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Absorption Spectrophotometry

ALTHOUGH THEY ARE SELDOM linked in people's minds, molecular and atomic absorption techniques show many common features. The basic optics of the instruments bear a certain resemblance. Both approaches excel at minor to trace level concentrations. And in their respective heydays, both techniques were promoted for their speed and selectivity. It seems natural to discuss them together in this brief survey of measurement techniques to compare and contrast them, as well as to illustrate the important roles that both continue to play in the metals laboratory.

UV/VISIBLE MOLECULAR ABSORPTION

Technically, molecular absorption spectrophotometry includes the important infrared region of the electromagnetic spectrum (0.78 to 1000 μm), where vibrational and rotational energy levels reveal so much about molecular structure. But the inorganic analytical chemist is generally much more involved with molecular absorption in the visible and near-ultraviolet (200 to 800 nm), where the incoming energy promotes changes in electron energy levels. Below 200 nm, air components begin to absorb significant amounts of radiation so that work there requires evacuated or helium-purged optical paths.

However, in the standard UV/visible region much can be accomplished. The quantitative relationship between path length through an absorbing medium and the absorbance of radiation was first defined by Bouguer in 1729; however, it is usually attributed to Lambert (1768). The connection with the concentration of an absorbing species was defined by Beer in 1859. The combination of these concepts takes different forms in the world literature, but in the United States the conventions derive from the Joint Committee on Nomenclature in Applied Spectroscopy (Society for Applied Spectroscopy and American Society for Testing and Materials), whose report was published in 1952 (Hughes, H. K., *Analytical Chemistry*, Vol. 24, 1952, p. 1349). It takes the form

$$A = \log(I_0/I) = abc_1 = \epsilon bc_2$$

where

A = absorbance,
I_0 = intensity (or power) of the incident light beam,
I = intensity (or power) of the transmitted light beam,
a = the absorptivity constant,
b = the light path in centimeters,
c_1 = concentration of the analyte species in grams/liter,
ϵ = the molar absorptivity constant, and
c_2 = concentration of the analyte species in moles/liter.

The quantity $\log(I_0/I)$, commonly called the absorbance, is also sometimes known as the "extinction" or the "optical density" of the solution. Analyte concentration is thus linearly proportional to absorbance for a constant light path length. Transmittance, today, is a less frequently used concept than absorbance even though the detector signal of most spectrophotometers is linearly proportional to it. It is related to absorbance by $A = \log(1/T)$, where T is the transmittance. The readout of some old filter photometers is in units of T, so calibration curves from these instruments are best plotted on log-linear graph paper.

Filter photometers are a comparatively primitive form of measuring device by today's standards, but they represented in their day a significant advance from color comparators, such as the Duboscq, which provided a standardized means of visually estimating color matches between unknown and standards. The Klett-Sommerson filter photometer was at one time the most widely used instrument of this type. It utilized a projection lamp, a photoresistor, a collection of narrow bandpass filters, and large-capacity, long path-length glass sample cells. The "Klett" was such a workhorse that its use persisted well into the modern spectrophotometer era, and it would not be surprising if some units were still in use today.

Spectrophotometers differ from filter photometers in that wavelength selectivity is achieved by means of a monochromator—comprised of either a prism or a diffraction grating and a network of mirrors and slits to direct the light. The bandpass of radiation reaching the sample chamber is typically much narrower with these instruments. Light throughput, however, may not be improved over a filter photometer. The detector may be a *phototube*, which is a vacuum tube with electrodes maintained at some potential between which a current flows if photons fall on the negative terminal. A more sensitive detector is a *photomultiplier*, which uses a cascade effect between a series of electrodes, each successive one at a higher potential than the last, to vastly amplify the sensitivity to impinging photons. A *photodiode array* is a solid state device that can be used to measure an entire wavelength region simultaneously.

Single-beam spectrophotometers have traditionally fallen into two classes: "workhorse" instruments (such as the Bausch & Lomb Spectronic 20™) and research-type instruments (such as the Beckman DU™). In their day, both of these devices were widely used. The Spectronic 20 was a grating instrument with a single test tube sample holder. The Beck-

man DU was a prism instrument with a four-cuvette sample holder. Today, computer-controlled photodiode array instruments represent the state of the art in both categories.

Another classification for spectrophotometers refers to their optical bench design. Single-beam instruments simply pass the monochromator-selected light through the sample cell and then into a detector. Dual-beam instruments split the monochromator-selected light into two beams. This is usually accomplished with a mechanical chopper, which is a rotating device that alternately presents a free path and a mirrored surface to the light beam. When the free path is present, the beam passes through the sample cell. When the mirror is present, the beam is diverted at a right angle to a series of other mirrors that direct it through the reference cell.

Both beams are then recombined at a half-silvered mirror that directs them to the detector. The detector then measures a "chopped" signal that alternates between the absorbance of the sample solution and the absorbance of the reference solution. The detector output is enhanced by an amplifier that is precisely tuned to the "chopped" frequency, extracting the two absorbances. In some configurations, this demodulated output drives a variable density filter in the reference light path to increase its absorbance and balance the two halves of the detector output. This version of a double-beam instrument is called an optical null design. There are other, quite distinct, designs as well. Some modern instruments using solid-state detectors simulate a dual beam instrument with a single-beam design by alternately scanning the reference and the sample and subtracting the complete spectra from each other, all under computer control.

The light source is usually a tungsten filament lamp for all measurements down to about 350 nm. Near-UV measurements between 350 and 200 nm usually employ a deuterium discharge tube with a quartz window. Light from the source enters the monochromator through an entrance slit and is then collimated by a lens system into a parallel beam that impinges on a prism or a grating. The dispersed light then falls on an adjustable exit slit. By turning the prism or grating, light of the appropriate wavelength can be made to pass through the slit. And by narrowing the slit width, a certain limited additional wavelength selectivity can be achieved.

Prisms do not disperse light as uniformly as diffraction gratings. Prism instruments tend to disperse light more broadly at the UV end of the spectrum and less broadly at the red end of the spectrum. Thus, with prism instruments, opening the slit when operating in the UV region allows more light energy to pass without diminishing wavelength selectivity.

A diffraction grating acts as a dispersing element by reflecting light from the spaces between its ruled parallel grooves. These thousands of reflections form an interference pattern that produces an orderly series of uniformly dispersed spectral lines (or slit images). With grating instruments, a given exit slit setting produces the same degree of selectivity (or bandwidth) across the entire wavelength region in which the spectrophotometer was designed to operate.

The sample chambers of commercial instruments take a number of forms. Perhaps the most common is designed to accommodate a cassette of four or more 1-cm square-sided glass cuvettes, which may have lids to slow the evaporative loss of volatile solvents. Other designs include cylindrical cells with flat optical faces at each end and path lengths of 2, 4, or 6 cm. Micro-cuvettes with extremely small internal volumes and "sipper" or flow-through cells are also available.

Other features of commercial instruments include external wavelength and slit controls and insertable filters for use in certain wavelength regions. In some designs, the phototube detector assembly is readily interchangeable to accommodate tubes sensitive to certain spectral regions. A light-proof shutter is generally the means of introducing the light beam to the sample chamber. With cassette designs, some means is provided for moving the individual cuvettes into the light path.

Spectrophotometric Measurements

UV/visible instruments are utilized in a number of different ways. First, there is the role as a qualitative identification tool, primarily of interest in organic analysis. Absorbance versus wavelength scans can be laboriously obtained with a conventional single-beam instrument (rezeroing the reference and measuring the sample absorbance at regular wavelength increments, then plotting the results), but they are best obtained on one of the recording designs (either double-beam or simulated double-beam). Many materials have a characteristic UV/visible spectrum that allows them to be "fingerprinted" by this means in a process analogous to qualitative infrared analysis.

Also, in developing a new spectrophotometric quantitative method, it is usually a good idea to record the spectrum of the colored species being measured in order to make the best decision on exactly where on the absorbance curve the readings should be taken. It should be noted that the best spot is not always on an absorbance maximum. If the maxima are sharp peaks, utilizing them may require an unrealistic degree of instrumental stability. Sometimes it is appropriate to also record the spectrum of the unreacted dye or the spectrum of the sample background in order to avoid regions of interference.

In the simplest quantitative measurements, a series of calibration standards is measured along with appropriate cell, sample, and reagent blanks, as needed. With the light-proof shutter closed, the instrument is first adjusted to infinite absorbance (or zero percent transmittance) with a potentiometer. This compensates for the "dark current" caused by thermal electron emission in the phototube or photomultiplier. Readings are then generally taken versus water or some simple solvent as a reference. Occasionally sulfuric acid is used as the reference.

After subtracting the appropriate blanks, the corrected absorbance is plotted on rectilinear coordinate graph paper versus concentration (or versus weight of analyte with an explicitly stated volume). Convention places absorbance on the ordinate. If the curve obeys Beer's law, the relationship is linear (ideally over the entire concentration range of interest), and its equation can be calculated by a simple least squares linear regression. Such an equation can be used to convert the corrected absorbances of unknown test solutions to concentrations of analyte.

If the curve is not linear over any portion of interest, it is usually best to read the values from the graph. If the only error associated with spectrophotometric measurement was that associated with reading an instrument scale, such as with

a dial analog readout, it would be possible to define an absorbance region of maximum precision, and it could be recommended that test conditions be adjusted so that all readings be taken in that region. In fact, with modern instruments the error limits of the measurement are defined by "shot noise" in the photomultiplier (a statistically distributed background emission of photoelectrons superimposed upon the "dark current").

Such a situation complicates the delineation of a region of maximum precision. It has been suggested, however, that such a region is defined by an inflection in the plot of log(concentration) versus the square root of the observed transmittance [see *Annual Book of ASTM Standards*, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1993, Practice for Photometric and Spectrophotometric Methods for Composition (E 60)].

Differential spectrophotometry provides a means of extending the usefulness of UV/visible molecular absorption techniques outside the low and trace concentration realm. In this variant, the reference solution is replaced by a synthetic standard accurately prepared at some concentration below that expected to be present in the unknown. The standard and the unknown are prepared identically. With the standard in the light path, the absorbance reading is adjusted to zero by opening the slit or increasing the gain on the detector amplifier.

Reading the absorbance of the unknown under these conditions of virtual scale expansion will often yield improved precision at high analyte concentrations. Even greater precision can be achieved by "pinning down" the infinite absorbance (0% transmittance) end of the scale with a synthetic standard prepared above the level of the unknown and adjusted to zero transmittance with the dark current control. While such techniques can improve precision significantly at high absorbance readings, they have limitations and should not be considered a substitute for good gravimetric or volumetric procedures, which excel at high analyte concentrations.

Multiple-component measurement is often feasible by reading absorbances at different areas of a test solution's spectrum. The technique is more frequently applied in quantitative organic analysis by infrared spectrophotometry, but it has also been usefully applied to metal analysis by UV/visible spectrophotometry (see example below). It is usually the case that the absorbance peaks of the components are not fully resolved from each other. That is, for a two-component system, A and B, A contributes some absorbance to B's absorbance peak at wavelength, λ_B, and B contributes some absorbance to A's absorbance peak at λ_A. With this situation, we prepare four calibration curves: A at λ_A, A at λ_B, B at λ_A, and B at λ_B; then we measure the unknown at λ_A and at λ_B. Let us here assume that all four calibration curves pass through the origin. In this case we can write

$$A_A = C_A S_{AA} + C_B S_{BA}$$

$$A_B = C_A S_{AB} + C_B S_{BB}$$

where

A_A = the unknown's absorbance at λ_A,
A_B = the unknown's absorbance at λ_B,
C_A = the concentration of A in the unknown,
C_B = the concentration of B in the unknown,
S_{AA} = the slope of A's calibration curve at λ_A,
S_{BA} = the slope of B's calibration curve at λ_A,
S_{AB} = the slope of A's calibration curve at λ_B, and
S_{BB} = the slope of B's calibration curve at λ_B.

All the quantities are known values except C_A and C_B. Their values can be found by solving these two simultaneous equations in two unknowns.

The process can sometimes be extended to a three-component system; however, beyond that, manual data manipulation becomes impractical. With computer-controlled diode array instruments that store the entire spectrum in memory, it is possible to calculate good approximations for many components by using software that applies iterative approximation techniques to a great many wavelengths.

Chemistry for Spectrophotometric Determinations

Up to this point we have confined the discussion to the measurement step itself. But before listing some illustrations, we should include a few remarks about the how and why of what we are measuring. There are thousands of compounds and complexes that are strongly colored or strongly UV-absorbing, but only a small percentage find utility in spectrophotometric methods. Still, this leaves quite a large number of specific and nonspecific reagents to sort through in selecting a suitable chromophore. Three texts can be unreservedly recommended in this regard: *Colorimetric Determination of Traces of Metals* by E. B. Sandell, 3rd ed., Interscience Publishers, New York, 1959, which is a classic and in its day an exhaustive treatment of its subject; *Colorimetric Determination of Nonmetals*, D. F. Boltz, Ed., Interscience Publishers, New York, 1958; and *The CRC Handbook of Organic Analytical Reagents* by K. L. Cheng, K. Ueno, and T. Imamura, CRC Press, Boca Raton, FL, 1982. Most questions concerning the spectrophotometric determination of the components of metals and alloys can be answered by consulting one or more of these books.

Table 13-1 lists some frequently utilized spectrophotometric reagents, the analytes they are often used for, and the recommended wavelength where measurements are made. In selecting a spectrophotometric approach, the analyst must keep a careful eye to a number of important parameters. If these are not fully described in the literature associated with a new method, he must do the experiments required to define them. Many of these hinge upon the *specificity* of the reagent. How many elements besides the analyte form colored species with it? How likely are these elements to occur in the intended sample matrix? Also, does the sample matrix contain elements that are likely to form turbidity in the measured solution? Are there simple chemical separation schemes for isolating the analyte that will not interfere with the color reaction?

Masking techniques are another alternative for dealing with interferences. These consist of the addition of one or more complexing agents to bind with problem matrix elements so that they do not react with the color reagent or precipitate in the solution. Compounds of cyanide, citrate, tartrate, oxalate, pyrophosphate, or chelating agents like EDTA are common masking agents used in many methods. The specific ones cho-

TABLE 13-1—Selected spectrophotometric methods.

Element	Reagent	Wavelength, nm	Reference	Remarks
Aluminum	8-Hydroxyquinoline	390	Chloroform	Extract after isolation
Antimony	Brilliant Green	645	Toluene	Extract after masking (pyrophosphate)
Arsenic	Molybdate	850	Water	Distill with HCl/HBr first
Boron	1,1-Dianthrimide	620	Sulfuric acid	Incubate at 100°C to develop color
Chromium	Diphenylcarbazide	540	Water	Good for tramp levels
Cobalt	Nitroso-R-salt	520	Water	ZnO separation common
Copper	Neocuproine	455	Chloroform	Extract after evolving Cr
Iron	1,10-Phenanthroline	510	Water	Reduce Fe; remove Cu
Lead	Dithizone	520	Chloroform	Extract after masking (cyanide)
Manganese	*meta*-Periodate	545	Water	Background: destroy color with NO_2^-
Molybdenum	Thiocyanate	475	Butyl acetate	Reduce Fe and Mo with $SnCl_2$
Nickel	Dimethylglyoxime	465	Water	Oxidizing conditions; extract with $CHCl_3$, then back extract
Niobium	Hydrogen peroxide	362	Sulfuric acid	High Ti interferes
Phosphorus	Molybdate	830 (650)	Water	Reduce with hydrazine sulfate
Silicon	Molybdate	815	Water	Extract with $CHCl_3$, reduce, then back extract
Tantalum	Pyrogallol	415	Water	Stabilize with tartrate
Titanium	Diantipyrylmethane	390	Water	Filter insolubles, ignite, fuse, and recombine
Tungsten	Dithiol	635	Butyl acetate	Extract after removing Mo

sen must, of course, be compatible with the intended chemistry.

Another important method parameter is the *blanking* approach required. All spectrophotometric methods have a cell blank if the cuvettes used for the reference and the test solution are not perfectly matched. This often-neglected step is simply accomplished by filling all the cells with the reference solution, adjusting the reference to zero absorbance, and reading the other cells against it. Much more important are the sample blank, that is, the test solution minus the color reagent; and the reagent blank, the reagents minus the sample. One or both of these may represent a significant part of the total absorbance, and it behooves the analyst to be aware of the relative importance of these blanks in each method.

If a blank reading is very significant, it is wise to average multiple blanks for the best accuracy. In a few methods, it is possible to easily and accurately measure the combined sample and reagent blank by destroying the colored complex after its absorbance is measured. Another important method parameter is color development time. Some reagents form a stable colored complex instantly, while others may require an hour (or incubation at a fixed temperature for a fixed time). And yet another parameter is the color stability once formed. Some colored species must be measured within a short window of time, while others can be measured one day and rechecked the next morning.

Important Details

It is important that the laboratory maintain a regular program of wavelength and absorbance checks on spectrophotometric equipment. This can consist of a wavelength scan (manual or automatic) using a standard holmium oxide glass cell (or other absorbance wavelength standard) to confirm that the maxima occur at the correct wavelength readings. Also, measurement of a graded series of standard filters will confirm measured absorbance response. Routine measurements in nonpolar solvents after a solvent extraction usually require some means of screening out errant water droplets from the light path. Separatory funnel stems are often stuffed with cotton or a rolled piece of filter paper. These are better for this purpose than Pyrex wool, which tends to contaminate cuvettes with tenaciously adhering fibers. Collection vessels—often a volumetric flask—may contain a pinch of anhydrous sodium sulfate to react with and hold any water that makes it that far.

Methods that utilize a sulfuric acid medium are a special problem. The analyst is confronted with filling a cuvette with a small opening and wiping the optical surfaces free of any drips without getting burned. The best approach is to keep a cloth or a paper towel thoroughly soaked with water, as well as a supply of dry lint-free wipers, close at hand. The optical surfaces are first wiped with the wet towel, then dried with the wipers.

Below 400 nm, quartz cells (with a much lower UV cut-off absorbance than borosilicate glass) should be used. All cuvettes should be thoroughly cleaned immediately after use. The cleaning must be tailored to the solutions used, of course, but heavily contaminated cells often yield to a 1:1:1 HCl: ethanol:water mixture.

Determination of Manganese (up to 1.6% Mn)

Weigh a 0.1-g sample of steel into a 250-mL Erlenmeyer flask . Dissolve in any combination of HCl and HNO_3. Add 5 mL of $HClO_4$ and heat to fumes of $HClO_4$. Cautiously, add HCl, dropwise, while fuming to evolve chromium. Cool, add 20 mL of water, and then 25 mL of H_2SO_4/H_3PO_4 mixture

(500 mL water + 500 mL H_3PO_4, cool, add cautiously, with stirring and cooling, 1000 mL H_2SO_4), then 25 mL of potassium *meta*-periodate solution (16 g KIO_4, 10 mL HNO_3, dilute to 2 L with water). Boil for 3 min and cool to room temperature. Transfer to a 100-mL volumetric flask, dilute to the mark, and mix well. Measure the absorbance versus water at 545 nm.

Add three drops of 10% (w/v) sodium nitrite solution to the cuvette. Mix by inverting, using a plastic finger cot, and then measure the absorbance of this blank at the same wavelength. Subtract the second reading from the first and calculate the manganese concentration from the calibration curve. [Note: For the most accurate work, it is best to use an aliquotting scheme with larger sample weights and to take separate sample aliquots for the sample reading and the blank.]

Determination of Copper

Weigh a steel sample containing 0.05 to 1.5 mg of copper into a 250-mL Erlenmeyer flask. Dissolve in any combination of HCl and HNO_3. Add HF dropwise to volatilize silicon. Cool, add 15 mL $HClO_4$, and heat to fumes of $HClO_4$. Cautiously, add HCl dropwise to the fuming solution to volatilize chromium. Fume until the volume has been reduced to approximately 10 mL. Cool, add 7 mL of water, and swirl to dissolve the salts. Add 1 mL of HCl and transfer the solution to a 100 or a 250-mL volumetric flask (depending on the copper level). Dilute to volume and mix.

Dry filter some of the solution into a 100-mL beaker and remove an aliquot of the filtrate containing 0.01 to 0.30 mg of copper, transferring it to a 150-mL beaker. To the aliquot add 5 mL of hydroxylamine hydrochloride solution (100 g/L) and 10 mL of citric acid solution (300 g/L). Stir well and adjust to pH 5.0 ± 0.1 with 1:1 NH_4OH: H_2O. Add 10 mL of neocuproine solution (0.1 g in 100 mL of absolute ethanol). Transfer the mixture to a 125-mL separatory funnel and add 15 mL of chloroform. Extract for 30 s and drain the (lower) organic layer through cotton into a 50-mL volumetric flask containing 7 mL of absolute ethanol. Add 10 mL of chloroform to the separatory funnel and extract again for 30 s. Drain the organic layer into the same flask. Discard the aqueous layer through the top and wash the separatory funnel and funnel stem with absolute ethanol into the volumetric flask. Dilute the flask to the mark with ethanol and mix. Read the absorbance at 455 nm versus chloroform. Subtract a reagent blank from the readings and calculate the percent copper by reference to a calibration curve.

Simultaneous Determination of Niobium and Titanium

Weigh a 0.2-g steel sample into a 250-mL beaker. Add (in this order) 25 mL of HCl, 5 mL of HNO_3, 25 mL of water, and 25 mL of solvent mix (400 mL H_3PO_4 + 300 mL water, stir well and cool, then cautiously, with stirring and cooling add 120 mL H_2SO_4; dilute to 1 L, cool, and mix). Heat slowly to dissolve the sample, then bring to light fumes. Fume for 1 min (no longer), cool for 1 min, then cautiously add 25 mL of dilution mix (cautiously with cooling and stirring, add 350 mL of H_2SO_4 to 600 mL of water; dilute to 1 L, cool, and mix).

Transfer to a 50-mL volumetric flask using 3.0 mL of HCl and 10.0 mL of stannous chloride tartaric acid solution (dissolve 88 g $SnCl_2 \cdot 2H_2O$ in 60 mL of HCl with warming; dissolve 50 g tartaric acid in 100 mL of water with warming; combine the two solutions and dilute to 250 mL with water) and enough dilution mix to dilute to the mark when cool. Mix well and transfer a 1.0-mL aliquot to each of two dry 50-mL beakers. To one beaker add 25.0 mL of H_2SO_4 and to the other add 25.0 mL of hydroquinone solution (15.0 g of hydroquinone + 450 mL H_2SO_4 in a dry 500-mL volumetric flask; add a stirring bar and close with a glass stopper; cover with a light shield, and stir magnetically until dissolved; remove the stir bar, dilute to the mark with H_2SO_4, mix well, and store in the dark. Prepare 24 ± 1 h before use in all cases).

Swirl to dissolve the white precipitate that forms and allow the solutions to stand for 10 min. Read the absorbance at both 400 and 500 nm versus H_2SO_4. Subtract the cell blank, the sample blank, and the reagent blank (prepared by substituting 1 mL of water for the sample aliquot) from the test solution reading at each wavelength. Assuming no intercepts, if S_A is the slope of the niobium calibration curve at 400 nm, S_B is the slope of the niobium calibration curve at 500 nm, S_C is the slope of the titanium calibration curve at 400 nm, and S_D is the slope of the titanium calibration curve at 500 nm, then

$$S_A W_{Nb} + S_C W_{Ti} = A_{400}$$

$$S_B W_{Nb} + S_D W_{Ti} = A_{500}$$

where

W_{Nb} = the weight of niobium in the final sample aliquot,
W_{Ti} = the weight of titanium in the final sample aliquot,
A_{400} = the corrected absorbance reading for the test solution at 400 nm, and
A_{500} = the corrected absorbance reading for the test solution at 500 nm.

It is a simple matter to solve these simultaneous equations for W_{Nb} and W_{Ti}. If tungsten is present, the approach fails because it absorbs at both wavelengths. However, if titanium is absent, niobium and tungsten can be determined in an identical manner. All three components can be analyzed by an elaborate scheme that involves separation of the tungsten by coprecipitation with molybdenum using alpha-benzoinoxime.

ATOMIC ABSORPTION

Ground state atoms absorb light just as molecules do. However, while molecules can be studied in solution, for analytical purposes the absorption of light by atoms must be studied in flames, vapors, and plasmas. Some of these are high-energy phenomena, where atoms tend toward excited and ionized states that *emit* light. To the extent possible, instruments and analytical schemes are designed to suppress such phenomena while maintaining an abundant population of ground state atoms. The seminal work in this field was published in 1955 (Walsh, A., *Spectrochimica Acta*, Vol. 7, 1955, p. 108); however, commercial instruments did not appear until the 1960s.

By now the basic principles of atomic absorption are familiar to most analysts. A high-intensity light source com-

prised of the emission spectrum of the element of interest is produced by either a hollow cathode or an electrodeless discharge lamp. Such lamps are designed to emit sharp spectra with narrow lines and a low background. The electrodeless discharge lamp (EDL) is a more intense light source than the hollow cathode lamp (HCL)— this usually results in better sensitivity since the detector amplifier can be operated at lower gain. However, EDLs are only available for a small number of elements (notably As, Bi, Ge, Hg, Pb, Sb, Se, Sn, Te, Tl, Cd, Zn, Ti, P, and certain alkali metals). HCLs, on the other hand, are available for most elements.

Some combinations of elements are also available in a single HCL, saving cost and lamp warm-up time. But these multi-element lamps occasionally generate difficulties due to spectral overlaps, and their intensities tend to be lower than that of single-element lamps. Whatever source is used, the light beam generally first passes into a mechanical chopper, such as that described above for a dual-beam UV/visible spectrophotometer. One portion of the light passes through the atomizer region (a flame, a graphite furnace, or perhaps a mercury cold vapor cell) where ground state atoms of the analyte absorb the characteristic energy.

The other portion of the light avoids this region. Another chopper alternately passes the reference and sample beams into a monochromator, where the analytical wavelength is selected and passed to a photomultiplier tube and its associated demodulating amplifier. Such an arrangement compensates for noisy, fluctuating source lamps (but not for noise from the flame or from furnace wall emission). The demodulator circuit generates an output signal proportional to the difference between the sample and reference beams, which is in turn proportional to the analyte concentration. There are, of course, numerous other instrument configurations.

Calibration Modes

Atomic absorption has a limited linear dynamic range when compared to some other techniques, like ICP-OES, but with careful multi-point calibration the nonlinear portion of the response curve can be utilized. Calibration curve quantification, either manual or by means of an "on-board" computer, is probably the most commonly used approach. However, if the analyst is willing to confine his work to the linear response concentration region, some additional options are open to him.

The *method of additions* is an extremely useful approach, especially in the presence of a heavy matrix or for trace level work with the graphite furnace atomizer. Two conditions are critical to this tactic: (1) the analyst must know the extent of the linear range so that the sample solutions all remain within it; and (2) a representative analyte-free blank must be available. In practice, one spikes several identical portions of the sample solution with exactly measured increments of pure analyte and measures these along with a representative blank.

The blank-corrected values are plotted versus concentration on linear graph paper divided into a positive and negative quadrant with corrected absorbance on the ordinate and the concentration of analyte running positive and negative from the centered origin on the x -axis. The added concentrations of analyte are plotted in the right quadrant, and the line is extended to $y = 0$ in the left quadrant of negative x-values. The negative x-value at $y = 0$ represents the unspiked analyte concentration in the test solution.

It is a relatively simple matter to automate this calculation using a computer or a statistical pocket calculator. Just perform a least-squares fit of the line and solve the resulting equation for $y = 0$. A very powerful simplified version of the same approach (sometimes referred to as the *spiking technique*) is simply a one-point method of additions. One merely splits the dissolved test portion into two equal volumes (or begins with two identical test portion weights), spikes one (often at about one half of the expected level of analyte concentration), and dilutes both to the same volume. This approach works well for both flame and graphite furnace work, although, of course, it is not as rigorous as the true multipoint method of additions.

The rationale behind both of these approaches is to compensate for matrix effects, which can be significant in certain complex alloy systems. If the analyst wishes to test for matrix effect, he can perform the following experiment: Add a series of increments of analyte to pure water, measure the absorbances, and draw the curve. Then add the same series of increments of analyte to the sample solution, measure the absorbances, and draw the curve on the same graph paper sheet. If the two curves are parallel, the sample shows no matrix effect. But if the curves are not parallel, a matrix effect exists with the sample solution. Some workers have also advocated determining the blank by a method of additions, but this approach can sometimes lead to seriously erroneous blank values. It is usually best to determine the blank directly from a synthetic matrix, using the average of several replicates.

The *bracketting* technique is a useful calibration approach at analyte concentrations above 1%, where a higher level of precision is always required. Prepare two standards, one at about 5% (of the amount present) *below* the level of analyte expected and one about 5% (of the amount present) *above* the level of analyte expected. The solutions are all diluted to the same final volume, which is selected to yield readings within the linear range and generally between 0.2 and 0.5 absorbance units. The solutions are measured in order of increasing concentration to effectively negate any memory effects. The blank-corrected absorbances can then be quantified graphically or by means of a simple algebraic expression (see Fig. 13-1).

Element Sensitivities

It is probably safe to say that a completely satisfactory theoretical explanation of the characteristic AA sensitivity of each element has not yet been formulated. There *is* considerable insight in this area, however, and trends can be delineated. Elements of lower atomic weight tend toward greater sensitivity than high atomic weight elements because under identical conditions there tends to be a higher population of light elements in the analytical light path. There are certain elements for which good ground state resonance lines do not exist except in a region obscured by molecular bands. Other elements have an abundance of low-lying energy states just above the ground state. Under any practical analytical condition, a significant portion of the analyte is distributed among these states and thus does not absorb at the ground

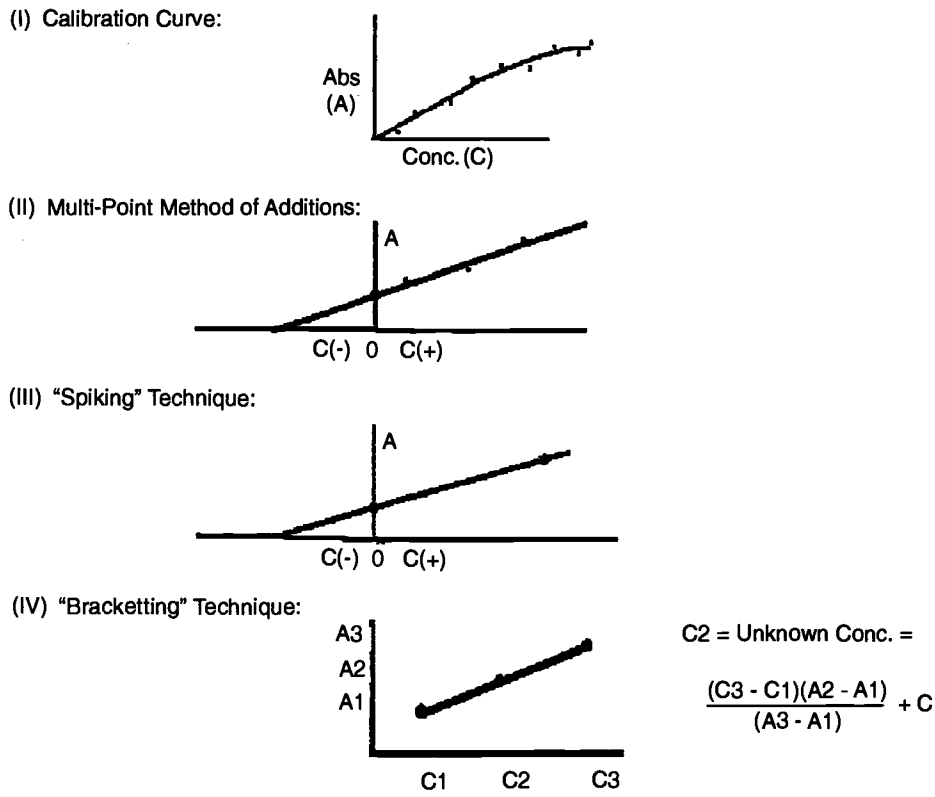

FIG. 13-1—Atomic absorption calibration options.

state resonance line. Many of the rare earth elements, for example, are very insensitive for this reason.

Also, there are a number of elements that tend to form thermally resistant oxides, nitrides, or carbides in either a flame or a graphite furnace atomizer. Examples of this effect are the poor sensitivities for niobium, tantalum, hafnium, zirconium, tungsten, and boron. It is interesting to note that atomic absorption becomes practical for many of these elements with an atomic absorption instrument fitted with a gas-jet-assisted plasma discharge lamp. In this device, a solid sample is sputtered by argon ions in the absence of any oxygen, nitrogen, or carbon.

Table 13-2 lists the relative sensitivities of the elements by atomic absorption of the more conventional flame and graphite furnace configurations. A more conventional means of expressing sensitivity is the concentration (in ppm), which produces 1% absorbance (0.0044 absorbance units). Such values vary between instruments and can be found in the manufacturer's literature.

Interferences

Like so many emerging methodologies, atomic absorption went through a period when it was touted as interference free. In fact, to this day it remains as one of the better instrumental techniques in this regard. But it is *not* interference free. Actually, several different classes of interferences can be delineated. *Physical effects* are one common source of error that leads to erroneous results. If the density, viscosity, and surface tension of the sample solution and the calibration solutions are not approximately the same, the transport rate into the flame or the deposition and subsequent atomization in the graphite furnace will differ, leading to error. Matching the sample matrix with synthetic standards is one solution to this problem, the method of additions is another. The simplest course is to dilute the sample until the physical effect becomes negligible, but this is only feasible where sufficient analyte sensitivity can be retained.

Chemical effects are interferences that result in a decrease in analyte signal. They are caused by the formation of compounds or complexes in the sample solution that reduce the population of ground state analyte atoms produced by the atomizer. A classic example is the reduction of calcium absorbance in an air/acetylene flame caused by the presence of phosphate in the sample solution. There are several different ways of dealing with interferences in this category. The simplest, which sometimes works, is to raise the atomization temperature. For example, phosphate has no effect on calcium in the hotter nitrous oxide/acetylene flame. Another approach is to add to both the sample and the calibration standards a reagent that forms a soluble complex with the analyte which is more stable than the interfering complex or compound but that releases the analyte thermally as a ground state atom. Similarly, a reagent could be added which reacts with the interferent, releasing the analyte. *Matrix modifiers* in graphite furnace AA are a group of reagents that are used to overcome chemical effects from undesirable side reactions, sometimes by forming a volatile species with the interferent that is removed during the "char" cycle before atomization occurs.

Ionization effects occur when analyte atoms are excited past the ground state to the free ion form. The formation of analyte

TABLE 13-2—Relative sensitivity of the elements by atomic absorption (*Note*: 0 = worst sensitivity; 4 = highest sensitivity).

Element	Wavelength, nm	Relative Sensitivity	Recommended Flame Oxidizer
Aluminum	309.3	3	Nitrous oxide
Antimony	217.6	2	Air
Arsenic	193.7	3	Air
Barium	553.6	3	Nitrous oxide
Beryllium	234.9	4	Nitrous oxide
Bismuth	223.1	2	Air
Boron	249.7	0	Nitrous oxide
Cadmium	228.8	4	Air
Calcium	422.7	4	Air
Cerium	[a]...	0	[a]...
Cesium	852.1	3	Air
Chromium	357.9	3	Nitrous oxide
Cobalt	240.7 (242.5)	3	Air
Copper	324.8	3	Air
Dysprosium	421.2	2	Nitrous oxide
Erbium	400.8	2	Nitrous oxide
Europium	459.4	2	Nitrous oxide
Gadolinium	407.9	0	Nitrous oxide
Gallium	287.4	2	Nitrous oxide
Germanium	265.1	2	Nitrous oxide
Gold	242.8	3	Air
Hafnium	286.6	0	Nitrous oxide
Holmium	410.4	0	Nitrous oxide
Indium	303.9 (325.6)	3	Air
Iridium	264.0	1	Nitrous oxide
Iron	248.3	3	Air
Lanthanum	550.1	0	Nitrous oxide
Lead	283.3	3	Air
Lithium	670.8	4	Air
Lutetium	336.0	0	Nitrous oxide
Magnesium	285.2	4	Air
Manganese	279.5	3	Air
Mercury	253.7	2	Air
Molybdenum	313.3	3	Nitrous oxide
Neodymium	463.4	0	Nitrous oxide
Nickel	232.0	3	Air
Niobium	334.4	0	Nitrous oxide
Osmium	290.9	0	Nitrous oxide
Palladium	247.6	2	Air
Phosphorus	213.6	0	Nitrous oxide
Platinum	265.9	2	Nitrous oxide
Potassium	766.5	4	Air
Praseodymium	495.1	0	Nitrous oxide
Rhenium	346.0	0	Nitrous oxide
Rhodium	343.5	3	Air
Rubidium	780.0	3	Air
Ruthenium	349.9	2	Air
Samarium	429.7	1	Nitrous oxide
Scandium	391.2	0	Nitrous oxide
Selenium	196.0	2	Air
Silicon	251.6	2	Nitrous oxide
Silver	328.1	4	Air
Sodium	589.0 (589.6)	4	Air
Strontium	460.7	4	Air
Tantalum	271.5	0	Nitrous oxide
Tellurium	214.3	3	Air
Terbium	432.6	0	Nitrous oxide
Thallium	276.8	3	Air
Thullium	371.8	3	Nitrous oxide
Tin	286.3	2	Nitrous oxide[b]
Titanium	365.3 (364.3)	2	Nitrous oxide
Tungsten	255.1	0	Nitrous oxide
Uranium	358.5 (351.5)	0	Nitrous oxide
Vanadium	318.3 (318.4, 318.5)	2	Nitrous oxide
Ytterbium	398.8	3	Nitrous oxide
Yttrium	410.2	0	Nitrous oxide
Zinc	213.9	4	Air
Zirconium	360.1	0	Nitrous oxide

[a]No absorbance has been measured.
[b]H_2/air shows better response but more interferences.

ions means that less analyte is available to absorb the ground state resonance line, and the analytical response is diminished. The best solution to this problem is to add to both sample and standards a fixed amount of an ionization suppressor reagent. This consists of an easily ionized element (sodium, strontium, or lanthanum solutions are often employed), which is, to some degree, ionized in place of the analyte.

Spectral effects consist of two types: atomic line interferences due to nonanalyte absorbance lines from the sample matrix components (or nonanalyte emission lines from the other elements in a multi-element lamp) and molecular band interferences and other forms of nonspecific absorbance (smoke, light scatter) that contribute to the spectral background. In the case of atomic line interferences, narrowing the slit or using an alternate resonance line usually solves the problem, although these remedies may decrease sensitivity. Of course, if the problem is a multi-element lamp, one can always substitute the single-element version.

If the problem is with the sample matrix, one can usually chemically separate the analyte from the offending element. Line interferences are comparatively rare in atomic absorption work. Nonspecific and molecular absorbance are much more common, but they can be corrected for using a number of different techniques, including the continuum-source, Zeeman, and Smith-Hieftje approaches.

In the *continuum-source background correction* system, a tungsten iodide lamp (for the visible region) or a low-pressure deuterium or hydrogen lamp (for the UV region) is used to produce a noncharacteristic (line-broadened and overlapped) light beam that a chopper sends through the atomizer in pulses. These pulses alternate with pulses of a line source (the HCL or EDL). Smoke, salt particles, and molecular vapors absorb both beams equally (provided that the beams have been initially balanced in intensity), so that the difference in the two sets of signals is the background-corrected analyte absorbance.

It should be noted that some atomic absorption *does* occur in the continuum beam since it does include the resonance wavelength, but it is a negligibly small fraction of the total absorption and has no influence on the correction process. Continuum-source background correction, unlike the other commonly employed schemes, results in no sensitivity loss for any analyte provided that the continuum beam and the line source beam are precisely aligned. Achieving such an exact alignment, however, is not always easy with the design of most commercial instruments. Continuum source correction presumes that the background is uniform across the bandpass of the slit width setting. If "structured" background occurs within the spectral bandpass (say, emission lines from a matrix element), then another correction system may be a better choice.

The *Zeeman background correction* system is not one, but several, instrumental schemes for compensating for background. The Zeeman effect, which describes the influence of a magnetic field on a beam of light, was sought in vain by Michael Faraday in 1862, but discovered in 1896 by Pieter Zeeman using more sensitive equipment. In the normal Zeeman effect, spectral lines are split into three components: the *pi line*, which remains at the original wavelength and is linearly polarized parallel to the magnetic field direction, and two *sigma lines*, which are displaced to the right and left an

amount proportional to the magnetic field intensity (e.g., about 0.1 A for 8 kG) and which are polarized perpendicular to the magnetic field direction. However, with many elements (e.g., Fe, Ni, Cu, Cr, and Hg) an anomalous Zeeman effect occurs in which, instead of two, an entire array of proportionately displaced sigma lines is generated.

The Zeeman effect is utilized in AA background correction schemes in a number of quite distinct designs. In one configuration, the atomizer is subjected to the magnetic field, which is cycled on and off at 60 times per second. The line source beam exiting the atomizer passes through a stationary linear polarizer, which passes the sigma components and rejects the pi component. When the magnet is on, the sigma components are shifted away from the resonant wavelength, where atomic absorption occurs and only the background is measured. When the magnet is off, both atomic absorption and background absorption are measured. Electronic subtraction of the two signals yields a background corrected output at the analytical wavelength.

Other configurations place the magnet around the line source rather than around the atomizer (these are termed "source-shifted" systems). Here, the pi components of the source are absorbed by both analyte and background, while the sigma components are absorbed only by the background. Some designs use a rotating polarizer to detect first one, then the other signal. Other arrangements use a Wollaston prism to direct the pi and sigma components to separate photomultipliers.

The Zeeman correction approach suffers some loss of sensitivity, and calibration curves tend to have a reduced linear region. Curves also "roll over" at high concentrations so that the same absorbance is obtained from two distinct analyte concentrations—one high and one low. The advantages tend to outweigh these problems, however. The signal-to-noise ratio is superior to most other systems, resulting in better precision and lower detection limits. The correction is generally very accurate, and structured background presents no special problem.

A third background correction system in commercial use is the *Smith-Hieftje* design. Here, a hollow cathode lamp is momentarily pulsed at a high input current level so that it produces a burst of line-broadened, self-absorbed continuum radiation. A cold atom cloud accumulates in front of the cathode, absorbing the intense line spectra emitted from the back of the cathode. Such continuum radiation is absorbed by the background, while the low current, narrow-line spectrum is absorbed by both the analyte and the background. Electronically subtracting the two signals yields the corrected absorbance. This approach is simple and requires less exact alignments than conventional continuum-source correction. Not all elemental line sources broaden effectively when their hollow cathode lamp is pulsed, however. For these cases, there is a significant loss of sensitivity.

Flame Atomic Absorption

Flame atomization atomic absorption was the first commercial form that this technique took, and it remains important as a comparatively inexpensive supplement and alternative to ICP-OES. The fuel is usually acetylene; the oxidizer is air or nitrous oxide. Occasionally, a hydrogen/air or an argon-sheathed hydrogen flame is used for special applications. The pre-mix burner, in which the gases are mixed before reaching the burner head, has become standard for most instruments. There are a number of different types of nebulizers These all utilize gas flow to aspirate the sample through a capillary and a cross-flow or impact bead to nebulize the solution, and they all incorporate a "spoiler" or other arrangement for rejecting all but the finest droplets.

The need for fine droplets is explained by the fact that within a relatively brief time over a short trajectory the droplets must be dried to minute salt crystals, which must then be vaporized into dissociated ground state atoms. Large droplets that did not completely vaporize would lead to burner clogging with the attendant danger of a flashback explosion as well as to erroneous measurements. Throwing away such a significant portion of the sample reduces the sensitivity, but increases the accuracy of the measurements, especially in the presence of a heavy matrix such as a dissolved metal alloy.

With a flame AA aspirating liquid, one is measuring a rate. Such signals can be conveniently filtered of a-c noise, making the readings more reproducible than is usually the case with discrete peak measurements, such as those measured in electrothermal AA. Each gas mixture utilizes a specially designed burner. The air/acetylene flame operates at about 2500°K and is suitable for all of the easily vaporized elements. The nitrous oxide/acetylene flame is about 500°K hotter and is usually reserved for refractory oxide-forming elements. Because of the greater tendency of this mixture to flashback, the flame is lit with air and switched over to nitrous oxide. When work is complete, the flame is switched back to air before it is extinguished.

Electrothermal Atomic Absorption

When one considers how little of the sample actually reaches the analytical measurement region in flame AA, it is no surprise that atomic absorption is in principle an exquisitely sensitive technique. When an instrument is configured to take full advantage of that inherent sensitivity, some truly remarkable detection limits can be achieved. Of the many designs developed, commercial electrothermal instruments have largely settled on the Massmann furnace used with the L'vov platform.

A hollow graphite tube (often manufactured of the thermally resistant pyrolytic graphite) is held in graphite cones connected to water-cooled copper contacts. The L'vov platform is a shallow boat (manufactured from the same material) that rests in the bottom center of the tube. The entire assembly is enclosed in a sealed chamber with optical quartz end windows to allow passage of the line source beam. Argon gas enters at the sides and exits through an aperture in the center of the tube where the sample (generally 5 to 40 μL) is injected by an auto-sampler.

In analyte-shifted Zeeman systems, the furnace is partially encircled by a magnet assembly. The furnace is programmed through a heating cycle consisting of a drying step to desolvate the sample, a "char" step to remove interfering volatiles and to place the analyte in a form suitable for atomization, and finally an atomization step wherein the ground state atom cloud is created and atomic absorption occurs. This thermal program may have a number of additional features:

precise rate-of-rise ramping between steps, gas flow interrupts (commonly, during the "char" step), and injections of reactive gases (e.g., oxygen or air to facilitate char or hydrogen to reduce oxides to metals).

The purpose of the L'vov platform is to delay the atomization of the analyte until the furnace atmosphere has achieved a high and stable temperature. For many elements, this discourages "memory" effects due to condensed analyte at the tube ends and leads to improved peak shape, sensitivity, and precision. With the graphite furnace atomizer, what is being measured is a discrete event—the atomization and atomic absorption of a large part of the total sample aliquot. The best results with the L'vov platform are usually from peak area, while atomization directly from the furnace wall with its faster atomization yields better results from peak height.

As mentioned above, there are numerous *matrix modifiers* that have been applied in furnace work. Chloride in the sample aliquot is a particular problem due to the formation of volatile analyte chlorides that are partially lost during the char cycle unless ammonium nitrate or diammonium EDTA is added. In both cases, with these additions volatile ammonium chloride is evolved away during the char step, leaving the analyte in the furnace in a form more amenable to atomization.

Nickel (generally in the form of nickel nitrate) is a valuable addition in many determinations and is particularly useful in tramp work with iron-base alloys. Compounds such as nickel selenide have favorable atomization characteristics. Magnesium nitrate and combinations of palladium and magnesium nitrate are highly advocated for numerous determinations. The choice of matrix modifier and the exact conditions, rates, plateau times, and temperatures of the program, including the choice of platform or wall atomization, are all highly empirical functions. The lore associated with electrothermal atomic absorption has begun to rival that associated with gas chromatography. However, instrument manufacturers provide a great deal of guidance to ease the burden of methods development.

Since the emergence of this technology in the 1970s, there have been various attempts to directly determine solids (particularly metal alloy chips), some of which have met with reasonable success. However, it must be remembered that the use of such minute samples as those required by a solids GFAA approach requires an extremely homogenous sample material if the results are to be truly representative.

Other Forms of Atomic Absorption

In 1939, atomic absorption was first described as an analytical technique for the detection of mercury vapor (Woodson, T. T. in *Revue of Scientific Instruments*, Vol. 10, 1939, p. 308), and to this day the cold vapor technique remains a highly sensitive and useful approach for that element. The chemically generated elemental mercury vapor is passed into a quartz cell in the instrument light path.

Hydride techniques came much later and have yet to be fully accepted due to precision problems. In hydride generation, a solution of sodium borohydride is used to generate selenium, arsenic, antimony, germanium, bismuth, lead, and tin hydride gases, which are passed by a flow of inert carrier gas to a flame-heated quartz tube in the light path or in other configurations directly into the burner flame itself. In some schemes, the hydrides are frozen out in a cold trap, which is subsequently heated rapidly to create an analytical signal pulse. Such systems produce extremely sensitive responses, but, unfortunately, often lack good reproducibility.

The use of a glow discharge sputtered source with solid samples is a recent advance since it allows sensitive determinations of boron, zirconium, and other elements that have been closed to AA determination. Since the argon-sustained plasma jet is free of oxygen, nitrogen, and carbon, refractory compound-forming elements have been opened to the advantages of AA determination. The disadvantage of a solids approach remains, however— the sample must be homogenous since only the solid surface will be sampled.

Chemistry for Atomic Absorption Determinations

There are those who believe that the only chemical manipulations involved in atomic absorption analysis are those reactions involved in the dissolution of the sample material. That perspective is unfortunate since the measurement technique can be enhanced substantially by the use of isolation and preconcentration steps, which will greatly extend its usefulness. A simple mercury cathode electrolysis can extend flame AA sensitivities so that 0.001% aluminum or titanium are easily quantified. Similarly, the determination of tin can be extended to 0.001% and below by aspirating MIBK/TOPO extracts into a flame AA.

Similar approaches are possible with electrothermal techniques, extending what are already high sensitivities into new realms. One important note that the analyst must remain aware of is that the new highly sensitive techniques do not usually preclude the application of old enhancement protocols. Thus, the potential remains to extend new approaches even beyond their instrumental promise. It is not always wise to think first in these terms, but the rapidly evolving requirements of material specifications mandate such contingency plans.

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