

Fraunhofer Effect Atomic Absorption Spectrometry

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The dark lines in the solar spectrum were discovered by Wollaston and cataloged by Fraunhofer in the early days of the 19th century. Some years later, Kirchhoff explained the appearance of the dark lines: the sun was acting as a continuum light source and metals in the ground state in its atmosphere were absorbing characteristic narrow regions of the spectrum. This discovery eventually spawned atomic absorption spectrometry, which became a routine technique for chemical analysis in the mid-20th century. Laboratory-based atomic absorption spectrometers differ from the original observation of the Fraunhofer lines because they have always employed a separate light source and atomizer. This article describes a novel atomic absorption device that employs a single source, the tungsten coil, as both the generator of continuum radiation and the atomizer of the analytes. A 25- μ L aliquot of sample is placed on the tungsten filament removed from a commercially available 150-W light bulb. The solution is dried and ashed by applying low currents to the coil in a three-step procedure. Full power is then applied to the coil for a brief period. During this time, the coil produces white light, which may be absorbed by any metals present in the atomization cloud produced by the sample. A high-resolution spectrometer with a charge-coupled device detector monitors the emission spectrum of the coil, which includes the dark lines from the metals. Detection limits are reported for seven elements: 5 pg of Ca (422.7 nm); 2 ng of Co (352.7 nm); 200 pg of Cr (425.4 nm); 7 pg of Sr (460.7 nm); 100 pg of Yb (398.8 nm); 500 pg of Mn (403.1 nm); and 500 pg of K (404.4 nm). Simultaneous multielement analyses are possible within a 4-nm spectral window. The relative standard deviations for the seven metals are below 8% for all metals except for Ca (10.7%), which was present in the blank at measurable levels. Analysis of a standard reference material (drinking water) resulted in a mean percent recovery of 91%. This report attempts to give an historical perspective on the development of a novel atomic spectrometer based on the Fraunhofer effect.

Atomic absorption spectrometry, or at least the serendipitous observation of the phenomenon, is now more than 200 years old.

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While the original source (our own sun) played the dual roles of generator of a continuum radiation and atomizer of the metal absorbers, all subsequent laboratory-based atomic absorption systems have employed separate and distinct light sources and atomizers. This paper will give a brief historical perspective as an introduction to a novel atomic absorption spectrometer that again combines source and atomizer in one unit: the tungsten coil.

Fraunhofer Lines. Even though Leonardo da Vinci, Rene Descartes, Isaac Newton, and many others had observed the spectrum of colors produced by passing sunlight through a prism, the dark lines in the solar spectrum were not discovered until 1802 by the retired physician William Hyde Wollaston.¹ Wollaston was the first to employ a narrow slit rather than a circular aperture, or pinhole, prior to the prism. With the slit positioned parallel to the refracting edge of the prism, he was able to observe a number of black lines in the spectrum. He surmised that these lines were the boundaries between the primary colors of the rainbow. He labeled several of the strong lines (A–E) and even some of the weaker ones with lower case letters. But Wollaston's interest was in the colors themselves, and not the dark lines, so he let the matter drop.

In 1814, Joseph von Fraunhofer, an optician, rediscovered the dark lines during his quest for monochromatic sources of radiation.² At the time he was seeking a means for measuring the dispersive power of various kinds of glass. As Wollaston had done 12 years earlier, Fraunhofer allowed sunlight to pass into a dark room through a narrow slit. Upon entering the slit, the light was collimated by a convex lens so that the rays struck the prism in a parallel fashion. The light was then refracted by the prism, and the spectrum was viewed with a telescope. Fraunhofer had hoped to reproduce the sharply defined bright yellow (or orange) streak that he had observed in flames and lamplight. To his surprise, the solar spectrum contained a very dark line at the position where he expected the bright yellow streak:

"I wished to see if in the color-image from sunlight there was a bright band similar to that observed in the color image of lamplight. But instead of this I saw with the telescope an almost countless number of strong and weak vertical lines, which are, however, darker than the rest of the color image; some appeared to be almost perfectly black."^{2,3}

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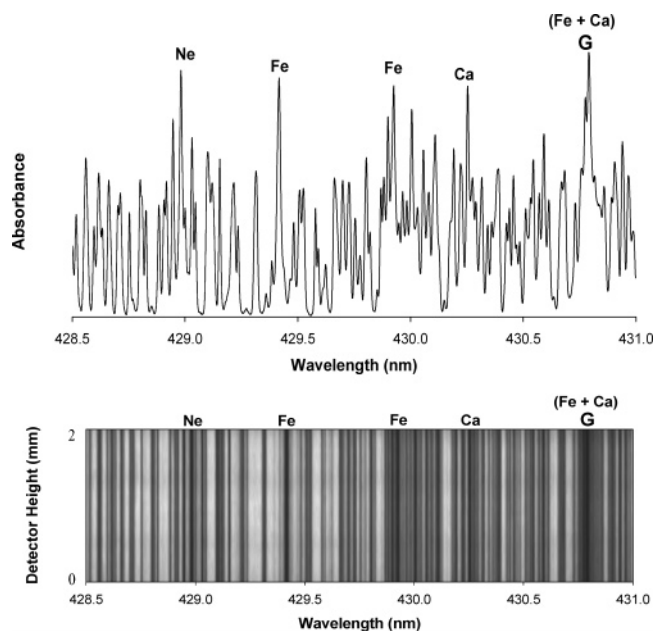


Figure 1. Fraunhofer effect spectrum of the sun including the G band. One end of a fiber-optic cable was oriented toward the sun, and the other placed near the slit of the high-resolution spectrometer depicted in Figure 3.

By using different prisms, he was able to show that the dark lines had fixed positions in the solar spectrum. He mapped their positions and labeled the most intense lines with the letters of the alphabet.⁴ Fraunhofer mapped no fewer than 576 dark lines in 1814. Copies of his map were readily available in the latter part of the 19th century,⁵ and his nomenclature for the “Fraunhofer lines” in the solar spectrum survives to this day.⁶ The lines are easily observed with a high-resolution spectrometer (Figures 1 and 2), with a greater abundance appearing at lower wavelengths. Fraunhofer, of course, only had access to the two-dimensional spectrum as shown in the lower portions of the figures. Thus, he had to estimate intensities based upon the degree of “blackness” of the lines. Modern technology, such as the CCD camera, easily converts these two-dimensional spectra to intensities and even to absorbance values at each wavelength (upper portion of each figure). Today, detailed, high-resolution solar spectra are readily accessible via the worldwide web.⁷

Once Fraunhofer had found his monochromatic source for the determination of the refractive indices of various materials at different wavelengths, he seemed uninterested in the further explanation of the dark lines. While many scientists embarked upon the quest for the origin of the Fraunhofer lines, the correct explanation is generally attributed to the physicist Gustav Robert Kirchhoff in 1859.⁸ In that work, Kirchhoff showed that the dark Fraunhofer D lines in the solar spectrum changed to bright ones

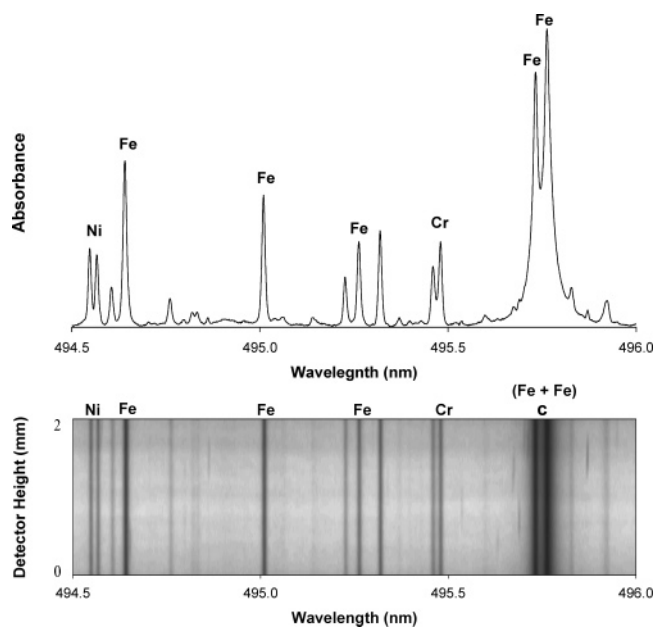


Figure 2. Fraunhofer effect spectrum of the sun including the c band.

if a flame colored by sodium vapor was placed in front of the slit.⁵ Kirchhoff had collaborated with Bunsen on the study of metal vapors in the flame. They would later report that the bright lines in each spectrum were characteristic of the metals in the flame.⁹ Kirchhoff surmised, then, that the solar atmosphere contained elements that absorbed characteristic wavelengths of the solar spectrum resulting in the dark Fraunhofer lines.¹⁰ To further prove this point, he created “artificial” sunlight using an oxyhydrogen limelight, which gave a spectrum with no dark lines. When this light was allowed to pass through a flame containing sodium, the dark Fraunhofer D lines appeared. The same effect was observed if the light source was a heated platinum wire through which an electrical current was passed.⁵

In short, Kirchhoff demonstrated that the Fraunhofer lines were the result of atomic absorption occurring when the continuum spectrum of the sun passed through its metal-containing atmosphere en route to the earth. The effect could be reproduced for any continuum source including a metal wire, if a metal vapor-producing atomizer was placed between the light and the observer. The sun, on the other hand, was itself both continuum source and atomizer.

Continuum Source Atomic Absorption Spectrometry (CSAAS) With Tungsten Filament Lamps. Tungsten filaments have been employed as light sources in CSAAS much less frequently than other sources, but their use spans more than a century. While the Fraunhofer lines are technically the first observations of the phenomenon of CSAAS, Kirchhoff's experiments using metal filaments as continuum sources for the observation of atomic absorption in a flame were the first laboratory-based observations of the method. His experiments differed from Fraunhofer's observations because they employed a separate light source and atomizer. In the early 1870s, Lockyer used an electric lamp (presumably with a metal filament), an iron

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tube furnace, and a spectroscope to observe the CSAAS spectra of sodium and iodine vapors.¹¹ A later version of this instrument employed an electric lamp powered by a 30-cell "Bunsen's battery", a furnace heated by an oxyhydrogen flame, and a spectroscope.¹² CSAAS spectra were observed for Ag, Na, Cd, Mn, Cr, Sb, Bi, Tl, Se, and iodine vapor.

In 1936, F. W. Paul employed the King furnace with a 500-W tungsten filament lamp for elements exhibiting CSAAS lines in the 340–800-nm region.¹³ Using a high-resolution spectrograph and a photographic plate, Paul was able to identify 600 absorption lines for Ce, 450 lines for Nd, and 1500 lines for Sm.

The analytical utility of atomic absorption techniques was generally recognized with the publication of the landmark 1955 paper entitled "The Application of Atomic Absorption Spectra to Chemical Analysis". In that work, Alan Walsh concluded that both the spectral resolution required to isolate the atomic absorption lines and the continuum source intensity necessary to produce an acceptable signal-to-noise ratio were beyond the capability of available instrumentation.¹⁴

"The accurate measurement of the profile of such a line would require a resolution of about 500,000, which is beyond the performance of most spectrographs. In addition, if it is desired to use photoelectric methods of intensity measurement, then it is scarcely feasible to use a continuous source, since the energy emitted over such a small spectral slit-width would be too small to give a high enough signal/noise ratio."

Seven years later, J. E. Allan reported CSAAS in a flame using a tungsten filament lamp at wavelengths above 340 nm for those elements for which hollow cathode lamps were not available.¹⁵ The system included a "Hilger large spectrograph" and a photographic plate. The absorbance signals observed in this manner required "concentrations substantially higher than required" for the hollow cathode lamp elements. Shortly thereafter, Gibson and co-workers reported the CSAAS spectra of Na, Ca, and Sn in a flame using a 180-W tungsten filament lamp as the light source.¹⁶ Their system employed a 0.5-m monochromator with a 30 000 grooves/in. grating and a photomultiplier tube detector. The goal of their work was to understand the fundamental processes of flame spectrometry such as analyte population distributions and flame temperatures. While they were not suggesting that their system be employed for chemical analysis in general, they did discuss the competition between analyte absorption and emission signals, and the dependence upon the relative temperatures of the light source and atomizer.

In 1965, Fassel and co-workers published a paper entitled "Evaluation of spectral continua as primary sources in atomic absorption spectroscopy".¹⁷ This work employed a 650-W tungsten filament lamp for those elements with absorption wavelengths above 370 nm. Three oxyacetylene flames were used in conjunction with a 0.5-m Ebert monochromator employing a 1250

grooves/mm grating. A photomultiplier tube was the detector, and the CSAAS spectra were recorded by scanning across the absorption profile. The tungsten lamp was used for the determination of many elements including Cs, K, Na, Ba, Li, Rb, Sr, and most of the lanthanides. Detection limits were in the part per million range for the lanthanides, and sub-ppm for the group I and II metals. Two of the suggested avenues for exploration were greater resolution in the spectrometer and better continuum primary sources. These are indeed the same limitations observed one decade earlier by Walsh.

Two years later, Winefordner and McGee reported a system similar to Fassel's that employed an extended flame cell or tube.¹⁸ This system also employed a 0.5-m Ebert monochromator with a 1250 grooves/mm grating. The light source for the 350–850-nm region was a tungsten filament lamp powered by a 6-V storage battery, and the detector was a photomultiplier tube. As with Fassel's system, the measured spectral bandwidth was on the order of 0.02 nm. Sub-ppm level detection limits were reported for Li, Na, K, Rb, Ca, Sr, Ba, Mn, Co, and Tl using the tungsten lamp.

Vickers and Marinkovic used a tungsten ribbon lamp for the CSAAS determination of Cr in a flame using a novel sample modulation device.¹⁹ They used a 1.0-m Czerny–Turner monochromator with a 1180 grooves/mm grating and a photomultiplier tube detector. At the 425.4-nm Cr line, the signal-to-noise ratio, the calibration sensitivity, and the detection limit were all significantly worse with the tungsten lamp than with either a Xe lamp or a hollow cathode. The tungsten lamp detection limit was a factor of 100 worse than the hollow cathode detection limit and a factor of 10 worse than the Xe lamp detection limit.

A 105-W tungsten–halogen lamp operated at 24 V was employed in a double-modulation CSAAS system by Elser and Winefordner.²⁰ A 0.5-m Ebert monochromator with a 1180 grooves/mm grating was employed along with a photomultiplier tube detector. The tungsten lamp in this work was used only for the determination of Ca at 422.7 nm. Even in this case, the lamp was used just for theoretical considerations, because it had a known spectral radiance that was roughly 6 times lower than that for the Xe lamp at the same wavelength. As with the others before them, the authors concluded that the "chief limitation has been the insufficient spectral radiance of the source employed." At this point in 1972, the higher intensity arc lamps clearly outperformed the tungsten filament lamps, as Walsh had suggested, and 30 years of the development of CSAAS using Xe short arc sources followed.^{21–24} During this time, the use of tungsten filaments as light sources for CSAAS waned (or disappeared altogether), but tungsten coils would soon find application as low-cost portable atomizers used in conjunction with more traditional AAS instrumentation.

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Tungsten Coil Atomic Absorption Spectrometry (WCAAS).

At roughly the same time that tungsten lamps disappeared as light sources for atomic absorption spectrometry, a commercial tungsten filament atomizer was described by Williams and Piepmeier.²⁵ They employed the spiral-wound tungsten filament from a 24-W commercial light bulb as the atomizer for an atomic absorption spectrometer using hollow cathode lamps. A similar system was described four years later.²⁶ Solutions containing Ag, Ca, Cr, Cu, Fe, Mg, Mn, and Sn were analyzed. Faithfull published a series of brief reports reviewing the use of tungsten filaments as electrothermal atomizers in AAS in the late 1970s.^{27–30} Those works suggested adding hydrogen to the argon purge gas to decrease the tungsten oxidation. In 1988, Berndt and Schladach described a simple low-cost tungsten coil atomizer that soon spawned significant interest in the technique.³¹ They used the coil from a 12-V, 150-W Osram projector bulb as the atomizer. Subsequent groups have published works using this atomizer with both home-built and commercial spectrometers.^{32–34} Portable battery-powered tungsten coil atomic absorption spectrometers have been described.^{35,36} A broad range of WCAAS applications has been reported: from the determination of Pb in blood^{37,38} to the determination of Yb in animal feces.³⁹ The reader is referred to recent reviews that contain many other specific applications of WCAAS.^{40–42} While a few papers have reported simultaneous multielement analyses using WCAAS systems, none have employed continuum sources.^{43,44}

Fraunhofer Effect Atomic Absorption Spectrometry (FE-AAS). The above discussions are intended to highlight the curious incident of the tungsten filament in analytical atomic absorption spectrometry: it alone has been employed as both a continuum light source and an atomizer for the technique. To date, however, there is no report of a dual W coil AAS system: one where one filament acts as light source and a second acts as atomizer. Neither, then, has any instrument been reported that uses a single W coil to perform both functions simultaneously. A device of this

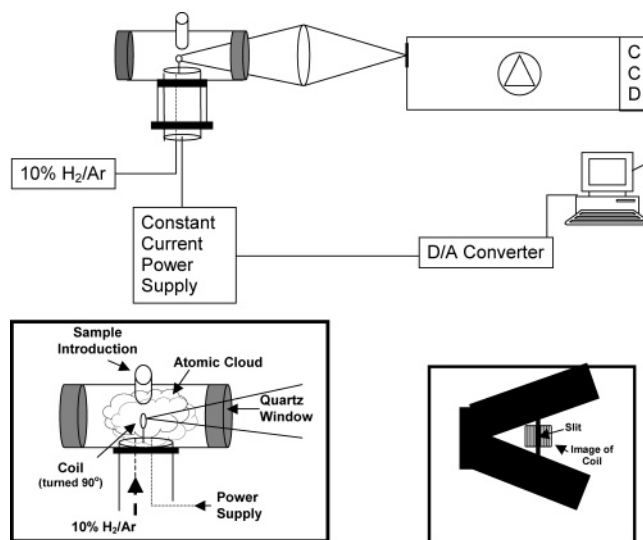


Figure 3. Schematic diagram of the FE-AAS instrument. Insets including a closeup of the atomization cell and a depiction of the coil image as projected on the monochromator entrance slit (with the v-shaped slit height adjuster in black).

nature is described and evaluated below. While the scale of the device is many orders of magnitude smaller than those celestial bodies that naturally produce the Fraunhofer effect, the principles involved are parallel. The result is perhaps the simplest design for an atomic absorption spectrometer reported to date.

EXPERIMENTAL SECTION

Instrumentation. Figure 3 is a schematic diagram of the FE-AAS spectrometer. The W coil atomizer used in this work, with the exception of the gas flow rate, has been described in detail elsewhere.⁴⁴ The filament is obtained by removing the quartz envelope from a common slide projector bulb (Osram Part HLX 64633) while leaving the two-pronged base intact. The bulbs are rated at 15 V and 150 W, and the manufacturer reports a 3400 K color temperature at full power. The filament is coiled in 10 turns. Viewing from the side, the turns are 3 mm high and together they occupy a width of 6 mm. Viewed end-on, the coils encircle an internal area ~ 1 mm in width and just less than 3 mm in height. The prongs of the bulb base are 7 mm apart and 10 mm long. They fit into a standard G6.35 two-prong ceramic bulb socket. The 19-mm-o.d. ceramic socket is countersunk into a 25-mm-o.d. aluminum rod so that the upper surface is flush. The bottom of the 5-cm-long rod is tapped for mounting onto an optical rail. The electrical leads to the socket, as well as a 3-mm-o.d. polyethylene purge gas supply tube, are threaded through the hollow center of the rod and out through a side port. The port is then sealed with epoxy to prevent air from leaking into the coil chamber. A continuous flow of 10% H_2/Ar is flushed through the tube at a rate of 1.0 L/min. This flow rate, while higher than some previously reported, is necessary to protect the coil during the 5-s atomization period at maximum power. A glass housing with two fused-silica windows and a sample introduction port protect the coil from oxidation. The purge gas escapes through the sample introduction port (Figure 3).

The tungsten filament is heated by a laboratory-constructed power supply. The supply consists of a line filter (Vicor Part 07818, Andover, MA), a harmonic attenuator module (Vicor Part VI-

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HAM) and a current source module (Vicor Part BatMod). The supply accepts a 0–5 VDC control signal from a D/A board in a personal computer and supplies a corresponding constant current in the 0–10-A range (at up to 15 VDC). A simple stepped coil heating cycle is achieved by delivering the appropriate control voltages for the requisite times.

The radiation emitted by the coil during the high-temperature atomization step is imaged onto the entrance slit of 1.33-m, $f/12$ McPherson model 209 Czerny–Turner monochromator using a fused-silica lens (25-mm o.d., 150-mm focal length). The 1:1 image of the coil on the slit is depicted in Figure 3. The slit is provided with a v-shaped adjustable slit height control. Given the size and shape of the coil, and the narrow dimension of the slit width, the proximity of the coil turns produces very little if any variation in the source intensity along the height of the slit. The monochromator is equipped with a 3600 grooves/mm grating (110×110 mm), resulting in a reciprocal linear dispersion of 0.21 nm/mm. This system has been employed previously for CSAAS measurements.^{45,46}

The detector is a thermoelectrically cooled charge-coupled device (CCD) (Princeton Instruments Spec-10, Roper Scientific, Trenton, NJ). The controller is the model ST-133A (Princeton Instruments) interfaced to a PC via a PCI card. The CCD consists of an array of 1340 by 100 pixels that are each $20 \times 20 \mu\text{m}$ in size. The detector thus provides a 26.8×2 mm imaging area. The sensor is back-illuminated with a UV-enhancement coating. The A/D converter has a 1.0-MHz digitization rate at 16 bits. The software allows the user to select three critical parameters: exposure time (t_e), number of successive exposure times to accumulate into a single spectrum (n_{acc}), and total number of spectra to be acquired at the trigger (n_s). The total time represented by a single spectrum is thus $t_e \times n_{\text{acc}}$, and the total amount of time represented by a series of spectra collected during a single sample atomization period is $t_e \times n_{\text{acc}} \times n_s$. Given the width of the imaging area of the detector and the reciprocal linear dispersion for the spectrometer, the system monitors a spectral window of ~ 5.6 nm at nearly normal angles of incidence for the grating. An entrance slit matched to the width of a single pixel ($20 \mu\text{m}$) should therefore provide a theoretical spectral band-pass of ~ 0.004 nm. In practice, the best full width at half-maximum for observed atomic absorption lines was between 2 and 3 pixels, so the practical spectral band-pass was closer to 0.01 nm. At higher angles of incidence, and longer wavelengths, both the spectral band-pass and spectral window decreased accordingly.

Method. Reference solutions were prepared from Ca, Co, Cr, K, Mn, Sr, and Yb stock solutions (1000 mg/L, SPEX CertPrep, Metuchen, NJ). The reference solutions were diluted with distilled–deionized water. Two drinking water standard reference materials were analyzed: trace metals in drinking water (High-Purity Standards, Charleston, SC) and primary drinking water metals (Peak Performance Certified Reference Materials, CPI International, Santa Rosa, CA). The standard reference materials were diluted with distilled–deionized water and a portion of the HPS standard reference material was spiked with 5.10 mg/L Co. The standard additions method was used to determine Co, Cr, Ca, and Sr in the water samples.

Table 1. Atomization Cycle for FE-AAS

applied current (A)	time (s) ^a	read
3.0	90	no
3.2	60	no
3.5	60	no
0	10	no
10.0	5	yes
0	30	no

^a The purge gas (10% H₂/Ar) flow rate was 1.0 L/min for all steps. Sample throughput for the program is 14 samples/h.

A constant atomization cycle was employed for all elements (Table 1), where the coil current in amperes (I) was related to its temperature (K) by the following equation:⁴⁷ $T = 309(I) + 325$. For each analysis, a 25- μL aliquot of solution was deposited directly onto the tungsten coil with an automatic micropipet. The H₂/Ar purge gas acted as coolant and also provided a reducing atmosphere to protect the tungsten coil and generate the atomic cloud. After three drying cycles with slowly stepped increases in current, a 10-s cooling period preceded the atomization step. The detector software was triggered to begin acquiring data at the initiation of the atomization stage. The W coil was heated to 10 A and glowed continuously for 5 s while data were acquired.

Detection parameters were adjusted to use the full range of the detector capacity without exceeding its saturation point, to maximize the signal-to-noise ratio (which increases with source signal). Depending upon the detection wavelength for a given element and the magnitude of the blackbody emission of the coil at that wavelength, the monochromator slit width and CCD exposure time (t_e) were optimized to give a signal approaching the saturation point. Once this was achieved, the number of exposures accumulated (n_{acc}) was increased as much as possible to allow larger signals to be achieved with improved S/N ratio, while maintaining a sampling rate fast enough to observe the shape of the atomization profile. The exposure time multiplied by the number of accumulations resulted in the overall integration time for a single spectrum, and then enough sequential spectra were stored into one data file to cover the entire atomization profile for the element in question. For example, cobalt at 352.7 nm required a 50- μm slit due to its relatively low wavelength, a 25-ms exposure time, 1 accumulation/spectrum, and 30 successive spectra stored in one file. The resulting 30 spectra therefore covered an atomization period of 750 ms. Strontium (460.7 nm) required a 20- μm slit, 3-ms exposure time, 9 accumulations/spectrum, and 25 spectra stored (thus covering an atomization period of 675 ms). Ytterbium (398.8 nm) utilized a 20- μm slit, 10-ms exposure time, 1 accumulation, and 60 spectra stored. Calcium (422.7 nm) and chromium (425.4 nm) were detected simultaneously in the same spectral window with a 20- μm slit, 6-ms exposure time, 6 accumulations/spectrum, and 15 spectra stored. Manganese (403.1 nm) and potassium (404.4 nm) were detected simultaneously with a 20- μm slit, 12-ms exposure time, 1 accumulation, and 40 spectra stored. So for those elements having accumulations greater than 1, the overall integration time per

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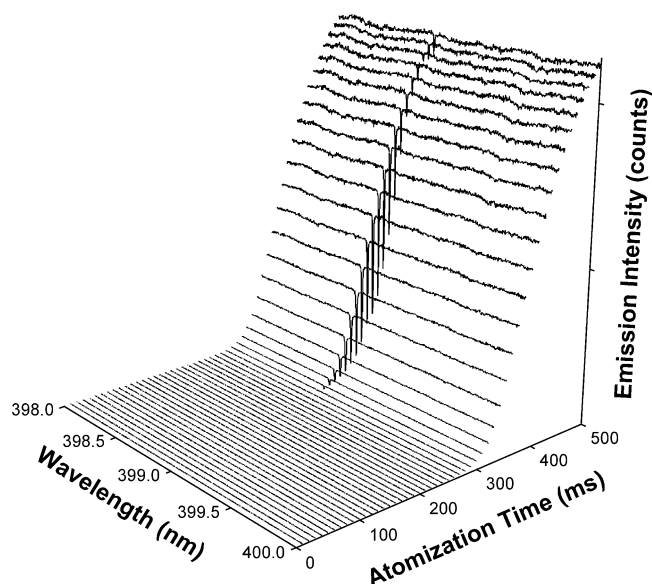


Figure 4. First 50 emission spectra collected during the W coil atomization of 25 μ L of a solution containing 1 mg/L ytterbium.

spectrum would result in detector saturation if the exposure time was simply set to this level. For instance, an exposure time of 27 ms for Sr would result in complete saturation and no usable signal.

Figure 4 is a 3-D image of the coil emission intensity collected during the atomization step for 25 μ L of a solution containing 1.0 mg/L Yb. At this wavelength (397–400 nm), the coil emission approaches saturation (16 bit–65 536 counts) at full power with a 10-ms exposure time and a 20- μ m slit width. So only a single exposure was accumulated for each spectrum shown in the figure. At the onset of the atomization step, the coil is at room temperature and the blackbody emission intensity is zero. At roughly 200 ms into the high-temperature step, the coil emission becomes observable, and the Yb absorption line first appears as a negative peak in the spectrum at 290 ms. The Yb absorption reaches a maximum at 340 ms and then wanes as the coil emission continues to rise with time. Raw data files such as this one were then converted to ACSII format, imported into a spreadsheet, and converted to absorbance. Both peak height and peak area absorbance values were plotted for calibration purposes. A blank solution was analyzed after each sample aliquot.

RESULTS AND DISCUSSION

Fraunhofer Spectra. Figure 5 exhibits two W coil Fraunhofer absorbance spectra: one showing the simultaneous detection of Mn and K (upper graph) and the other showing Ca and Cr. The 2-D CCD images, which are not shown, resemble those of Figures 1 and 2 with the presence of the elements as dark vertical lines amid the otherwise bright blackbody emission background. Clearly the tungsten coil is acting both as light source and as sample atomizer. In Figure 5, manganese lines appear at 403.1, 403.4, and 403.5 nm, while potassium lines occur at 404.4 and 404.7 nm. In addition, a bright tungsten emission line is just perceptible at 404.1 nm. The absorption lines appear as positive peaks, and the emission lines appear as peaks in the negative direction. The spectrum of Ca and Cr is less complicated, showing only the Ca and Cr peaks at 422.7 and 425.4 nm, respectively.

Analytical Figures of Merit. FE-AAS analytical figures of merit were determined for the seven test elements: Ca, Cr, Co,

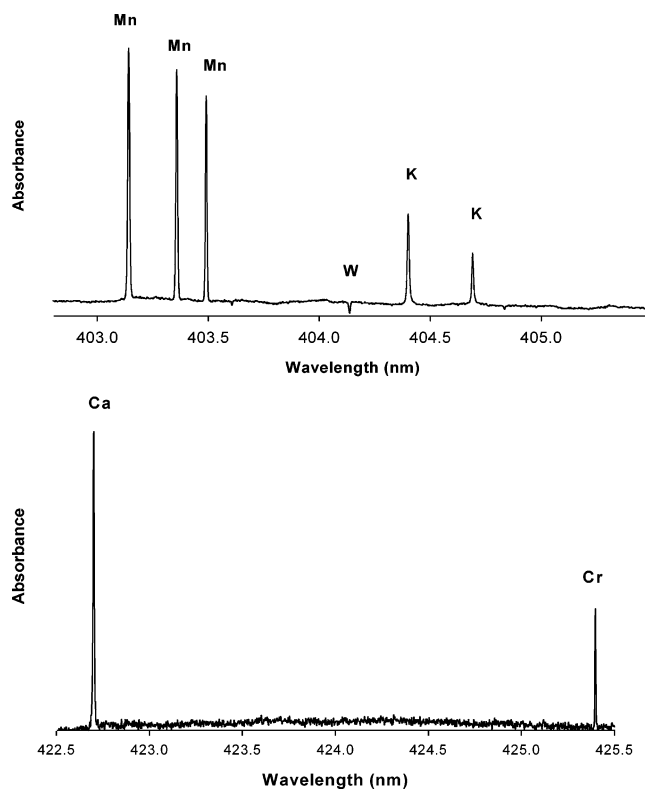


Figure 5. FEAS spectrum of 10 mg/L Mn and 10 mg/L K (upper graph). The total time represented by the spectrum is 12 ms, and the spectrum was collected 150 ms after the onset of atomization. FEAS spectrum of 1 mg/L Ca and 5 mg/L Cr (lower graph). The total time represented by the spectrum is 36 ms, and the spectrum was collected 180 ms after the onset of atomization.

Mn, K, Sr, and Yb. This suite of metals was chosen to provide a range of elements having different boiling points and atomic masses that also had absorption wavelengths spanning the range of utility for the system: the brightness of the W coil is prohibitively low below 350 nm, and the spectrometer has an upper wavelength limit of 520 nm (Table 2). For Yb, Sr, and Ca, the measurement wavelength is the most intense AAS wavelength for the element. In the case of Co, the most sensitive AAS wavelength (240.7 nm) is in the ultraviolet region at a wavelength where only minimal blackbody emission is observed at the highest tungsten coil temperature. The Co AAS line at 352.7 nm occurs at a wavelength observable by the FE-AAS system, but the sensitivity of this wavelength is 15 times worse than that of the primary AAS wavelength.⁴⁸ Similarly, the Cr line at 425.4 nm exhibited a higher S/N than the primary line at 357.9 nm with the FE-AAS system, despite the fact that the primary line is more sensitive by a factor of 2.⁴⁸ The Mn and K absorption lines utilized are respectively 10 and 333 times worse than those of the primary wavelengths. Figure 6 shows the atomization profiles for each element at the conditions stated in Table 1. The absorbance for each metal reaches a peak and then returns to near zero in less than 500 ms. The appearance time of the peak absorbance value in the FE-AAS atomization profile varies for each element despite the constant atomization parameters. The peak absorbance time does not appear to be directly proportional to either the boiling

(48) Robinson, J. W. *Undergraduate Instrumental Analysis*, 5th Ed.; Marcel Dekker: New York, 1995; p 366.

Table 2. Analytical Figures of Merit for FE-AAS

	Co	Yb	Sr	Ca	Cr	Mn	K
absorption wavelength (nm)	352.7	398.8	460.7	422.7	425.4	403.1	404.4
peak FE-AAS absorbance time (ms) ^a	375	340	200	270	200	348	300
boiling point (K)	3143	1466	1657	1757	2945	2235	1047
relative atomic mass	58.93	173.04	87.62	40.08	52.00	54.94	39.10
recommended GFAAS atomization temp (°C) ^b	2400	2300	2400	2500	2300	1900	1500
FE-AAS LOD (ng) ^c	2	0.1	0.007	0.005	0.2	0.5	0.5
GFAAS LOD (ng) ^d	0.1	0.0005	0.001	0.0005	0.003	0.02	0.1
upper limit of linear range (ng)	400	3	1	0.1	30	500	600
precision (% RSD) ^e	3.8	6.1	1.8	10.7	6.7	4.5	7.8
certified value for drinking water std (mg/L)	5.1 ^f		0.015	0.50	0.50		---
FE-AAS determined value (mg/L)	5.1		0.0090	0.60	0.57		---

^a See Figure 6. ^b Recommended by The Perkin-Elmer Corp. ^c Based on 3 standard deviations in the blank signal and a 25- μ L sample volume. ^d Based on 3 standard deviations in the blank signal and a 50- μ L sample volume (see refs 48 and 49). ^e The precision was measured at the following analyte concentrations: 0.1 mg/L Yb, 10 mg/L Co, 0.05 mg/L Sr, 3.0 μ g/L Ca, 1.0 mg/L Cr, 1.0 mg/L Mn, and 15 mg/L K. ^f This sample was spiked with 5.1 mg/L Co.

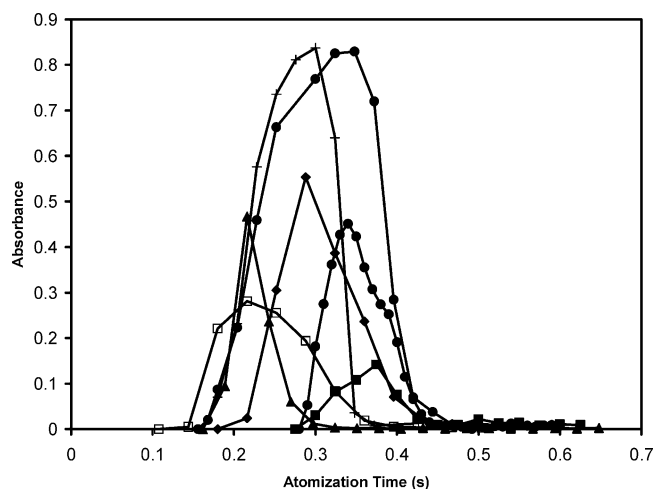


Figure 6. Atomization profiles for 0.05 mg/L Ca (\blacklozenge), 100 mg/L Co (\blacksquare), 0.05 mg/L Sr (\blacktriangle), 0.5 mg/L Yb (\bullet), 1.0 mg/L Cr (\square), 10 mg/L Mn (\circ), and 10 mg/L K (+).

point, the atomic mass, or the recommended graphite furnace atomization temperature for the metal. Nevertheless, both peak absorbance and peak area were used in calibration curves, and both were linear for each metal, resulting in very similar limits of detection (LODs).

Limits of detection were determined by the IUPAC method: $3\sigma/m$, where σ is the standard deviation in the blank signal and m is the calibration sensitivity. The LODs for FE-AAS are greater than the best LODs reported for GFAAS by a factor ranging from 4 to 200.⁴⁹ All GFAAS LODs were obtained with a 50- μ L sample volume, and the LODs for Co, Cr, Mn, and K have been increased by factors of 15, 2, 10, and 333, respectively, to account for the difference in sensitivity between the wavelengths employed and the primary wavelength for each metal.⁴⁸ The LOD values in Table 2, therefore, should be directly comparable. The elevated LODs reported for FE-AAS might be attributed to a combination of factors: (1) a relatively low intensity continuum light source was employed (W coil) instead of the spectrally narrow hollow cathode lamp, (2) the W coil atomizer is "open" as opposed to the closed

graphite tube, and (3) the high-resolution monochromator has a relatively poor throughput due to its large f -number (12) and small slit width. Similar to other AAS techniques, the linear dynamic range for FE-AAS is between 1.5 and 3.0 orders of magnitude.

The precision of the FE-AAS technique was determined with aqueous standard solutions having the following concentrations: 0.1 mg/L Yb, 10 mg/L Co, 0.05 mg/L Sr, 3.0 μ g/L Ca, 1.0 mg/L Cr, 1.0 mg/L Mn, and 15 mg/L K. Repetitive analyses of equivalent aliquots of these solutions resulted in relative standard deviations (RSD) between 1.8 and 10.7%. The accuracy of the FE-AAS method was tested with the drinking water standard reference materials. Ca, Cr, Sr, and Co were all present in a reference material. Ca, Cr, and Sr were present at detectable levels; therefore no dilution or spiking was necessary. Cobalt was present at a level below the LOD for FE-AAS, so the standard reference material was spiked with 5.1 mg/L Co for detection purposes. Ytterbium was not present in either reference material, and thus was not determined. As previously reported for W coil AAS, the standard additions method was applied to the analyses of drinking water.⁵⁰ The recoveries reported in Table 2 are quite respectable. The accuracy is poorer at concentrations very near the detection limit (Sr) and for Ca (which was present in the diluent water).

Conclusions. Atomic absorption spectrometry using a single device for both light source and sample atomizer has been described for the first time since the explanation of the Fraunhofer lines in the solar spectrum. While this technique is interesting from a purely historical point of view, it also opens the door for a potentially simple portable spectrometer. The tungsten coil, as a continuum light source, can replace the different hollow cathode lamps needed for multielement analysis by traditional AAS. And since the coil requires low power and is an inexpensive but efficient sample atomizer, a very simple instrument could be powered by a single car battery. The source/atomizer combination greatly simplifies the optical arrangement of the instrument by eliminating a source, a power supply, and a focusing lens. The design also reduces the typical three-component alignment problem (light source—atomizer—detector) to a much more straightforward two-component problem (tungsten coil—

(49) *The Guide to Techniques and Applications of Atomic Spectroscopy*; The Perkin-Elmer Corp.: Norwalk, CT, 1997; p 5.

(50) Bruhn, C. G.; Ambiado, F. E.; Cid, H. J.; Woerner, R.; Tapia, J.; Garcia, R. *Anal. Chim. Acta* **1995**, *306*, 183–192.

detector). In fact, a very compact system could be composed of a single tungsten coil, a fiber-optic cable, and a compact echelle monochromator/CCD combination. In its current state, FE-AAS has figures of merit approaching, but not as good as those of traditional atomic spectrometry techniques. The method is also limited to wavelengths above 350 nm for now, but the simplicity of the design and the potential for simultaneous multielement determinations may make the approach attractive for specific field applications.

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