EDX in particular goes hand-in-hand with the development of new instrumental features and methods such as trace analysis, microanalysis, imaging, confocal depth profiling, and various industrial specialties; among the interesting mathematical/methodical developments are reference-free methods (including the “pre-calibration” and “truly reference free” variants), Monte Carlo methods, and the combination of XRF with statistical methods and chemometrics (occasionally conflicting with the advantageous principles of fundamental parameter methods). While the high long-term stability of modern instruments in combination with pre-calibration using dedicated type standards (matching the intended application by the user) gives the comfortable

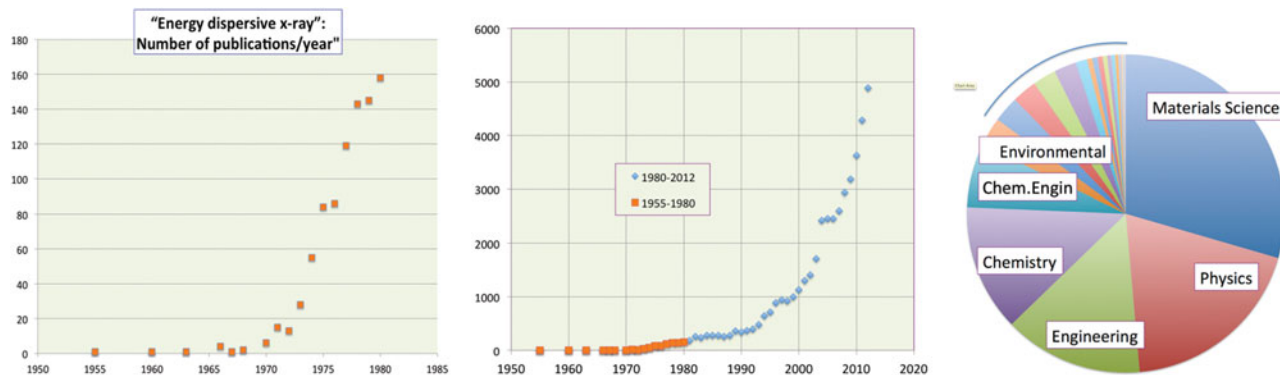


Figure 5. (Color online) Number of publications/year with keywords “Energy dispersive” and “X-ray” in title or abstract. Right: Frequency of publications in field-specific journals (main areas). Statistics using Scopus/Elsevier.

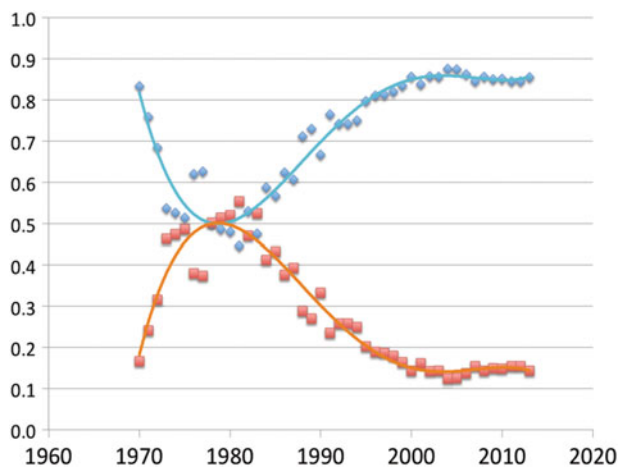


Figure 6. (Color online) Fraction of publications per year in technically oriented (blue) and non-technical journals (red) (keywords and reference as in Figure 5).

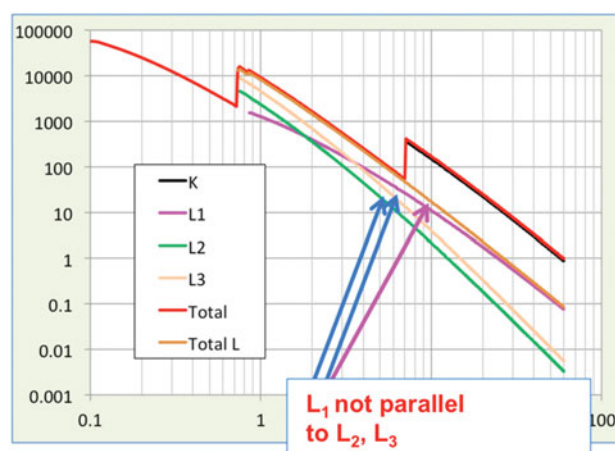


Figure 7. (Color online) L -range of μ/ρ (Cu). Non-parallel lines indicate energy-dependent subshell ratios (Cullen 1997).

impression of reference-free analysis, the scientific “truly reference free” methods require calibration of all components of a setup vs. metrological standards (i.e., effectively against the international unit system, not against application oriented reference samples). Only a few laboratories have these abilities, but are the final reference for obtaining (best possible) unbiased fundamental parameter values.

In all fundamental parameter methods, the quality of the parameters themselves is a key factor. While most K -line related parameters are quite well known except for low atomic numbers this is by far not always the case for L - and M -lines. Besides individual numerical values is sometimes also the method of definition and determination that requires critical investigation as shown below for the subshell photo-absorption coefficients.

The L -subshell ratios $\tau_{L1}:\tau_{L2}:\tau_{L3}$ of photo-absorption are conventionally assumed to be constants (determined as the ratio of the high- and low-energy values in the vicinity of the subshell edges); however, theoretical computations show clearly energy dependence (Figure 7). Recently experimental data became available that confirm the theoretical values; (Hönicke *et al.*, 2012; Doi *et al.*, 2013). In context of the often complex rearrangements within the electronic structure

after an initial ionization in an inner shell such studies and the application of the findings are relevant in practical applications.

Trying to extrapolate the developments into the future reveals a pattern of challenges, not all with entirely optimistic expectations. On one hand, the assumption that instruments will become more powerful, the methods more advanced, and applications more versatile is reasonable – but at the same time the average future user tends to be less frequently a specialist in analytical sciences and more dependent on automated black-boxed procedures designed by programmers and instrument developers who are not necessarily specialists in the intended field of application. The situation becomes even more complex by the simultaneous application of different analytical techniques. As already mentioned the frequently observed cooperation of experts with different background (such as technical/non-technical) will be increasingly helpful and will need its mirror on the side of developers of instruments and methods.

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