

A Timeline of Atomic Spectroscopy

This timeline provides a short history of the experimental and theoretical development of atomic spectroscopy for elemental spectrochemical analysis. Included are the instrumental techniques of optical emission (flame, arc/spark, inductively coupled plasma, glow-discharge, and laser-ablation), atomic absorption, and X-ray fluorescence spectroscopy. An attempt has been made to bring together the history of these apparently disparate spectrometric techniques: It's all about electron transitions, whether outer-shell (atomic absorption and optical emission) or inner-shell (X-ray fluorescence).

Volker Thomsen

While perhaps the most extensive such timeline to date, it is surely not complete. Sources for further information have been provided.

1666: Isaac Newton (1642–1727) (Figure 1) shows that the white light from the sun could be dispersed into a continuous series of colors. He coined the word “spectrum.” His apparatus, an aperture to define a light beam, a lens, a prism, and a screen, was the first spectroscope. He suggested that light was composed of minute corpuscles (particles) moving at high speed.

1678: Dutch mathematician and physicist **Christian Huygens** (1629–1695) proposes the wave theory of light.

1729: French mathematician and scientist **Pierre Bouguer** (1698–1758) notes that the amount of light passing through a liquid sample decreases with increasing sample thickness.

1752: **Thomas Melville** (1726–1753) of the University of Glasgow, Scotland, observes a bright yellow light emitted from a flame produced by burning a mixture of alcohol and sea salt. When the salt is removed, the yellow color disappears.

1760: German mathematician and scientist **Johann Heinrich Lambert** (1728–1777) publishes his “Law of Absorption.”

1776: Italian physicist **Alessandro Volta** (1745–1827) (Figure 2) uses his “perpetual electrophorus” device for producing static electric charges to spark various materials. He notes different colors with different materials. Eventually he is able to identify certain gases by the colors emitted when sparked.

1786: American astronomer and instrument maker **David Rittenhouse** (1732–1796) produces the first primitive diffraction grating with parallel hairs laid across two screws.

1802: English scientist **William Hyde Wollaston** (1766–1828) is the first to observe dark lines in the spectrum of the sun.

1814: The German optician **Joseph von Fraunhofer** (1787–1826) invents the transmission diffraction grating and makes a detailed study of the dark lines in the solar spectrum.

1826: Scotsman **William Henry Fox Talbot** (1800–1877) observes that different salts produce colors when placed in a flame.

1851: **M.A. Masson** produces the first spark-emission spectroscope.

1852: German scientist **August Beer** (1825–1863) publishes a paper showing that the amount of light absorbed was proportional to the amount of solute in aqueous solutions.

1859: The German physicist **Gustav Robert Kirchoff** (1824–1887) and chemist **Robert Wilhelm Eberhard von Bunsen** (1811–1899) (Figure 3) discover that spectral lines are unique to each element.

1860–1861: **Kirchoff** and **Bunsen** discover the elements cesium and rubidium using their new technique of spectral analysis.

1861: The element thallium is discovered by Sir **William**



Figure 1: Sir Isaac Newton.



Figure 2: Alessandro Volta.



Figure 3: Gustav Kirchoff (left) and Robert Bunsen.

Crookes (1832–1919) (Figure 4) using the method of spectral analysis.

1863: The element indium is discovered by German professor of physics Ferdinand Reich (1799–1882) and German metallurgical chemist Theodor Richter (1824–1898), also by the method of spectral analysis.

1868: The element helium is discovered through its characteristic spectral lines in the spectrum of the sun. The discovery was made independently by French astronomer Pierre Janssen (1824–1907) and English astronomer Joseph Norman Lockyer (1836–1920). It was named for the Greek term for sun, Helios. (Note: Lockyer is knighted shortly after this discovery. Also, he founded the journal *Nature* in 1869. See also 1873–1874.)

1868: Swedish physicist Anders Jonas Ångström (1814–1874) (Figure 5) publishes a detailed study of the wavelengths of solar spectral lines, expressed in units of 10^{-10} meters. This unit is now known as the angstrom (Å). He is considered one of the fathers of modern spectroscopy.

1869: Ångström produces the first reflection grating.

1873–1874: Sir Joseph Norman Lockyer (see 1868) (Figure 6) observes that

the (complex) spatial structure of the atomic emission within the high-voltage spark-induced plasma is a function of the concentration of the emitting element. Furthermore, he shows that improved quantitation is possible by comparing the analyte emission with that of another element in the sample

(an early example of “internal standardization”).

1877: L.P. Gouy introduces the pneumatic nebulizer for transferring liquid samples into a flame.

1882: American physicist Henry A.

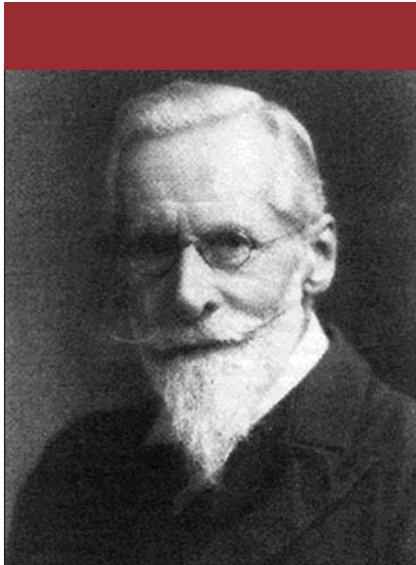


Figure 4: Sir William Crookes.

Rowland (1848–1901) (Figure 7) produces greatly improved (curved) diffraction grating using his new grating “ruling machine” at Johns Hopkins University (Baltimore, Maryland). Gratings produced in his laboratory became the standard throughout the world.

1882: W.N. Hartley of Dublin conducts a systematic study of change in spectral line intensity with concentration. Later, he produces the first semi-quantitative spectrographic analysis (determination of beryllium in cerium compounds).

1885: Johann J. Balmer (1825–1898) (Figure 8), a Swiss high school teacher and adjunct university mathematics pro-



Figure 5: Anders Ångström.

fessor, shows that the wavelengths of the visible spectral lines of hydrogen could be represented by a simple mathematical formula. These lines are now known as the Balmer series of hydrogen.

1888: Swedish physicist Johannes Rydberg (1854–1919) generalizes Balmer’s formula to: $1/\lambda = R_H [(1/n^2) - (1/m^2)]$, where n and m are integers and $m > n$. (For the Balmer series, $n = 2$ and $m = 3$.) The constant, R_H , is now called Rydberg’s constant.

1895: German physicist Wilhelm Conrad Röntgen (1845–1923) (Figure 9) discovers X-rays and experiments extensively to discern their properties. He is awarded the first Nobel Prize in

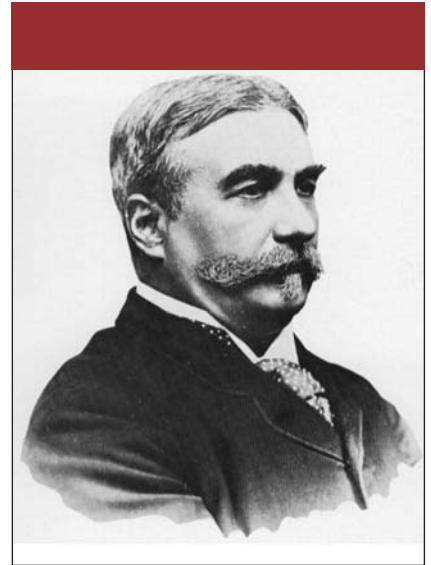


Figure 6: Sir Joseph Lockyer.

physics for his discovery (1901).

1896: Pieter Zeeman (1865–1943), Dutch physicist, observes splitting of spectral lines by a magnetic field. He receives the 1902 Nobel Prize in physics for his work.

1896: The French physicist Antoine Henri Becquerel (1852–1908) discovers radioactivity. He shares the 1903 Nobel Prize in physics with Pierre and Marie Curie for their work on radioactivity.

1897: The electron is discovered by British physicist Joseph Thomson (1856–1940). He is awarded the 1906 Nobel Prize in physics for this discovery and his investigations on the conduc-



Figure 7: Henry A. Rowland.

tion of electricity in gases.

1900: German physicist **Max Planck** (1858–1947) introduces the quantum concept. He is awarded the 1918 Nobel Prize in physics.



Figure 8: J.J. Balmer.

1900: **Frank Twyman** (Adam Hilger Ltd., London, UK) produces the first commercially available quartz prism spectrograph.

1900: First work on time-resolved optical emission spectroscopy is reported

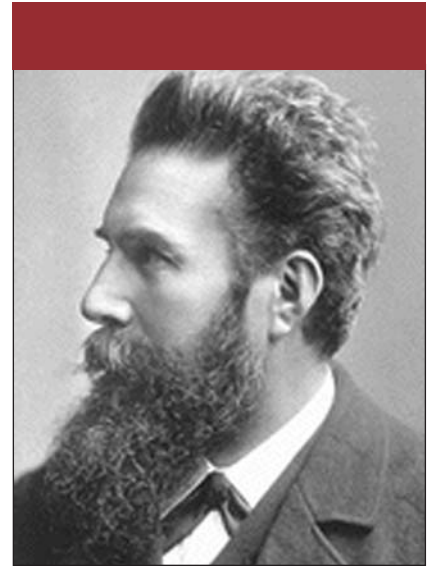


Figure 9: Wilhelm C. Röntgen.

by **A. Schuster** and **G. Hemsalech**. Their technique involves moving the photographic film in the focal plane of the spectrograph.

1906: American physicist **Theodore Lyman** (1874–1954) discovers ultraviolet

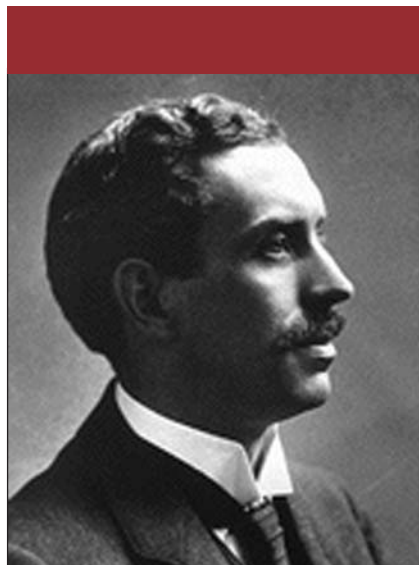


Figure 10: Charles Barkla.

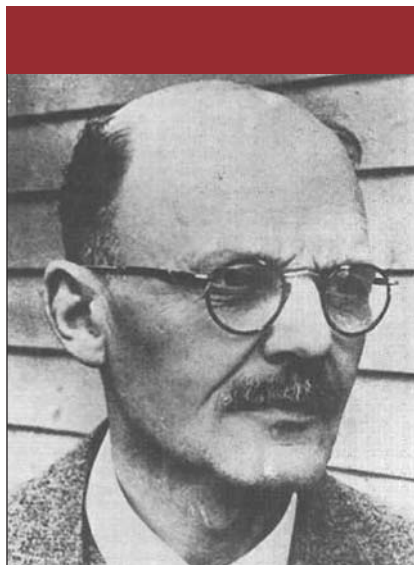


Figure 11: Hans Geiger.



Figure 12: Niels Bohr.

let series of hydrogen lines. They fit the Rydberg formula with $n = 1$ and $m = 2$.

1905: Albert Einstein (1879–1955) explains the photoelectric effect, for which he was awarded the Nobel Prize in 1921. His theory explains that when a photon strikes the surface of some

materials, an electron is ejected. This same year, he publishes his “Special Theory of Relativity.”

1906: British physicist Charles Barkla (1877–1944) (Figure 10) discovers that each element has a characteristic X-ray and that the degree of penetration of

these X-rays is related to the atomic weight of the element. He is awarded the Nobel Prize in 1917.

1908: Swiss theoretical physicist Walter Ritz (1878–1909) proposes his Combination Principle (also known as the Frequency Sum Rule), which notes that the spectral lines of any element include frequencies that are either the sum or difference of two other spectral lines.

1908: German physicist Hans Geiger (1882–1945) (Figure 11) develops a device for detecting radioactivity (“Geiger counter”).

1912: German physicist Max von Laue (1879–1960) suggests using crystals to diffract X-rays. He is awarded the Nobel Prize in 1914.

1912: Two German physicists, Walter Friedrich and Paul Knipping, acting on the suggestion of von Laue, diffract X-rays in zinc-blende (sphalerite).

1913: Danish physicist Niels Bohr (1885–1962) (Figure 12) presents his theory of the atom, which explains the Rydberg formula of simple spectra. He receives the 1922 Nobel Prize in physics.

1913: The British father and son team of William Henry Bragg (1862–1942) and William Lawrence Bragg (1890–1971) work out the condition for



Figure 13: Henry Moseley.

X-ray diffraction (Bragg's law). They are awarded the 1915 Nobel Prize in physics.

1913: British physicist **Henry Moseley** (1887–1915) (Figure 13) establishes that atomic number is more fundamental than atomic weight by observations of the X-ray spectra of the elements.

Moseley generally is considered the founder of X-ray spectrometry.

1913: German physicist **Johannes Stark** (1874–1957) discovers the splitting of spectral lines in an electric field, now called the Stark effect. He was awarded the 1919 Nobel Prize in physics.

1913: American physicist **William David Coolidge** (1873–1975) introduces the hot filament, high-vacuum X-ray tube.

1914: **W.H. Bragg** (1890–1971) and **S.E. Pierce** discover that the decrease in X-ray absorption is proportional to the cube of the energy (Bragg–Pierce law).

1915: **W. Duane** and **F.L. Hunt** discover the short-wavelength limit in X-ray generation.

1916: German physicist **Walter Kossel** (1888–1956) is the first to realize that X-ray spectra are due to the removal of inner shell electrons from the atom.

1919: German physicists **Arnold**

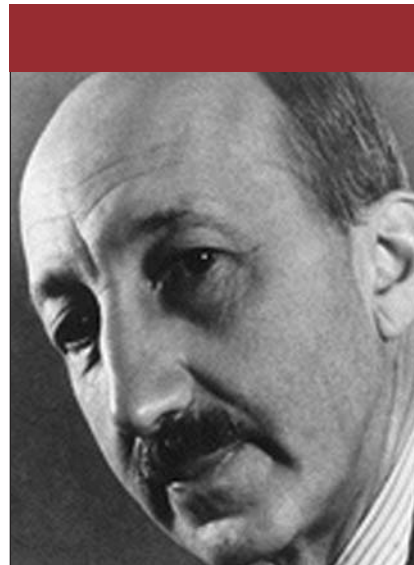


Figure 14: George von Hevesy.

Sommerfeld (1868–1951) and **Walter Kossel** note that the spectral lines of any atom are qualitatively similar in character (wavelength) to those of the ion of an element one atomic number higher (“Verschiebungsgesetz”).

1920: **Adam Hilger Ltd.** produces the



Figure 15: Louis de Broglie.

first evacuated spectrograph for the determination of sulfur (180.7 nm) and phosphorus (178.2 nm) in steel.

1921: C. Ramsauer and F. Wolf investigate the time-resolved spectroscopy of the alkali and alkaline earth metals using a slotted rotating disk in the light path to the spectroscope.

1922: American physicist **Frederick Sumner Brackett** (1896–1972) discovers the infrared series of hydrogen lines that now bear his name.

1922: American spectroscopist



Figure 17: Werner Heisenberg.

William Frederick Meggers (1888–1966) and coworkers (**Kiess and Stimson**) publish their paper, “Quantitative Spectroscopic Analysis of Materials,” attempting to bridge the gap from semiquantitative to quantitative analysis. Meggers is often considered the “dean of American spectroscopists.”

1922: American physicist **Arthur Holly Compton** (1892–1962) studies X-ray photon scattering by electrons (Compton effect). He receives the 1927 Nobel Prize in physics for his work.

1922: **A. Hadding** first applies X-ray spectra to chemical analysis (of minerals).

1923: Hungarian-born chemist **George von Hevesy** (1885–1966) (Figure 14) and coworker Dutch physicist **Dirk Coster** (1889–1950) discover hafnium, the first element identified by its X-ray spectrum.

1923: **George von Hevesy** proposes quantitative analysis by secondary excitation of X-ray spectra. (Von Hevesy received the 1943 Nobel Prize in chemistry for his work on using radioisotopes as tracers to study chemical processes.)

1923: French physicist **Louis de Broglie** (1892–1987) (Figure 15) proposes wave-like nature of electron. He received the Nobel Prize in physics in 1929.

1923: Austrian physicist **Lise Meitner** (1878–1968) (Figure 16) discovers the radiationless transition now known as the Auger effect (see 1925).

1923: **R. Glocker** and **W. Frohnmeyer** apply X-ray absorption edge spectrometry.

1924: German physicist **Wolfgang Pauli** (1900–1958) formulates the exclusion principle to explain the Zeeman effect. He is awarded the Nobel Prize in 1945.

1924: Swedish physicist **Karl Manne Georg Siegbahn** (1886–1978) receives the Nobel Prize in this year for his measurements of the X-ray wavelengths of the elements.



Figure 16: Lise Meitner.

1924: **W. Soller** constructs an X-ray spectrometer using parallel foil collimators.

1925: German physicist **Friedrich Hund** (1896–1997) presents empirical rules for atomic spectroscopy (Hund’s rules).

1925: German physicist **Werner Heisenberg** (1901–1976) (Figure 17) establishes matrix mechanics. He receives the Nobel Prize in 1932.

1925: French physicist **Pierre Victor**



Figure 18: Erwin Schrödinger.



Figure 19: Walther Gerlach.

Auger (1899–1993) rediscovers the Auger effect (autoionization).

1926: German physicist **Erwin Schrödinger** (1887–1961) (Figure 18) develops wave mechanics and presents the equation that now bears his name. He is awarded the Nobel Prize in physics in 1933.

1926: **Schrödinger** shows that his wave mechanics and Heisenberg's matrix mechanics are mathematically equivalent.

1927: **Heisenberg** develops his uncer-



Figure 20: Alan Walsh.

tainty principle, which explains the natural linewidth of spectral lines.

1928: **Hans Geiger** (see 1908) and **W. Müller** improve the gas-filled radiation detection tube.

1929: **H. Lundegårdh** significantly advances flame emission spectroscopy by coupling an air–acetylene flame with a pneumatic nebulizer for sample introduction and a spray chamber for sample conditioning.

1930: The German physicists **Walther Gerlach** (1889–1979) (Figure 19) and **Eugen Schweitzer** develop the concept of internal standard and the method of intensity ratios. The concepts of “homologous” and “fixation” spectral line pairs are introduced.

1930: Dutch scientists **Kipp** and **Zonen** produce the first recording microphotometer for the measurement of spectral line intensities on photo-

graphic plates.

1936: **Thanheiser** and **Heyes** use phototubes to measure intensities.

1937: First commercial grating spectrograph produced by **Maurice Hasler** of Applied Research Laboratories (ARL).

1938: First commercial X-ray spectrometer introduced by **Hilger and Watts, Ltd.**

1939: Publication of M.I.T. wavelength tables by **George R. Harrison**.

1940: Photomultiplier tube is developed.

1944: **R.W. Wood** produces blazed gratings.

1947–1948: First commercially available “direct-readers,” optical emission spectrometers using photomultiplier tubes as detectors (ARL and Baird Atomic). These instruments reduce the multielement analysis of metals from hours to minutes (and later, to seconds).

1947: Synchrotron radiation first observed at General Electric.

1947: American physicist **Willis E. Lamb** (b. 1913) discovers the Lamb shift, the small energy difference between the 2s and 2p electron shells in hydrogen. He is awarded the Nobel Prize in physics in 1955.

1948: **H. Friedman** and **L.S. Birks** build prototype of first commercial wavelength dispersive X-ray secondary emission spectrometer with sealed-off X-ray tube.

1948: The transistor is invented by American physicists **William Shockley**, **John Bardeen**, and **Walter Brattain**. All share the Nobel Prize in 1956.

1949: **Paul T. Gilbert** creates a flame emission attachment for the popular Beckman DU spectrophotometer.

1949: **R. Castaing** and **A. Guinier** build the first electron-probe microan-

alyzer.

1949: **Kenneth McKay** investigates germanium point contact diodes as radiation detector for alpha particles.

1955: Australian spectroscopist **Alan Walsh** (1916–1998) (Figure 20) develops atomic absorption spectroscopy (AAS), which has been described as “the most significant advance in chemical analysis” in the 20th century.

1955: **J. Sherman** develops “fundamental parameters” method providing theoretical relationship between analyte concentration and X-ray intensities.

1956: First commercially available vacuum optical emission spectrometer (ARL Quantovac).

1956: First X-ray spectroscopy experiments with synchrotron radiation by **Tomboulion** and **Hartman** at Cornell electron synchrotron.

1958: American physicists **Arthur L. Schawlow** (1921–1999) and **Charles H. Townes** (b. 1915) publish “Infrared and Optical Masers,” describing the basic principles of the laser. Schawlow receives the Nobel Prize in 1981 with **Nicolaas Bloembergen** (b. 1920) and **K.M. Siegbahn** (see 1981). Townes shares the 1964 Nobel Prize in physics for fundamental work in quantum electronics leading to the maser-laser principle.

1959: **E.M. Pell** first applies lithium doping of semiconductor detectors to compensate for impurities in silicon and germanium.

1960: First operational (ruby) laser produced by American physicist **Theodore Maiman** (1927–) working at Hughes Research Laboratories.

1961: Russian scientist **B.V. L'vov** develops graphite furnace for atomic absorption spectroscopy.

1962: First portable X-ray fluorescence (XRF) analyzers (Columbia Scientific Industries and Texas Nuclear).

1962: Lithium-drifted germanium

detector first used for gamma-ray spectroscopy.

1963: First computer-controlled optical emission and X-ray spectrometers.

1963: British chemist **Stanley Greenfield** and coworkers invent the annular inductively coupled plasma (ICP). (This instrument has had a huge impact on the development of instrumental analysis.)

1964: **A.A. Sterk** first applies ion (proton) excitation of X-ray spectra to actual chemical analysis.

1966: French physicist **Alfred Kastler** (1902–1984) receives Nobel Prize in physics this year for optical methods of studying atomic energy levels.

1966: **Harry Bowman** and colleagues at U.C. Berkeley publish the first energy-dispersive X-ray fluorescence (EDXRF) results.

1966: **Max Amos** and **John Willis** introduce the nitrous oxide–acetylene flame.

1966: “The Breakdown of Noble and Atmospheric Gases by Ruby and Neodymium Laser Pulses” published by **R.G. Tomlinson**, **E.K. Damon**, and **H.T. Buscher**, possibly the first paper on laser-induced breakdown spectroscopy (LIBS).

1967: **W. Grimm** invents the glow-discharge source.

1968: **John W. Criss** and **LaVerne Stanley Birks** produce first computer program for fundamental parameters calculations in X-ray fluorescence (NRLXRF).

1969: American spectrochemist **Velmer A. Fassel** and Dutch chemist **P.W.J.M. Boumans** develop low-power ICP.

1970: **Greene** and **Whelan** report first depth profiling with the Grimm glow-discharge source.

1971: Total reflection of X-rays, first demonstrated by **A.H. Compton** in 1923,

is applied to EDXRF by **Yoneda** and colleagues.

1972: First commercially available portable arc/spark optical emission spectroscopy (OES) spectrometer is introduced (Hilger, Ltd.). It uses fiber optics to provide light transfer from “probe” to optic.

1973: Maturity of EDXRF as an analytical technique demonstrated by **R.D. Giaugue** and colleagues at U.C., Berkeley with the determination of elements at *trace* levels.

1974: First commercially available ICP spectrometers introduced.

1975: **J. Robin** and **C. Trassy** first use end-on observation in ICP.

1976: The concept of capillary optics for focusing X-rays originated at the U.S. Naval Research Laboratory (**D. Mosher** and **S. Stephanakis**).

1976: **J.P. Walters** and colleagues at the University of Wisconsin produce a controllable waveform high-voltage spark excitation source.

1977: **Jaklevic** first applies microbeam technique to EDXRF (analysis of human hair).

1981: Swedish physicist **Kai M. Siegbahn** (b. 1918) receives the Nobel Prize in physics for high-resolution electron spectroscopy.

1984: Introduction of the silicon drift detector for position sensing applications.

1988: First commercially available optical emission spectrometer with electronic time-resolved spectroscopy capability (Spectro A.I.).

1988: **M. Chevrier** and **Richard Passetemps** invent the radio-frequency glow-discharge source.

1990: Practical capillary optics real-

ized in Russia by **M.A. Kumakhov** and **F.F. Komarov**.

1990: Introduction of nitrogen-flushed UV optical system to eliminate vacuum pump oil vapor back-diffusion problems (Spectro A.I.).

1992: First commercially available spectrometer with charge injection device (CID) solid-state detector (the IRIS from Thermo Jarrell Ash).

1993: First commercially available one-piece, handheld XRF analyzer (NITON).

1993: Nitrogen-filled UV optical system with recirculating system is patented (Spectro A.I.)

1997: Digitally controlled waveform source for arc/spark spectrometry (ARL and Spectro A.I.).

2000: Miniature, low-power X-ray tube developed.

Acknowledgment

Some of the above entries related to X-ray spectrometry were compiled while the author was Senior Applications Scientist at NITON LLC, Billerica, MA, now part of the Thermo Electron Corp. This earlier timeline can be accessed at www.niton.com.

Sources for the History of Atomic Spectroscopy

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