

Infrared Solves Some Unusual Problems for the Film Industry

Paul A. Wilks

Having recounted in my previous guest editorials some of the past history of the evolution of infrared instrumentation and how it has begun to move out of the laboratory into the real world of materials analysis (1, 2), I thought it might be interesting to describe three analytical problems

in a while there is a mix-up in the shop and we lose track of the film orientation, which could lead to a disaster if film with the wrong orientation is used in further processing.

“Can you provide us with some sort of equipment that will quickly tell us which side is which?”

We happened to have a Thunder Dome ATR attachment supplied by Thermo Spectra-Tech (Madison, WI), which was being evaluated for another purpose. We found that there was such a concentration of IR energy at the upper surface of the spherical element in the Thunder Dome that one needed only to press a piece of the film

“... Our extruder was functioning erratically, and we have produced several hundred rolls of film that may or may not have the correct thickness moisture barrier. How can we check these rolls to determine which has the correct barrier thickness and which doesn't?”

that came to us from the plastic film industry and discuss how infrared techniques solved them.

Wilks Enterprise was approached several months ago by a manufacturer of plastic films for packaging with the following problem:

“We manufacture a film that is basically polyethylene with a sealant layer on one side. Trouble is, you can't tell which side is which by just looking at the film. Although we take great care in our processing to make sure we know which side is up, every once

Although each material had characteristic infrared absorption bands, taking transmission spectra would obviously not help in film orientation. Attenuated total reflectance (ATR) sampling would, however. The trouble was that the one usable band in the sealant spectrum was rather weak and conventional horizontal ATR sampling methods, even with the clamp set at fairly high pressures, did not show significantly different absorption at the wavelength of the characteristic sealant band. (We managed to break a ZnSe ATR plate in the evaluation process!)

on the spherical surface with one's thumb and there would be a strong positive reading from the infrared fultometer if the sealant surface was down, and a much weaker reading from the other side. A reading takes less than 30 s. The film orientation problem was solved and the infrared fultometer, with spherical ATR surface on the “thumb sampler” is now in use in the film processing plant.

A short time later, another film maker approached us with another problem:

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Walther Gerlach and the Foundations of Modern Spectrochemical Analysis

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The author discusses the life and sometimes-overlooked work of German scientist Walther Gerlach.

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Almost without exception, all precision quantitative analysis using emission spectra is based on some variant of the internal-standard principle first enunciated by Walther Gerlach (1).

It seems strange, therefore, that so little is known today about the founder of modern optical emission spectrochemical (OES) analysis. Aside from an excellent biography in German (2), little else is available; his name appears in a 110-word entry in *Encyclopedia Britannica*, Vol. 5, 15th Edition (1994), but he is not noted in any of the

many compilations of scientific biographies.

For most scientists, the name Gerlach brings to mind only the classic Stern–Gerlach experiment of atomic physics. It is not generally appreciated that Gerlach, a first-rate experimental physicist, transformed the spectrographic technique from a qualitative or semiquantitative tool into a quantitative method of instrumental chemical analysis. He did this by introducing the internal standard method, which remains central to modern spectrometric analysis, whether the excitation is by

thereof are generally conceded to begin with the work of Bunsen and Kirchhof (1). Their 1860 publication (3) showed that qualitative chemical analysis was feasible. One year later, the authors proved this rather conclusively by discovering two new elements — cesium and rubidium — by spectroscopic analysis.

Attempts to produce quantitative analyses using photographic film (spectrograph) rather than the human eye (spectroscope) ran into grave problems, caused by the number of variables associated with the

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arc/spark or the more recent inductively coupled plasma (ICP).

Historical Development

Although spectroscopy has a long history going back to Newton, the chemical applications

intensity of the spectral lines produced by a given material. These included excitation source instability and variable photographic film sensitivity.

Several researchers achieved semiquantitative results in the

Table I. Improvement in precision using internal standardization.

Spectral line pair	Intensity analyte (%RSD)	Intensity ratio (%RSD)
Si(I) 251.6/Fe(I) 281.3	0.82%	0.18%
	0.85%	0.22%
Cr(II) 289.8/Fe(II) 273.0	0.44%	0.17%
	0.95%	0.24%
Mn(II) 293.3/Fe(II) 273.0	0.72%	0.28%
	0.98%	0.28%

late 19th and early 20th centuries. The work of W.N. Hartley in Dublin, Ireland, is noted, as his 1882 study appears to have been the first systematic study of the change in spectral line intensity with concentration. He also made the first quantitative spectrographic analysis (determination of beryllium in cerium compounds [1]).

De Gramont in Paris, France, was a driving force for the development of spectrographic methods as a quantitative technique for chemical analysis (1). In the United States, Meggers, Kiess, and Stimson attempted to bridge the gap to quantitative analysis in their 1922 paper (4). However, Meggers and co-workers relied on constant excitation conditions, extremely difficult to produce experimentally at that time (5).

In Germany, Gerlach made the real breakthrough to quantitative analysis. In 1929 Gerlach and co-worker Eugen Schweitzer introduced the method of internal standards along with the concepts of homologous spectral lines and fixation pairs (6). Although his name seldom surfaces in today's spectrochemical literature, it was very prominent in the spectroscopy texts of the 1940s (1, 5, 7).

Internal Standard Method

The early spectrographic attempts at quantitative analysis were plagued by multiple problems, running the gamut from unstable excitation sources to the response of the photographic plate or film itself. Gerlach solved these problems by introducing the *internal standard method*: Ratio the intensity of the analytical spectral line to the intensity of a spectral line of another component of the material. Then plot this ratio

against the concentration of the standards to produce a working (calibration) curve.

Two types of internal standard lines can be used:

- A weak (nonsensitive) spectral line of the major component of the sample. This approach is most common with arc/spark spectrometry.
- A strong (sensitive) line of an element such as strontium or yttrium that is not initially present, but added to the sample. This approach is generally used today in ICP spectrometry.

How does this technique work? Let a measurement of a spectral line of an analyte, A, be $I_A = 1000$ counts. The internal standard spectral line, measured at the same time, yields $I_{STD} = 10,000$ counts. The intensity ratio is $I_A/I_{STD} = 0.10$. Now a second measurement is made at some time later: $I_A = 950$ counts and $I_{STD} = 9500$ counts. Note that despite the change in measured values, the intensity ratio remains the same. This simple yet powerful technique compensates for both short and long-term changes in the measuring instrument, the spectrometer.

The improvement in precision through the use of internal standards is shown in Table I with arc/spark OES measurements made on low alloy and stainless steel samples (8). The center column gives the precision of the analytical spectral line alone, while the next column shows the precision of the intensity ratio.

Homologous and Fixation Line Pairs

Two allied concepts arise naturally from the method of internal standards, both introduced by Gerlach. They are

homologous and fixation spectral line pairs. Gerlach was the first to call spectral line pairs *homologous* if they worked well together to compensate for changes in excitation conditions. It is important to note that not all line pairs of an analyte and matrix are homologous. For example, an ionic line of the matrix element does not couple well with an atomic analytical spectral line.

What defines a pair of homologous spectral lines? No set of necessary and sufficient conditions exists, as more research in this area is required. We can state, however, that their excitation potentials must be similar; or, in the case of ionic lines, their combined excitation and ionization energies must be similar. Beyond this, we must turn to experimentation. Several types of tests may be performed.

The basic definition of homologous spectral line pairs, due to Gerlach, is that they compensate for changes in the excitation energy. The simplest test to determine if a line pair meets this criterion is to make measurements at different power levels.

Homologous spectral line pairs improve the precision of analysis, generally by a factor of about three or four. Table I shows some examples. A counter example is W(I) 400.8/Fe(I) 360.8 in tool steel where the %RSD of the analytical spectral line alone was found to be 0.75% and that of the intensity ratio 0.70%. This test is simple to perform.

It has also been found that homologous line pairs improve the calibration and show less interelement (matrix) effects. Some examples from arc/spark OES are noted here (8):

- The use of the Al(I) 305.9-nm spectral line rather than Al(I) 308.2-nm line improves the calibration for high aluminum concentrations in zinc alloys by a factor of three as measured by the standard error of estimate of the calibration curve. The internal standard line in both cases is Zn(I) 267.0 nm.
- Consider the spectral line pairs Ni(I) 380.7/Cu(I) 296.1 and Ni(II) 376.9/Cu(I) 296.1. Using the first pair, the nickel silvers (Cu–Zn–Ni) and cupro nickels (Cu–Ni) plot to-

Table II. Change in fixation pair intensity ratio with excitation.

Peak current (A)	Intensity ratio [Fe(II) 273.0/ Fe(I) 360.8]
130	4.029
110	3.885
57	2.902

gether nicely. With the second pair, an interelement correction for zinc, or the use of two separate calibration curves, is necessary.

We can summarize the characteristics of homologous spectral line pair ratios:

- They correct for changes in source excitation (the basic definition)
- Their excitation potentials (and ionization energies) are similar
- Their precision is better
- They improve the calibration
- They show less interelement (matrix) effects.

A *fixation pair* is the opposite of homologous spectral line pairs. Here we choose an atomic and ionic spectral line of the matrix or base element. The ratio of the two will provide a sensitive indicator of any changes in excitation source conditions.

A fixation pair may be monitored to ensure that the excitation remains constant. If the excitation is stable, then the ratio of the fixation pair will also remain constant. Table II shows the variation in the Fe(II) 273.0 nm/Fe(I) 360.8 nm intensity ratio with change in the peak current of the spark-like excitation (8).

Biographical Notes

Walther Gerlach was born 1 August 1889, in Biebrich am Rhein, Germany. He studied physics at the University of Tübingen and received his PhD in 1912 under Friedrich Paschen. His dissertation concerned blackbody radiation and a means to determine the Stefan-Boltzmann constant.

From 1913–1915 Gerlach, together with colleague Edgar Meyer, produced a series of publications on the photoelectric effect. They described their observations of this effect on microscopic

metal pieces and also at low pressures. Their results confirmed Einstein's theory of the photoelectric effect over an alternate proposed by Sommerfeld and Debye.

Gerlach completed his "habilitation," a requirement to teach at German universities, in 1916 and became a lecturer at Tübingen University. After service in World War I, Gerlach spent a year (1919–1920) in industry, working in the Physics Laboratory of Farbenfabriken Elberfeld.

In 1920 Gerlach became professor at the Institute for Experimental Physics in Frankfurt. Max Born, head of the institute, wrote Einstein to express his delight in acquiring Gerlach: "We now have the famous Gerlach here. He is energetic, knowledgeable, ingenious, and helpful" (2).

That same year, his colleague Otto Stern approached him for assistance in an experiment he had designed. "Together they succeeded in proving the reality of space quantization and in measuring the magnetic moment of the silver atom" (9). Five papers were published during the years 1921–1924, four of them jointly, on what came to be known as the Stern–Gerlach experiment. Stern later received the Nobel Prize in Physics in the year 1943 for the detection of the magnetic moment of protons.

In 1924, when Alfred Landé asked who should be considered for the opening in experimental physics at the University of Tübingen, Albert Einstein replied, "In my opinion, Mr. Gerlach would be the correct successor to Paschen. Among the younger German experimental physicists who might be considered, he is the best" (2). Gerlach returned to the University of Tübingen in 1925 as professor of physics.

His last move came in 1929 when he joined the University of Munich. He remained there until his retirement in 1957.

It is not generally known that Gerlach's work on spectrochemical analysis resulted in three volumes of *Die chemische Emissionsspektralanalyse*, published in English translation in 1929, 1934, and 1936 (6, 10, 11).

Amidst all this spectroscopy, Gerlach found the time to write a textbook on magnetism, *Magnetismus*, published in 1931. A decade earlier (1921), Gerlach had published his text on quantum mechanics, *Grundlagen der Quantentheorie (Foundations of Quantum Theory)*.

After World War II, Gerlach was interned with fellow German scientists Werner Heisenberg, Carl von Weizsaecker, Otto Hahn, and six others at Farm Hill in England. Details of this internment and insights into the Nazi atomic bomb effort are only now coming to light. (Gerlach's name surfaces in several publications as one of the 10 German physicists interned at Farm Hill in England at the end of World War II. See, for example, A.D. Beyerchen, *Scientists Under Hitler* [Yale University Press, New Haven, CT, 1977]; M. Walker, *Nazi Science: Myth, Truth, and the German Atomic Bomb* [Plenum Press, New York, 1995]; and K. Hentschel, ed., *Physics and National Socialism: An Anthology of Primary Sources* [Birkhauser, Boston, 1996].)

In 1950 Gerlach published a philosophical work, *Humaniora und Natur (Humanity and Nature)*. Gerlach retired from the University of Munich in 1957. In 1973 he published an historical study, *Kepler und die Copernicanische Wende (Kepler and the Copernican Revolution)*.

Gerlach died in Munich on 10 August 1979, only days after his 90th birthday.

Conclusions

The internal standard principle of Walther Gerlach lies at the heart of modern spectrometric analysis. It was most important in elevating the spark optical emission method of spectrochemical analysis from semiquantitative to quantitative analysis status. Today, this principle is a standard part of the arsenal of the modern chemist using instrumental methods for quantitative chemical analysis.

However, the twin concepts of homologous spectral lines and fixation pairs introduced by Gerlach seem to have been forgotten by most or simply lost over time. Perhaps their reexamination by today's practicing spectro-

chemists may provoke theoretical studies and promote instrumental advances.

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"Guest Editorial"

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"We make a film with a moisture barrier with a layer of polyethylene on either side. We recently discovered that our extruder was functioning erratically, and we have produced several hundred rolls of film that may or may not have the correct thickness moisture barrier. How can we check these rolls to determine which has the correct barrier thickness and which doesn't?"

It turned out that the barrier layer material had a strong carbonyl absorption band — the polyethylene didn't — so it was easy to determine the barrier layer thickness by transmission. However, it wasn't very practical to cut a lot of pieces from the rolls and put them individually into the infrared filtometer to check the barrier layer thickness.

Our solution was to take the source and detector out of the body of the filtometer and mount them on either side of a U-shaped holder, so that the film could be passed continuously through them and the layer thickness measured continuously. The arrangement worked

so well that, after the previously extruded rolls were checked, the manufacturer decided to mount the filtometer permanently after the extruder to monitor barrier-layer thickness of newly extruded film.

And finally, a third film problem came to us — this one also to provide a thickness measurement of an inner layer — in this case, nylon — in a film that eventually became bubble wrap. Because nylon has a very strong band at $3\ \mu\text{m}$ ($3333\ \text{cm}^{-1}$), it was easy to obtain a precise measurement of its thickness in an infrared filtometer equipped with a $3\text{-}\mu\text{m}$ detector. The problem was that the plant procedure was to take a piece of film, weigh it, then strip off the polyethylene and weigh the residue. In this way, the thickness of both components could be determined. The procedure was time consuming and, furthermore, required the use of hazardous reagents. By combining the infrared measurement for the nylon thickness and measuring the overall film thickness with a micrometer, the time-per-analysis was greatly reduced and the need for a reagent was eliminated.

Hence, these are three real-world process quality control problems that

were solved by infrared analysis. The original infrared evaluation was done with conventional laboratory spectrometers but the ultimate plant procedures were carried out by dedicated infrared filtometers.

All three problems were solved using absorption bands in the mid-IR region, where they are generally isolated and free from interference. This is usually not the case with NIR absorption bands, which frequently overlap and interfere with each other. Furthermore, those three solutions illustrate the fact that, if measurement of an infrared absorption band can be used for quality control or process management, then simple, reliable, inexpensive filter instruments can be used successfully in plant environments.

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