resource paper

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Principles, Methodologies, and Applications of Atomic Fluorescence Spectrometry

Atomic fluorescence involves photon excitation of atoms to produce excited atoms which undergo radiational deexcitation over a short time period (order of nanoseconds) after excitation . . . . The intensity of the fluorescence depends critically upon the intensity of the light source at the exciting wavelength and the concentration of analyte atoms.

Atomic fluorescence spectrometry (AFS) is an analytical spectrometric method based upon physical principles put forth in the 1800's by Kirchhoff, Bunsen, and others (*1–5*). Walsh (*6*) and Alkemade (*7*) first utilized these physical principles in atomic absorption spectrometry, which is currently the most used single element, trace analysis method. The physical principles of AFS were first noted in the early 1900's by Wood (*8*) who observed that sodium vapor could be excited to produce atomic fluorescence. However, little research on the physical aspects of AFS was reported in the literature until the 1930's, and no research on the analytical aspects of AFS resulted until the 1960's (*9–11*).

Nichols and Howes (*12*) in a 1924 paper described the atomic fluorescence characteristics of Ba, Ca, Li, Na, and Sr in flames. However, the classic 1929 paper by Badger (*13*) who studied the flame atomic fluorescence characteristics of Ag, Cd, Cu, Hg, Mg, Na, and Tl and the prediction by Alkemade (*14*) at the 10th Spectroscopicum International Colloquium led Winefordner and coworkers (*9–11*) to the first analytical use of atomic fluorescence spectrometry. In the early 1960 studies by Winefordner and coworkers and by West and coworkers (*15, 16*) at Imperial College in London, turbulent flames as atomizers and low intensity metal vapor discharge lamp sources were used to produce atomic fluorescence. The atomic fluorescence was observed in those studies with a single channel, high luminosity, inexpensive monochromator-photomultiplier detector and dc electronic processing. Since those early studies, acetylene flames (separated and not-separated), chamber type nebulizers, electrothermal furnace atomizers, higher intensity sources, including electrodeless discharge lamps (EDL)—pulsed and cw, hollow cathode discharge lamps (HCL)—pulsed and cw, dye lasers—pulsed and cw, multichannel TV image detectors, rapid scan spectrometers, and phase sensitive (lock in), boxcar, and photon counting measurement systems have been used.

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"Principles, Methodologies and Applications of Atomic Fluorescence Spectrometry" is the first of a new series of Resource Papers aimed primarily at college teachers and planned to give up-to-date summaries of the state of the science and the art in critical areas of chemistry today. Other papers in the series will appear in subsequent months. The publication of Resource Papers is supported in part by a grant from the Research Corporation.

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In this review, the most significant aspects of the physical principles, the instrumentation, the methodologies, the applications, and possible future developments will be discussed. Adequate references will be given for the reader to refer to. General references on AFS are those by: Winefordner, Schulman, and O'Haver (*17*), Sychra, Svoboda, and Rubeska (*18*), Winefordner (*19*), and Winefordner (*20*), and the reader is referred to them for a more detailed discussion of the principles, instrumentation, methodologies, and applications.

Principles

Basis of Method

Atomic fluorescence involves photon excitation of atoms to produce excited atoms which undergo radiational deexcitation over a short time period (order of nanoseconds) after excitation. The source of excitation can be either a narrow line source (spectral half width of exciting radiation is narrower than the absorption line of the analyte atoms in the atomizer), or a continuum or pseudocontinuum source (spectral half width of exciting radiation is broader than the absorption line of the analyte atoms in the atomizer). The atomizer is any device which converts the sample into atoms, such as a flame or a furnace. The intensity of the fluorescence depends critically upon the intensity of the light source at the exciting wavelength and the concentration of analyte atoms.

Transitions

Atomic fluorescence transitions (*21*) are generally categorized as resonance, direct-line, or stepwise line. These are shown in Figure 1. If the photon energy of fluorescence is less than the photon energy of absorption, the process is called Stokes (*type*) fluorescence. If the reverse is true, the process is called anti-Stokes (*type*) fluorescence. If only excited states are involved in the absorption and fluorescence processes, then the word *excited* is introduced in front of the name. If after excitation, thermal assistance populates a higher or lower level from which fluorescence occurs, then the phrase *thermal assistance* is inserted prior to the name of the fluorescence process.

Intensity Expressions (*22–26*)

It is beyond the scope of this paper to give formal derivations of the intensity expressions. However, the results of the derivations will be given and discussed.

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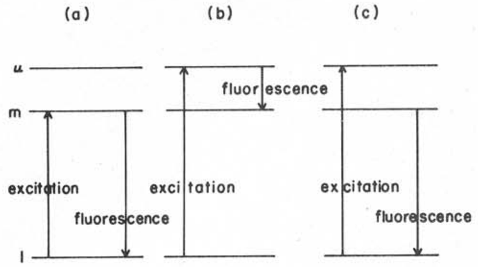

Figure 1. Types of atomic fluorescence transitions (a) Resonance (b) Direct line (c) Stepwise line. Key: u = upper excited state, m = intermediate excited state, l = lower (usually ground) state.

In the treatment to follow, it has been assumed that the atom under consideration has only two levels, i.e., ground, 1, and first, 2, excited states (the higher, 3, 4, . . . energy levels are assumed not to influence the population of state 1; the atoms are uniformly distributed in the atomizer; the atomizer has a uniform temperature, T, and all species are in thermodynamic equilibrium; the light source radiation impinging upon the gaseous species does not affect the energy distribution, the velocity distribution, or the atomizer temperature; the analyte atoms are present as a trace component in the atomizer (low optical density case); the radiation density of the source is spatially uniform and constant while traversing the atomizer; and finally polarization and coherence effects are negligible.

The basic fluorescence radiance expression is given by

$$B_{\mathrm{F}} = \left(\frac{l}{4\pi}\right) Y_{21} E_{\nu_{12}} \int_0^\infty k_\nu \mathrm{d}\nu \tag{1}$$

where

l = path length in direction of detection system, m
4π = number of steradians in a sphere (fluorescence is isotropic), sr
Y_{21} = fluorescence power (quantum) efficiency, W fluoresced/W absorbed
$E_{\nu_{12}}$ = spectral irradiance of exciting radiation at absorption line, ν_{12}, W m^{-2} Hz^{-1} (1 W = 1 Js^{-1})
$\int_0^\infty k_\nu \mathrm{d}\nu$ = integrated absorption coefficient over absorption line, m^{-1} Hz

The product $E_{\nu_{12}} \int_0^\infty k_\nu \mathrm{d}\nu$ is the power absorbed (W) from the source radiation by the analyte atoms per unit volume (m^3) of atomizer species. The product of Y_{21} and $E_{\nu_{12}} \int_0^\infty k_\nu \mathrm{d}\nu$ converts the power absorbed per unit volume to power fluoresced per unit volume. The product of l and $Y_{21} E_{\nu_{12}} \int_0^\infty k_\nu \mathrm{d}\nu$ converts the power fluoresced per unit volume to power fluoresced per unit area of the atomizer. Finally, dividing by 4π sr gives the power (W) fluoresced per unit area (m^2) per unit solid angle (sr). The integrated absorption coefficient is given by

$$\int_0^\infty k_\nu \mathrm{d}\nu = n_1 \left(\frac{h\nu_{12}}{c}\right) B_{12} \left[1 - \frac{g_1 n_2}{g_2 n_1}\right], \mathrm{m}^{-1}\ \mathrm{Hz} \tag{2}$$

where

n_1 = concentration of analyte atoms, m^{-3}
$h\nu_{12}$ = energy of the exciting photon, J
c = speed of light, m s^{-1}
B_{12} = Einstein coefficient of induced absorption, m^3 J^{-1} s^{-1} Hz
g_1, g_2 = statistical weights of states 1 and 2, respectively, dimensionless
n_1, n_2 = concentration of states 1 and 2, respectively, m^{-3} (note that $n_1 + n_2 \cong n_T$, the total concentration of atoms in all states)

The B_{12} factor is the number of absorption transitions per unit time per unit spectral energy density per absorbing species. The product $B_{12} h\nu_{12}/c$ is the reciprocal spectral quantum irradiance per absorbing atom, i.e., the number of absorption transitions per unit cell area (m^2) per unit spectral quantum flux (photons Hz^{-1}) per absorber. The product $n_1 B_{12} h\nu_{12}/c$ is the total number of absorption transitions per unit cell length per unit spectral quantum flux (m^{-1} Hz). The factor in brackets accounts for the absorption decrease via induced (stimulated) emission at the same frequency, ν_{12}.

Utilizing the steady state approach, where the excitation rate equals the de-excitation rate, i.e.

$$\left(k_{12} + \frac{B_{12} E_{\nu_{12}}}{c}\right) n_1 = \left(k_{21} + A_{21} + \frac{B_{21} E_{\nu_{12}}}{c}\right) n_2 \tag{3}$$

where

k_{12}, k_{21} = excitation and de-excitation non-radiational (collision) rate constants, s^{-1}
A_{21} = Einstein coefficient of spontaneous emission, s^{-1}
B_{21} = Einstein coefficient of induced emission, m^3 J s^{-1} Hz
B_{12} = Einstein coefficient of induced absorption, m^3 J s^{-1} Hz
n_1, n_2 = concentrations of electronic states 1 and 2, m^{-3}
c = speed of light, m s^{-1}

The fluorescence power (quantum) efficiency Y_{21} is defined as

$$Y_{21} = \frac{A_{21}}{A_{21} + k_{21}} \tag{4}$$

and A_{21} is related to B_{21} and B_{12} by

$$A_{21} = \left(\frac{8\pi h\nu^3{}_{12}}{c^3}\right) B_{21} = \left(\frac{8\pi h\nu^3{}_{12}}{c^3}\right) \left(\frac{g_1}{g_2}\right) B_{12} \tag{5}$$

where h is the Planck constant. Combining expressions, B_{F} for all the two level atoms is given by

$$B_{\mathrm{F}} = \left(\frac{l}{4\pi}\right) Y_{21} E_{\nu_{12}} \left[n_1 \left(\frac{h\nu_{12}}{c}\right) B_{12} \left(\frac{E^{*}{}_{\nu_{12}}}{E^{*}{}_{\nu_{12}} + E_{\nu_{12}}}\right)\right] \tag{6}$$

where

$$E^{*}{}_{\nu_{12}} = \frac{cA_{21}}{B_{21} Y_{21}} \tag{7}$$

and in terms of the saturation spectral irradiance, $E^{s}{}_{\nu_{12}}$, i.e., the source irradiance which results in a fluorescence radiance 50% of the maximum possible value

$$E^{s}{}_{\nu_{12}} = E^{*}{}_{\nu_{12}} \left(\frac{g_1}{g_1 + g_2}\right) \tag{8}$$

and substituting for n_1 in terms of n_T, B_F is given by

$$B_{\mathrm{F}} = \left(\frac{l}{4\pi}\right) Y_{21} E_{\nu_{12}} n_{\mathrm{T}} \left(\frac{h\nu_{12}}{c}\right) \left[\frac{B_{12}}{1 + \dfrac{E_{\nu_{12}}}{E^{s}{}_{\nu_{12}}}}\right] \tag{9}$$

Several interesting conclusions can be made concerning the fluorescence radiance, B_{F}

1) B_F is linear with n_T as long as the optical density is low, i.e., $k_\nu l \gtrsim 0.05$. The linearity of B_{F} with n_T (analytical calibration curve) is greater as $E_{\nu_{12}}$ increases; i.e., as $E_{\nu_{12}}$ increases, n_T must increase for $k_\nu l$ to exceed 0.05.
2) B_{F} is linearly dependent upon the source irradiance and the fluorescence quantum efficiency as long as $E_{\nu_{12}} \ll E^{s}{}_{\nu_{12}}$; i.e.

$$B_{\mathrm{F}} = \left(\frac{l}{4\pi}\right) Y_{21} E_{\nu_{12}} n_{\mathrm{T}} \left(\frac{h\nu_{12}}{c}\right) B_{12} \tag{10}$$

which is the case for conventional source excitation of atoms.

3) B_F is independent of the source irradiance and the fluorescence quantum efficiency if $E_{\nu_{12}} > E^{s}{}_{\nu_{12}}$, i.e., saturation of the upper state is essentially achieved (B_F is the maximum possible value for a given n_T)

$$B_F = \left(\frac{l}{4\pi}\right) Y_{21} E^{s}{}_{\nu_{12}} n_T \left(\frac{h\nu_{12}}{c}\right) B_{12} \tag{11}$$

or substituting for $E^{s}{}_{\nu_{12}}$ from eqns. (7) and (8)

$$B_F = \left(\frac{l}{4\pi}\right) h\nu_{12} A_{21} n_T \left(\frac{g_1}{g_1 + g_2}\right) \tag{12}$$

The fluorescence radiance is therefore determined only by well-known atomic parameters, A_{21}, g_1, g_2, and $h\nu_{12}$ and by n_T. Thus if one measures B_F (steady state conditions), n_T can be *absolutely* determined (*22, 27, 28*) at a given location in the atomizer. Also in analytical spectrometric studies, B_F will be independent of any source fluctuation (unfortunately scatter of source radiation does follow the source fluctuations) and in-

Table 1. Instrumental Components Used in Atomic Fluorescence Spectrometric Systems

Sources	Status/Comments	References
Vapor Discharge Lamps	These sources were convenient to use in the early work in AFS but are not used now because of their tendency to emit broad and self-reversed lines.	(*34, 35*)
Cd		
Zn		
Hg		
Ga		
In		
Tl		
Na		
K		
Hollow Cathode Lamps	These sources are seldom used anymore in AFS because they are expensive and relatively low in intensity compared to other sources.	(*34–44, 97–100*)
1. cw or modulated		
"High" intensity HCL		
a. Flame Atomizers		(*36–38, 42–44*)
b. Furnace Atomizers		(*39–40*)
2. pulsed		(*41, 97–100*)
Exploding Wires	Status unknown.	(*45*)
Electrodeless Discharge Lamps	These sources have been the most used AFS sources. However, they are tedious to produce and no reliable production and operation methods are available for all elements. The use of these sources has dropped off in the past two years.	(*46–53*)
[Coupling of Lamp to Microwave (Lamps not thermostated)]		
1. Antenna		(*46–48*)
2. Cavity		(*49*)
3. Thermostated Lamps		(*47*)
4. Lamp Preparation/Optimization		(*47–50*)
5. Modulation Methods		(*47–51*)
6. Pulsing Methods		(*52, 53*)
Xenon Arc Continuum	These sources were used in the early stages of AFS and then not used for $\sim$5 years. Now the Eimac Xenon arc lamp is used in several multielement AFS systems.	
[Power]		(*44, 54–57*)
1. 150W		(*44, 54–57*)
2. 450–500W		(*44, 54–57*)
Lasers	These sources are potentially the best for AFS because of their high intensities (produce near saturation), narrow spectral bandwidth (scatter is less), and collimation (simple optics). However, such sources are expensive ($\gtrsim \$15{,}000$) and only recently have they been efficiently doubled to give wavelengths down to $\approx$220 nm.	(*58–68*)
1. cw-Tunable		(*58–60*)
2. Pulsed-Tunable		(*61–68*)
Flame Atomizers	The early studies in AFS utilized turbulent H_2-based flames with total consumption burners. These flames are noisy and inefficient atomizers. Most recent studies have utilized C_2H_2/air and C_2H_2/N_2O separated flames which are less noisy and efficient atomizers for most elements. Separation of the secondary reaction zone with a stream of Ar reduces the flame background.	(*69–76*)
1. C_2H_2-Based		(*69–72, 76*)
2. H_2-Based		(*72–76*)
Furnace Atomizers	Furnace atomizers are only useful if the sample is too small for flame atomization and/or if the sensitivity of measurement is not adequate. Matrix interferences are great and difficult to compensate for (Hg is exception).	(*73–96*)
1. C-Filament/Rod		(*73–81*)
2. Pt Loop		(*82*)
3. C-Tube		(*83*)
4. Continuous Flow		(*84–87*)
5. Sputtering Chamber		(*88*)
6. Arc Pulse		(*89–91*)
7. Reduction/Aeration-Hg Only		(*92–96*)
Optical Systems	Most AFS systems have used small, high throughput monochromators. Because of the simplicity of AFS spectra, slew scanning of these monochromators is simple if relatively large slit widths are used. Non-dispersive (no monochromator) systems are sensitive but more susceptible to interferences.	(*34, 35, 57, 97–103*)
1. Single Channel		
a. Single Element Spectrometric Detection		(Most papers) (*34, 35*)
b. Multiple Element Spectrometric Detection (slew scan)		(*57, 97–102*)
c. Non-Dispersive		(*115, 116*)
2. Multiple Channel (TV Tube Detector)		(*103*)
Detectors	All studies except the ones designated have used photomultipliers and single channel detection.	
1. Photomultiplier		(Most papers)
2. TV Image Detector		(*157, 158*)

Table 1. Continued

Sources	Status/Comments	References
Electronics	Early studies in AFS used either dc amplifiers or a chopped source with an ac amplifier. Recent studies have involved the use of modulated sources with lock-in amplification. Several studies have utilized dc or ac photon counting. All pulsed AFS studies have used boxcar integrators.	
1. DC-Amplifier		(Early papers)
2. AC-(non synchronous) Amplifier		(Early papers)
3. AC-(synchronous) Amplifier (Lock-in)		(Recent papers)
4. DC-Photon Counter		(Recent papers)
5. AC-(synchronous) Photon Counter		(Recent papers)
6. Pulsed-Boxcar Integrator		(Laser papers)

dependent of flame chemistry, i.e., flame gas composition which influences Y_{21}.

4) If the concentration, n_T, is increased (*17, 29*) greatly, then B_F does *not* follow the expressions above but rather is related to the $\sqrt{n_T}$.
5) If a narrow line source (*30–32*) is used for excitation and if all other assumptions given above are valid, then the exact expression for B_F is more complex than those listed in eqns. (*9–11*) but is in general similar; e.g., B_F is still linearly related to n_T, but now the source irradiance absorbed is determined by the width and profile of the exciting line, the velocity distribution of the absorbers, and the broadening mechanism for the absorbers.

Concentration of Atomic Absorbers

The analyte concentration (species/m^3) in all electronic states, n_T, is determined by the atomizer used. If an analyte solution is aspirated into a flame atomizer (*17*) then

$$n_T = \frac{N_A F_S C \epsilon \beta}{F_G e_f} \qquad (12)$$

where

N_A = Avogadro's number (6×10^{23}); molecules/mole
F_S = solution aspiration (transport) rate, m^3 s^{-1}
C = analyte concentration of simple solution being aspirated, moles m^{-3}
ϵ = efficiency of nebulization, i.e., the ratio of the amount of analyte entering the flame (per s) to the amount of analyte being aspirated (per s), dimensionless
β = overall atomization efficiency, i.e., the amount of analyte as atoms (per s) to the amount of analyte entering the flame (per s), dimensionless
F_G = flow rate of unburnt gases into the flame, m^3 s^{-1}
e_f = flame gas expansion factor (the unburnt gases expand from room temperature to the flame temperature), dimensionless

The efficiency of nebulization, ϵ, is dependent upon the characteristics of the solution being nebulized, upon F_S, and upon the nebulizer-chamber characteristics. The overall atomization efficiency, β, is dependent upon the factors affecting

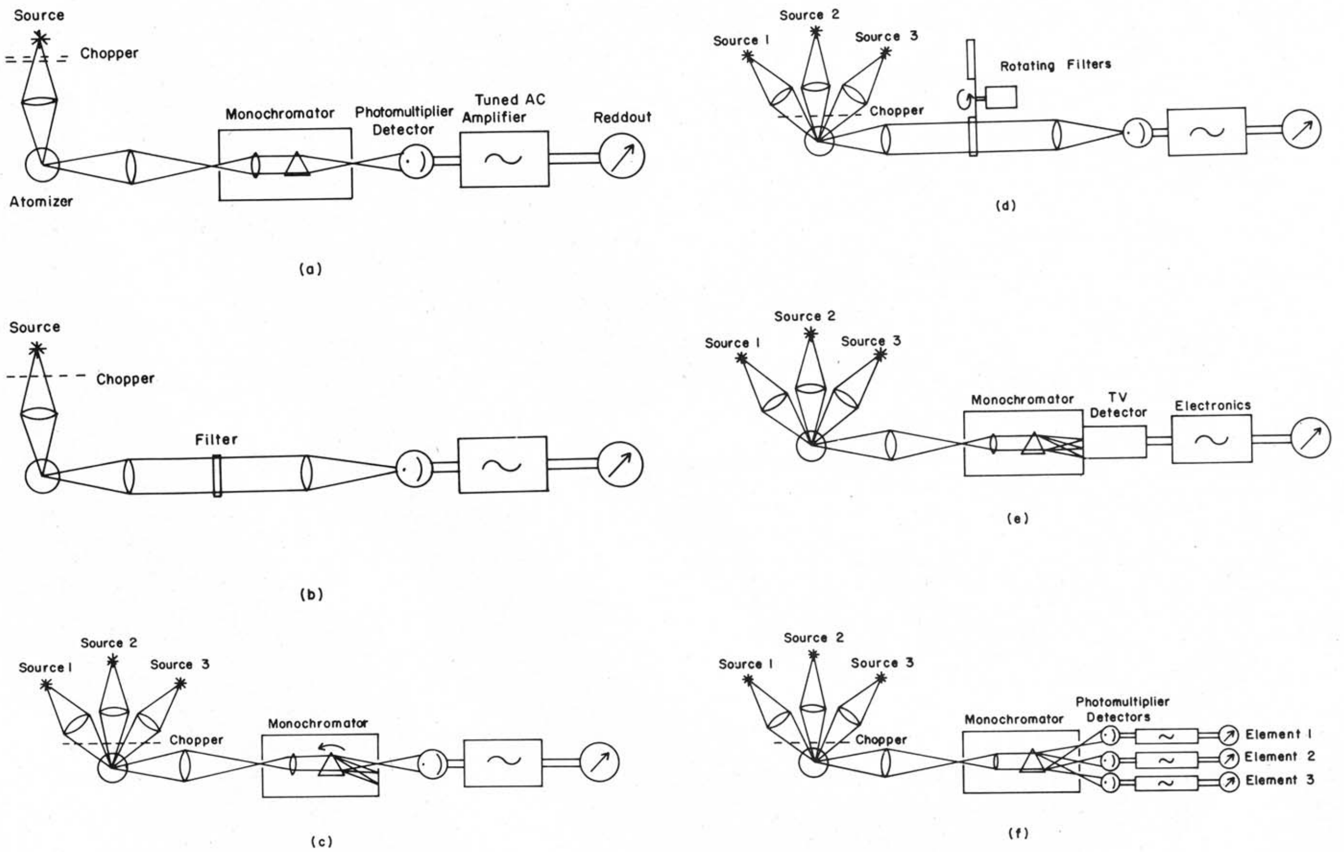

Figure 2. Types of atomic fluorescence spectrometric systems (a), (b) Single channel dispersive (a) or Filter (b) AFS-electrodeless discharge lamp, xenon continuum source, or tunable laser, (c), (d) Multielement dispersive AFS-stacked electrodeless discharge lamps or pulsed hollow cathode lamps or one eimac xenon continuum source with rapid scan (programmed) dispersive spectrometer (c) or rotating filter (d), (e), (f) Multielement dispersive AFS-stacked electrodeless discharge lamps, pulsed hollow cathodes, or one eimac xenon continuum source with TV tube detector (e) or direct reader with individual photomultiplier tube-electronic measurement systems for each spectral line (f).

Under ideal circumstances, the sensitivity of atomic fluorescence spectroscopic methods makes it possible to detect as few as 100 atoms of sodium/cm^3 in a sodium vapor cell.

solvent evaporation from the droplets produced in the nebulizer-chamber, vaporization of the solute particle resulting when solvent evaporation is complete, and equilibrium processes affecting atom ionization and compound formation with flame gas species, as O, OH, H, etc.

The analyte concentration (*17, 33*) within furnace atomizers depends upon the sample characteristics, the rate of heating of the furnace, the thickness of the sample on the furnace walls, and the environment within and type of furnace. In atomic fluorescence spectrometry, filament atomizers have been primarily used (sample is placed in a small indentation on the surface of the graphite filament which is heated at a low temperature to evaporate the solvent, at a higher temperature to ash the sample matrix, and at a much higher temperature to produce atoms which are excited by means of an imaged light source just above the filament). In such systems, the total concentration, $n_T(t)$ will be a function of time. Experimentally, either the peak signal or the peak area is measured. There is no general expression describing the variation of $n_T(t)$ with experimental parameters.

Instrumentation

The basic instrumental system in AFS is shown in block manner in Figure 2. As can be seen, the instrumental set up is similar to solution fluorimetry except that a flame is used as a "cell" rather than a quartz cuvet and generally *no* excitation filter or monochromator is used. The type of instrumental components utilized in AFS are listed in Table 1 with appropriate references and comments.

The criteria of importance in choosing sources, atomizers, and optical components are given in Tables 2, 3, and 4, respectively. A comparison of single- and multi-element AFS systems is given in Table 5.

In the above tables, only the most recent references, i.e, those since Browner's (*34*) excellent review of AFS and West's (*35*) flame review on a comparison of AFS with atomic absorption spectrometry, as well as several especially significant older references are listed.

Methodologies and Applications

In Tables 6 and 7, relative and absolute detection limits for

Table 2. Criteria of Importance in Choosing an Excitation Source for AFS

(1) High radiance over absorption line (pulsed laser > cw laser > EDL, HCL, Xenon arc)
(2) Good short and long term stability (Xenon arc, HCL, cw laser $\gtrsim$ EDL, pulsed laser)
(3) Simplicity of operation and setting up (Xenon arc > HCL, EDL > cw laser $\gtrsim$ pulsed laser)
(4) Low cost and long lifetime (Xenon arc > EDL, HCL > cw laser $\gtrsim$ pulsed laser)
(5) Usefulness for all spectral lines (Xenon arc > EDL, HCL $\gtrsim$ pulsed laser $\gg$ cw laser)
(6) Freedom from stray light (pulsed laser, cw laser > EDL, HCL > Xenon arc)

The use of > means that the figure of meit listed is better for the source listed at the left and worst for the source at the right.

Table 3. Criteria of Importance in Choosing an Atomizer

(1) High β Value (β = overall atomization efficiency)—C_2H_2/N_2O flames are generally more reducing (and hotter) than C_2H_2/air and C_2H_2/air is more reducing than H_2-based flames. Furnaces are good atomizers for most elements—exceptions are elements in a volatile molecular form as chlorides or elements forming carbides with the furnace (graphite or carbon).
(2) High stability for continuous atomization—flames are quite stable atomizers especially where chamber type nebulizers are used. Continuous flow furnaces are also quite stable.
High reproducibility for discrete atomization—furnaces are less reproducible than flames—this is partly a result of less precise sample introduction and of sample spreading and vaporization/atomization on and off the surface.
(3) Low background emission—flames have a background associated with the flame species. C_2H_2 flames have molecular species such as OH, C_2, CH, and CN producing a background; H_2-based flames have only the OH species producing significant background. Furnaces have a high blackbody emission if observations are made near or within the furnace and low background if observations are made above the furnace.
(4) Freedom from physical and chemical interferences—C_2H_2/N_2O flames have few sample matrix interferences except for ionization of some elements; C_2H_2/air is a fine atomizer for some elements but others are atomized only partially, namely, the strong oxide formers (e.g., Ba, Sr, Al, Ti, W, Zr, etc.); furnaces with inert atmospheres have complex interactions between sample matrix species and the analyte often causing large errors.
(5) Low concentration of quenching species and low atomizer temperature. Flames have many quenchers, as CO, CO_2, N_2, etc. Furnaces have few quenchers.
(6) Long residence time of atoms in the optical path. Flames have short residence times (few milliseconds) for any given species. Furnaces have longer residence times (order of seconds).

Table 4. Criteria in Choosing Optical Components

Entrance Optics Between Source and Atomizer
(1) Collect large solid angle of source radiation and impinge on atoms.
(2) Use fewest optical components (mirrors, lenses) as possible to avoid optical losses (reflection, absorption).

Optics Between Atomizer and Dispersing System
(1) Collect much fluorescence radiation from region where the fluorescence to background intensity ratio is greatest.
(2) Use fewest optical components as possible to avoid optical losses.

Dispersing System
(1) Filters—Use narrow band interference filters (multielement analysis can be performed by placing filters in a rotating wheel and sequencing the electronic measurements) (*115, 116*).
(2) Nondispersive (no filter or monochromator)—Use pure line sources and solar-blind photomultiplier if spectral line of concern is in uv (*115, 116*).
(3) Monochromator—Use large throughput (small *f*-number), medium resolution spectrometer (programmable slew scanning of wavelength is needed for multielement work).

Detectors
(1) Photomultipliers—Use ones with high gain, low dark current, wide spectral range.
(2) TV Image Devices—Use SIT or ISIT (silicon intensified target vidicon or intensified silicon intensified target vidicon). However, these devices (state of art) have poor resolution (500 channel devices have actually ~200 "real" channels and so in AFS studies, one can only cover 20–40 nm in any spectral window. If 200–800 nm were to be covered in 40-nm segments, the grating of the monochromator would still have to be slewed to 15 different positions) (*157, 158*).

Electronics
(1) DC Amplifier—Use with unmodulated source; large time constant—dark current, amplifier, source, atomizer drift problems.
(2) AC Amplifier (non-synchronous)—Use with modulated source; large time constant—source, atomizer drift cause problems; detuning due to chopper frequency drift; if time constant—small or electrical bandwidth is wide, then shot noise problems.
(3) AC Amplifier (synchronous)—Use with modulated source; no frequency drift problems as in ac non-synchronous amplifier; need large time constant to reduce shot noise; source, atomizer drift cause problems.
(4) Boxcar Integrator (gated detector)—Use for pulsed sources; dark current—atomizer induced shot noise is small but source drift causes problems.

Table 5. Comparison of Instrumental Systems

Single Element

- Monochromator System
  1. flexible in wavelength coverage and ease of wavelength selection
  2. stray light is small
  3. cost is significant
  4. lower optical throughput (radiation collected and passed to detector)
- Non-Dispersive System
  1. simple and low in cost
  2. large optical throughput
  3. stray light is a problem
  4. sources must be of pure element or interference filters must be used
  5. multiplexed systems as Michelson interferometers give poor signal-to-noise ratios

Multi-Element

- Monochromator System
  1. With slew scanning controlled by computer, system is flexible in wavelength coverage and simple to select wavelength
  2. Sequential selection of wavelengths is versatile, low cost, and fairly fast (direct readers with individual detectors for each line of interest use much lower throughput optics causing analysis time to increase for any given set of elements—the analysis time per element is less than with the sequential selection if the number of elements exceeds ~3)
- Non-Dispersive System
  - A rotating filter which with separate excitation source for the elements of interest is a simple, inexpensive method. Such a system has a large optical throughput but is more prone to stray light and atomizer noise (*115, 116*)

Table 6. Relative Detection Limits (Aqueous Solution) Obtained by Atomic Fluorescence Spectrometry and by Several Other Methods

	Detection Limit (ng/ml)				
	AFS				
Element	Line Source[a]	Continuum Source[b]	Laser[a]	AAS[c]	AEICP[d,e]
Ag	0.1(2)	1.⟨0.7⟩	4.*	2.	0.2**
Al	100.	200.	0.6*	20.	0.4
As	100.[0.1]	...	...	400.	2.
Au	1,000.	150.	...	200.	...
Ba	...	...	8.*((2))	20.	0.01**
Be	10.	15.	...	2.	...
Bi	10.(2)	...⟨10⟩	3.*	30.	...
Ca	20. . .	...	0.08*	2.	0.0001**
Cd	0.001	6.⟨1⟩	8.*	1.5	0.07
Ce	...	...	500.	...	0.4**
Co	5.	15.	200.	15.	0.1
Cr	50.	1.5⟨40⟩	1.*	3.	0.06**
Cu	1.	1.5⟨2⟩	1.*	2.	0.04
Dy	...	...	300.	...	...
Er	...	...	500.	...	...
Eu	...	...	20.	...	...
Fe	8.	10.⟨20⟩	30.*	10.	0.09**
Ga	10.	...	0.9*	...	0.6
Gd	...	...	800.	...	0.5
Ge	15,000.	...	...	...	...
Hf	...	...	...	200.	...
Hg	80.	...	...	...	...
Ho	...	...	100.	...	...
In	100.	25.⟨10⟩	0.2*	...	...
Li	...	...	0.5*	1.	...
Lu	...	...	3,000.	...	...
Mg	1.	0.1⟨3⟩	0.2*	0.1	0.003**
Mn	6.	2.⟨5⟩	0.4*	3.	0.02**
Mo	500.	100.	12.*	20.	0.3**
Na	100,000.	...	<0.1*	0.5	0.02**
Nb	...	...	1,500.	...	0.2
Nd	...	...	2,000.	10.	...
Ni	3.	25.⟨30⟩	2.*	...	0.2**
Os	...	...	150,000.	15.	...
Pb	10.(10)	50.⟨10⟩	13.*	...	1.
Pd	1,000.	100.	...	...	2.**
Pr	...	...	1,000.	...	...
Pt	50,000.	700.	...	...	...
Rh	3,000.	...	100.	...	...
Ru	...	...	500.	...	...
Sb	...[0.1]	...	50.	30.	...
Sc	...	...	10.	...	...
Se	40.[0.06]	...	...	250.	1.
Si	600.	...	...	100.	...
Sm	...	...	100.	...	...
Sn	30.(10)	150.⟨20⟩	...	70.	3.**
Sr	30.	0.9	0.3*	1.	0.003**
Tb	...	...	500.	...	...
Te	5.(10)[0.08]	...	...	70.	...
Ti	...	200.	2.*	80.	0.03
Tl	8.(6)	6.	4.*	30.	...
Tm	...	...	100.	...	...
V	70.	30.	30.*	50.	0.06**
Yb	...	...	10.	...	...
Zn	0.02	15.⟨5⟩	...	1.	0.1**

[a] All values come from references within [Winefordner, J. D., *Chem. Tech.*, 123, (1975)] except those in ( ).

[b] All values come from Johnson, D. J., Plankey, F. W., and Winefordner, J. D., *Anal. Chem.*, **46**, 1858 (1974).

[c] All values come from Pekin Elmer atomic absorption commercial literature on the Model 460.

[d] All values without double asterix come from [Olson, K. W., Haas, W. J., and Fassel, V. A., *Anal. Chem.*, **49**, 632 (1977)].

[e] All values with double asterix (**) come from [Boumans, P. W. J. M., and de Boer, I. J., *Spectrochim. Acta*, **30B**, 309 (1975)].

[ ] These values were taken from [Thompson, K. C., *Analyst*, **100**, 307 (1975)]. Results are for the hydride generation method. ( ) These values were taken from [Molnar, C. J., and Winefordner, J. D., *Anal. Chem.*, **46**, 1419 (1974)]. * Values from [Weeks, S. J., Haraguchi, H., and Winefordner, J. D., *Anal. Chem.*], submitted. ⟨ ⟩ These values taken from [Clyburn, S. A., Bartschmid, B. R., and Veillon, C., *Anal. Chem.*, **46**, 2201 (1974)]. (( )) Value taken from [Green, R. B., Travis, J. C., and Keller, R. A., *Anal. Chem.*, **48**, 1954 (1976)].

a number of elements measured by AFS are given. In Table 6, the influence of source type as well as comparisons with several other methods are given. In Table 7, a comparison of the AFS absolute detection limits with those by two other well-established methods is given.

In Table 8, the elements of interest and the areas of application of AFS are listed.

Finally, it is interesting to note the extremely high sensitivity of atomic fluorescence under ideal circumstances. Fairbank et al., (*112*) report a detectable atomic fluorescence signal using cw dye laser excitation from 100 atoms of sodium/cm^3 in a sodium vapor cell and interestingly, they predict a detection of 0.1 Cs atom/cm^3. Gelbwachs, et al., (*113*) and Smith and Winefordner (*114*) were able to detect $\sim 10^4$ atoms/cm^3 and $\sim 10^2$/atoms/cm^3 via a flashlamp pulsed tunable dye laser and a cw tunable dye laser, respectively; both studies utilized flame atomizers (C_2H_2/air). Gelbwachs, et al., predict a detection limit of ~ 10 atoms (Na)/cm^3 for Na in a closed cell (glass) and an ultimate detection limit of 10^{-4} atom within the interaction volume.

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Table 7. Absolute Detection Limits (Aqueous Solution) by Atomic Fluorescence Spectrometry and by Several Other Methods

Element	Detection Limit (pg)		
	AFS[a,c]	AAS[a,d]	AEICP[b,e]
Ag	0.4	0.2	200.
Au	4.	10.	...
Bi	6.[*]	7.	...
Cd	0.0015	0.1	70.
Co	20.	6.	100.
Cu	0.3	7.	40.
Fe	...(0.75)[Δ]	3.	90.
Ga	50.	20.	600.
Hg	7.	100.	...
Mg	1.	0.06	3.
Mn	5.	0.5	20.
Ni	5.	10.	200.
Pb	10.(0.2)[†](0.075)[Δ]	5.	1,000.
Sb	100.[*]	30.	...
Sn	100.	60.	3,000.
Tl	20.	3.	...
Zn	0.02	0.08	100.

[a] All values come from references within [Browner, R. F., *Analyst*, **99,** 617 (1974)] except those with *, †, Δ.

[b] All values come from [Fassel, V. A., Special Technical Publication 618, American Society for Testing Materials, Philadelphia, PA, 19103, 1977].

[c] 1 μl sample sizes.

[d] 5 μl sample sizes.

[e] 1 ml sample size.

[*] Values come from [Molnar, C. J., and Winefordner, J. D., *Anal. Chem.*, **46,** 1807 (1974)].

[†] Value taken from [Neumann, S., and Kriese, M., *Spectrochim. Acta*, **29B,** 127 (1974)].

[Δ] Values taken from [Bolshov, M. A., Zybin, A. V., Zybina, L. A., Koloshnikov, V. G., and Majorov, I. A., *Spectrochim. Acta*, **31B,** 493 (1977)].

Table 8. Applications of Atomic Fluorescence Spectrometry[a]

1. Ag, Cu, Fe, Mg, Ni, Pb, and Sn in Lubricating Oils (*34, 35, 102*).
2. As, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Se, Si, Te, and Zn in Metallurgical Samples (*34, 35, 165*).
3. Co, Cr, Cu, Fe, Hg, Mn, and Zn in Sea Water (*34, 35*).
4. Cd, Cu, Mg, Ni, Pb, and Zn in Biological Samples (*34, 35, 106–111*).
5. Hg in Foods, Rocks, and Sediment (*34, 35*).
6. Cd and Mn in Graphite (*34, 35*).
7. Cu, Hg, Mg, Mn, and Zn in Agricultural Samples (*34, 35, 106, 108, 111*).
8. Flame Gas Diagnostics (*22, 27, 28*)—Determination of flame temperatures and concentrations of flame gas species as C_2, CH, NO, NH, CN, etc.

[a] References (*34*) and (*35*) give many references to AFS applications.

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