ANALYTICAL REVIEW

Spectrophotometric Methods—Part I

Calorimetry and UV-Vis Spectroscopy

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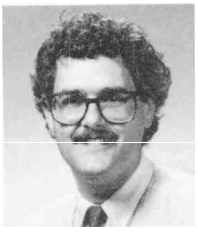

Up to now, the columns in this series have described the common, well-established methods usually lumped together and referred to as wet analytical techniques. These methods are characterized as relatively "low-tech" and low-cost. For many labs, wet techniques are perfectly adequate to provide the information necessary for process control. However, a growing number of shops are taking the plunge, opening their wallets and investing in a black box with bells and whistles. Is this a smart move? Which black box is best for the job? Beginning this month, we'll try to answer these questions while we slowly accelerate into the fast lane of instrumental analytical techniques.

The most common instrumental techniques found in process control labs are those depending on interaction of the analyte with energy in the electromagnetic spectrum. I'll use the term *spectrophotometric* to describe these methods, which are also referred to as various forms of spectroscopy. Whatever the tag, an understanding of these techniques requires a quick introduction to quantum theory.

Many visitors to plating shops are struck by the brightly colored baths, particularly those containing copper, nickel and chromium. It seems intuitively evident that for these analytes, the more concentrated the solution, the more intense the color. This observation has long been used to monitor rinse tanks visually. Unfortunately, though our eyes are able to distinguish subtle changes in color, they aren't calibrated to measure concentration.

The bath appears colored because of absorption of specific wavelengths of visible light by the components of the solution. Each molecule or ion has many distinct energy levels characteristic of that analyte. When we say that light (or any form of electromagnetic energy) is absorbed, we mean that part of the light has the correct amount of energy to cause a transition from one energy level to another. The specific amount of energy absorbed depends on the size of the gap between the analyte's energy levels. Spectrophotometric methods can be classified by the part of the electromagnetic spectrum having the right range of energy. Analytical techniques use virtually the entire spectrum, but this month our attention is focused on UV-visible spectroscopy.

Report card	UV-Visible Spectroscopy
acids/bases/pH	F
plating metals	B-
contaminant metals	D
common anions	C-
chelating agents	C-
plating additives	D
wastewater	B

The connection between the absorbance of light energy and the concentration of the absorbing analyte is provided by the Beer's Law equation:

$$A = I_0/I = ebc$$

where A is the absorbance, or the ratio of light intensity before (1.) and after (1) it passes through the sample, b is the distance light travels through the sample (contained in a transparent cell), c is the concentration of the absorbing analyte, and e is a constant. This constant is sometimes called the extinction coefficient although it is more properly known as the molar absorptivity.

Each analyte has a characteristic energy level gap corresponding to a particular wavelength of light. If the light source is tuned to that wavelength, the absorbance of the analyte is maximized, providing the greatest sensitivity to the analyte concentration. Commercial spectrophotometer are capable of tuning a desired wavelength by filtering out all other wavelengths. Light intensity is measured with a photomultiplier.

Optimum wavelength and molar absorptivity are unique for each analyte, but they are also extremely matrix dependent. The color differences between a cupric chloride etchant, an electroless copper bath and an acid copper bath illustrate this point. The optimum wavelength for a given type of solution environment can be found by looking for the maximum absorbance. There are reference tables giving values of the molar absorptivity, but these are based on standard solutions having little similarity to the complex mixtures found in plating baths.

Fortunately, the analyst doesn't need to know the molar absorptivity in order to use Beer's Law. The equation predicts a linear relationship between absorbance and analyte concentration. A calibration curve can be prepared by measuring the absorbance at the optimum wavelength for a series of standards with known concentration. The standard solutions should approximate the actual sample matrix as closely as possible. Although it takes only two points to define a line, at least three standards should be used to create the calibration curve to reduce experimental error. The standard concentrations should also bracket the expected sample concentration to avoid extrapolation. Once a calibration curve is available, the measured absorbance of an unknown sample can be quickly converted to analyte concentration.

Some sample preparation is often required prior to the absorbance measurement. At high concentrations (usually above one g/L), absorbance starts to fall below the Beer's Law line, indicating the upper limit of the calibration curve. This non-linearity means that samples containing high

concentrations of analyte must be diluted to the useful Beer's Law range. Samples at lower concentrations, such as rinse water or some wastewaters, can often be measured directly.

Analytes that are non-absorbing or weakly-absorbing in the UV-visible spectrum can be converted to a more useful form by introducing an organic ligand that binds to the analyte to create a strongly-absorbing complex. Calorimetric determination of chromium (VI) in wastewater, using diphenylcarbazone, is a modification of this strategy. Sub-ppm levels of chromium can be measured by this technique.

UV-visible spectroscopic methods are available for most of the common plating metals (copper, nickel, iron, chromium, zinc, cadmium, tin, lead) as well as for a handful of anions. Because of the nature of the energy transitions in this part of the spectrum, absorption of different analytes can have significant overlap. For this reason, samples should contain only one strongly-absorbing analyte. Sample preparation is usually easy, commercial instruments are relatively cheap, and a single analysis takes only a few minutes. Many procedures can be completely automated for high sample throughput.

Several modifications of this basic approach are common. On the high tech side, one can buy a scanning spectrophotometer that gradually steps through the UV-visible range, measuring the absorbance at each wavelength stop and plotting the resulting spectrum. The spectrum reveals the optimum wavelength for maximum analyte absorption. Some have suggested using the spectrum as a "fingerprint" of the sample to detect subtle changes in the solution. This approach has shown promise in real time sensor applications. Diode array spectrophotometer can obtain the entire absorbance/wavelength spectrum at once, without stepping.

On the low tech side, portable calorimetric kits are available for remote analysis. A water sample is mixed with a pre-measured portion of color-developing reagent specific for the analyte of interest. The color of the solution is compared with a reference card having printed bands corresponding to different analyte concentrations. This technique yields surprisingly accurate results—and the cost and ease of use can't be beat.

Next month, we'll take a look at two of the most powerful and versatile instrumental techniques available to the analytical chemist: atomic absorption and atomic emission spectroscopy. •

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