

The**SPEX**

INDUSTRIES INC. 300 PARK AVENUE BETHLEHEM, PENNSYLVANIA 18018-0001

Speaker**SPECTROSCOPY AT BETHLEHEM STEEL**

Over the past four decades, optical emission and x-ray spectroscopy have emerged as standard techniques for control of the composition of steels. Highly automated, dependable and swift, today's analytical instrumentation is responsible for a great boost in the productivity of the steelmaking process and an equally great boost in the uniformity of the hundreds of types of steel produced. Nowhere are these facts more evident than at the sprawling Bethlehem Steel plant in Bethlehem, Pennsylvania. The author's visit began in the basic oxygen furnace (BOF) shop.

Basic Oxygen Furnace - Steelmaking

Fitted with hard hats and protective goggles, we enter a room so cavernous that a couple of ocean liners could be comfortably berthed inside. Up a flight of stairs and 100 yards along a gangway a huge cauldron laden with 200 tons of molten iron is held by a gigantic overhead crane. The shop is getting ready to charge fresh raw materials into the 35-foot high, 25-foot diameter BOF steelmaking vessel for the next heat. First the vessel is tilted partway on its side, its deep orange glowing contents spewing heat in all directions. Quickly, a special machine resembling an oversize dump truck on rails unceremoniously deposits 75 tons of scrap into the vessel. Then, after the scrap charging machine is moved away, the ladle of molten iron, held high with ropes of steel, is quickly emptied on top of the scrap through the gaping mouth of the vessel. Immediately the vessel is turned to a vertical position. Without hesitation, a 60-foot long, water-cooled lance blowing oxygen at a scarcely believable rate of 25,000 cubic feet per minute is lowered into the vessel.

The refining of a new batch of steel is underway. Above the vessel a roaring flame dances in disco-bright colors as it sprays sparks and belches gases through a fume hood and up a towering chimney to a gas cleaning station. For nearly 20 minutes the roar forces the

hosts to shout explanations to the awe-struck visitor while the oxygen reacts exothermically to reduce the amount of carbon, silicon and other elements in the bath. Simultaneously the concentration of sulfur and phosphorus is reduced to acceptable levels by flux reaction with the slag. Then suddenly the noise dies down, the vessel tips, and a furnace crewman dashes over, dipping a spoon on a 20-foot handle into a fiercely radiant pool. Sixty seconds later, the sample has been cast into a 1½" diameter disc, plunged into water and placed into a pneumatic carrier which propels it several hundred feet to the spectroscopy lab. Immediately after the sample is removed from the vessel, another 20-foot steel rod containing a thermocouple is plunged into the molten steel to determine if temperature is acceptable—usually 2900F for medium carbon grades of steel.

In the laboratory a waiting technician, alerted by call box three minutes earlier, grabs the sample, drops it onto a magnetic clamp, grinds off about ⅛", then belt-sands it smooth, and rushes it next door to the operator of the optical emission spectrometer (OES). Elapsed sample preparation time: about 45 seconds.

Having already run a standard similar to the grade being processed, the spectrometer operator has assured himself that his entire complex computerized analytical system is "Go." He now gaps the counter electrode of thoriated tungsten, positions the sample above it, closes the lid of the spark stand and presses START. The computer takes over. After a few seconds of preburn, it opens the shutter; about 15 seconds later, the computer, having established that the integrated intensity of the reference spectral line of iron had reached a pre-determined level, stops the spark. As the unseen computer digests and interprets the raw spectral data, the operator adjusts the sample for a duplicate analysis.

Now the teletype is clanking out the first results: concentration values for carbon, manganese, phosphorus, sulfur, silicon, nickel, chromium, copper, molybdenum, tin and aluminum. Another 30-second wait and then the second set of values is typed, revealing almost identical values for the 11 elements. Nodding approvingly, the operator reaches for the convenient phone to jargon the analysis to the steelmaking shop. Simultaneously, the computer transmits the analysis to a teletypewriter in the "pulpit," the furnace control room. Total time for conventional spoon sampling plus analysis is about 6 minutes.

The melter, the man in charge of the furnace, checks the analysis to decide if the element compositions are within specifications and if the temperature is correct. Typically only about ⅓ of the heats finish within specifications at the end of the original oxygen blow because both the composition and temperature specifications are extremely tight. If either composition or temperature is not correct, the melter initiates corrective action by reblowing with oxygen for up to a minute or by adding coolant, usually in the form of iron ore. In some instances, both remedial actions must be taken. For this particular heat, a short reblow is needed. Again the roar. In 30 seconds it's all over. The sampling and analysis are repeated. This time the temperature is correct and the analysis reveals all elements centered comfortably within the desired specification.

"Get ready to tap" cries the Melt Supervisor. Obediently—so it appears—the vessel tips in the opposite direction, emptying its contents into a large ladle. Alloying elements are added as the ladle fills. As soon as it is full, the ladle is picked up by crane and moved over a trainload of molds. The steel in the ladle is teemed into those molds. After partial solidification, the ingots of steel are hauled away for removal of the molds enroute to the rolling mills.

What we have experienced is a heat, or batch, of carbon steel as it is formulated in a modern basic oxygen furnace. While older open-hearth furnaces took 6 to 8 hours from tap-to-tap, the BOF procedure takes only about 40 minutes. Little wonder, then, that the Bethlehem Plant phased out all of its open-hearth furnaces over eleven years ago in favor of two basic oxygen furnaces. Complementing these are five electric-arc furnaces dedicated to the production of alloy or specialty steels. Feeding the basic oxygen furnaces are two blast furnaces which smelt the prime ingredient of steel—molten pig iron—from ore, coke and limestone.

BOF Improvements

Slashing the elapsed time for making a heat of steel was one of the compelling reasons for switching to the BOF process. But even 40 minutes is far from the goal. Sampling, analysis and corrective action account for 20 to 25% of those 40 minutes, so that engineers are constantly studying and inventing means to shave even seconds from the cycle time. Every minute of saved time represents a considerable saving to Bethlehem Steel.

As pointed out earlier, the cycle involves several minutes of time waiting for analytical results. Equally significant, each heat entails at least one, and sometimes as many as three analyses, before it is correctly formulated and approved. The incentive is obviously great for the first analysis to be the only analysis. Because of the potential time and energy savings, the heat should be proved to conform to specs as fast and as reliably as possible.

With all this in mind, one of the two BOF furnaces at the Bethlehem works has been extensively modified over the past few years. Alongside the lance that admits oxygen to the vessel is another, a so-called sensor lance (Fig 1), which holds a multi-element sensor. One element of the sensor is a thermocouple so it will be hot enough to be tapped and teemed without solidifying prematurely and low enough to insure high quality steel ingots. The second sensing element is more complex, consisting of a specialized differential thermal analyzer (DTA) that, with the assist of the computer, is able to determine the carbon content of a small sample of metal from its "liquidus arrest," the discontinuity of the cooling curve.

The third element in the sensor is a sampler. Instead of having to tilt a lumbering vessel for manual sampling after interruption of the oxygen blow, a

sample slug is cast automatically within the sensor itself. The lance is then quickly withdrawn, pulling the spent sensor with its sample above the top of the vessel and hood. Here, a saw buzzes through the sample slug which drops through a chute to the floor 60 feet below. Still glowing red, the sample is picked up with tongs, inserted into a special heat-sink carrier which, in turn, is dropped into a pneumatic tube to be shot to the lab. All this is done in about one minute, without tilting the huge vessel or turning off the blast of oxygen.

Analysis of Lance Samples

Initially, results from the vacuum OES on lance-cast samples were disappointing. Run under the identical conditions developed for conventional cast samples, the precision turned out to be unacceptable, in fact, decidedly worse than expected. Although the problem turned out to be simply solved, tracking down its source and instituting a cure took a good deal of time and concern. The problem was finally traced to microscopic inclusions of slag introduced because, with faster sampling, the slag lacked sufficient time to float to the surface of the molten metal. Once diagnosed, the malady was successfully treated by increasing the preburn time—time before exposure—from 3 to 15 seconds, thereby decomposing the inclusions without letting them interfere with the analytical results.

Retrofitting sensor lances to existing BOFs is expensive, but it is estimated that the sensor lance has a relatively

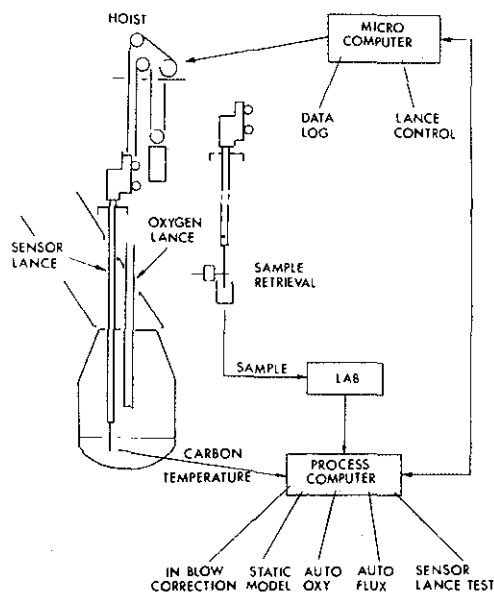


Figure 1 Sensor-lance system. Dropped in the bottom of the BOF vessel by a rapid-moving hoist, the lance assumes three functions: to measure the heat temperature, to approximate its carbon content, and to remove a sample swiftly for spectrometric analysis.

short payback period. With it, sampling time has been reduced about 4 minutes. Even more important, however, is the fact that the lance allows almost twice the number of BOF heats to be tapped at the end of a single blow without corrective action. The analysis, in other words, usually confirms that the heat meets specifications the first time around.

Mixups

As long as people are human, occasional mixups will continue to be inevitable. And when the unidentifiable materials are look-alike steels, the effect can be decidedly serious. Weld two different grades of steel together and one runs a considerable risk of intergranular corrosion and eventual failure. Support a building with compositionally-wrong beams, and the structure may sag or collapse. Quite apart from such catastrophic consequences, industry depends on uniformity to maintain its productivity. Auto manufacturers need to form sheets into complex shapes with the same tools and under identical conditions, irrespective of the source of the steel. Hardware manufacturers need to turn, drill, thread, cut, mill, broach, and otherwise machine rods on automatic machines that are set up once and for all at identical feed rates and spindle speeds. Metal finishers need to be assured that, treated identically, all replicate castings or forgings will be hardened, annealed, coated, or plated properly. All of these stipulations rely primarily on the compositional constancy, the same elemental makeup of the steel.

On a tonnage basis, the element of most concern, by far, is carbon. Close to 100 grades of steel, differing principally in their carbon content, which can vary from less than 0.1% to over 1%, are listed by AISI. Faced with their expense and the prospect of worldwide depletion of alloying ingredients such as chromium, vanadium, tungsten, molybdenum and nickel, metallurgists have, over the years, learned how to create steels with greatly varying chemical and mechanical properties simply by varying the carbon content. Sorting most steels thus boils down to determining their carbon content. Despite necessity, the only invention yet mothered for on-site determination of carbon is an ancient one. Visually examining the pattern of sparks flying off a grinding wheel, an experienced "spark tester" can instantly distinguish low from medium or from high carbon steels. Although the method is undeniably inexpensive, it is wholly subjective, depending on the alertness of a competent technician. Furthermore,

carbon differences of 0.05% often cannot be detected visually and low-alloy steels containing the same carbon content cannot be differentiated. De and Sitek (2) estimate that only about 65% of mixups can be unsnarled by the most careful "sparking."

A careful statistical study by Linde showed that this 65% could be improved to almost 90% by determining manganese in addition to carbon. With this incentive in mind, Bethlehem's Research Department set about developing an on-site manganese analyzer. Portable, easy to operate by unskilled workers and, in 10 seconds, posting concentration figures accurate to 60.1% over the range 0.3-1.7% manganese, the analyzer is now a commercial reality (Fig 2). It is basically a single channel, direct-reading optical emission spectrometer. A low-power dc arc is struck between an electrode and the surface of the questionable steel. Vapors from the arc are aspirated into a flame fed by a bottle of propane. Interference filters isolate a manganese line and a section of the spectrum's background, the intensities of which are ratioed. The method boasts better detectivity than energy-dispersive x-ray techniques which require radioactive sources.

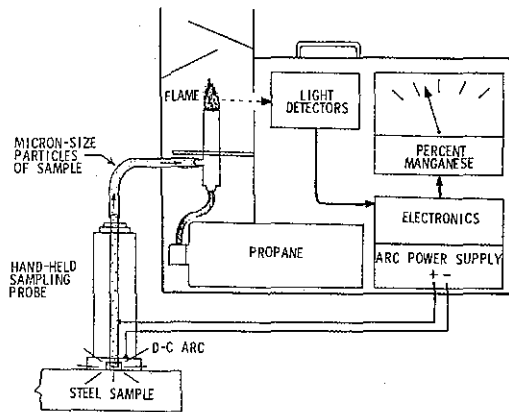


Figure 2 On-site manganese analyzer. The hand-held probe is held against the steel piece in question. A dc arc is struck and the resulting vapor aspirated into a propane-fed flame. A simple interference-filter optical spectrometric system converts the intensity of a manganese line into percent concentration.

is added during tapping to "kill" (deoxidize) the steel.

Just as optical emission spectroscopy has emerged as the accepted technique for the determination of most elements in carbon steel, x-ray spectrometric analysis has taken hold as the preferred tool for analyzing most of the other materials involved in steelmaking. At the Bethlehem Plant, several x-ray spectrometers are the workhorses. Integrated emissions at characteristic wavelengths for each element are ratioed against lines from a reference sample. Calibration curves in resident software provide rapid and accurate concentrations. Technicians have prepared separate calibration curves for slags, ores, sinter, refractories and other materials to assure freedom from matrix effects. Elements routinely determined are Ca, Si, Fe, Mn, P, Cr, Al, Ti, V and Mg. Modern vacuum x-ray spectrometers are so sensitive that even light elements such as Mg, At. No. 12, can be measured down to 0.2%.

One sample preparation technique that has gained a firm foothold in conjunction with x-ray spectroscopy involves fusion. Mixed in a ratio of one to anywhere between 4 and 10 with a fluxing material, the sample is fused and then cast into a disc ready for insertion in the spectrometer.

But even within Bethlehem Steel, the sample preparation approach is subject to variations; production favors one, research another. And with good reason. For efficient production control, the speed of analysis of a single sample is paramount; for efficiently analyzing research samples, minimizing the overall time per sample for a batch of samples is the primary consideration. Every day the analysts working for Robert Leciston, General Foreman of the Production Control Laboratories,

routinely furnish analyses within 10 minutes from the submission of the sample. At a better overall preparation and analysis rate per sample, the analysts working for Randy Fike in Research typically fuse samples in groups of 8 at a time, then analyze all prepared samples in one batch later that day.

The production-control procedure for slags involves a mixture of Spex HiPure 90% lithium tetraborate and 10% lithium carbonate as the fluxant. First, chunks of the slag are powdered in a swingmill (Spex SHATTERBOX). Taking a few seconds, this assures a representative sample and adequate mixing with the fluxant. Then a total of about 10g of the fluxant and analyte is placed in a 5%Au-95%Pt crucible, a drop or two of HBr is added as a wetting agent, and the material rapidly heated in a single-station induction furnace. In 5 minutes the temperature is raised to around 1300C, the crucible removed and its contents poured into a dish of the same platinum alloy. Leciston points out that the casting dish should be quite thick in order to prevent cracking and facilitate release of the disc.

By contrast, in research, a slower Globar resistance furnace holding a number of samples is preferred. Instead of the mixed flux, neat lithium tetraborate is added to the sample. In their applications, it is not necessary to add a wetting agent to prevent sticking to the crucible. Fike has found it advisable to wet-sand the cast bead sample smooth before analysis to improve precision. Of course, consistent precision and accuracy are highly dependent on all phases of the analysis.

Bethlehem's research has found the fusion method applicable for the analysis of (1) iron, manganese, tungsten and titanium ores, (2) BOF, BF and ESR slags, (3) dolomite and calcite, and (4) alumina, silica, magnetite and firebrick refractories. By changing the flux/sample ratio and applying proper calibration curves, the method has been developed so it is almost universal.

Specific Elements

Carbon remains a tricky element for optical emission spectroscopy. Today's direct readers are evacuated and the optical path from the sample to the spectrometer bathed in argon to prevent absorption of the carbon line at 193 nm. Special spark conditions have been developed and counter electrodes, of thoriated tungsten or fine silver, have been selected after numerous trials with other materials. Yet, no steel laboratory

For the remaining 10% of steel mixups, mobile, direct reading spectrometers have recently become available commercially for on-site analyses. In operation, the technician first standardizes the mobile instrument with a reference sample. When a suspect sample is analyzed, in seconds the instrument will reveal whether or not its silicon, manganese, chromium, nickel, molybdenum and other element contents fall within a pre-set tolerance of the reference values. Unlike the manganese analyzer which transports vapor for subsequent analysis, the mobile spectrometer probe conducts light itself. A fiber optics bundle transmits the light 10 feet to a concave grating that disperses the radiation to a series of photomultipliers. A "Yes-No" indication on the probe removes any subjectivity from the measurement.

Alloy Grades

Where OES has become dominant for the analysis of carbon steels, it has yielded to x-ray spectroscopy (XES) for determining the higher concentrations of elements in alloy steels produced by the electric-arc furnaces. Carbon in alloy steels, however, is still determined by the primary combustion method. Other than carbon, only aluminum is determined (down to below 0.005%) by a vacuum direct reading OES. Aluminum, incidentally,

is complete without its bank of combustion analyzers. Whether for back-up verification or as a primary reference method, carbon is measured by inductively melting the sample in an atmosphere of oxygen, converting the carbon to CO₂ and measuring the amount of released CO₂.

Philip F. Yongken, Chief Chemist at the Bethlehem Plant, reports that all carbon steels containing less than 0.5% carbon are routinely determined by OES.

Above that value, the chemists resort to the combustion method which takes about 1½ minutes. Carbon in all alloy steels, as well as the 4 to 5% carbon in molten iron from the blast furnaces is determined by the combustion method.

Boron is another troublesome element to the analyst. In recent years, boron additions have been found to be an inexpensive way of improving the hardenability of steel. (Hardenability is a measure of the depth to which a metal can be hardened.) As little as 0.001% boron can increase the hardenability to the same extent as far greater concentrations of more expensive manganese, chromium, or molybdenum. However, only that portion of the boron that is in metallurgical solid solution with the steel is effective. Any boron present in other forms, usually oxide inclusions, is inert.

Unfortunately, OES, while sensitive down to ppm levels, measures only the total boron concentration in solid samples. OES determinations, therefore, cannot always be correlated with hardenability. A more reliable correlation is presently favored by Dean A. Flinchbaugh, Supervisor of Laboratory Analytical Services at Bethlehem Steel's Homer Research Laboratory. The method is to extract phosphoric acid-soluble boron and determine its concentration with a direct current plasma (DCP) spectrometer.

Boron concentrations must also be controlled in certain slags, for example that protecting the molten metal in continuous casting molds. This slag contains boric acid at levels of 8-10%.

Although the other elements present—calcium, aluminum and silicon—can be measured by conventional vacuum x-ray spectroscopy, boron again is an exception, this time because its k-alpha line is emitted in the soft x-ray region, too weak to be detected. Again DCP appears to be the preferred technique for its measurement.

The analysis of certain specialty steels falls outside the scope of ordinary spectroscopy. Sulfur below 0.007% was called for in the Arctic pipeline which, of course, is subject to extremes in ambient temperature. Sulfur at this level is usually determined by combustion. Low levels of hydrogen, oxygen and nitrogen are desired in steels destined for high-stress applications. These elements are normally determined by inert gas fusion: melted in an inert gas atmosphere, the steel releases the gases which are then separated and measured by infrared or thermal conductivity methods.

Standards

Most instrumental analyses are secondary: they do not measure the concentration of an element directly, but instead, a parameter relative to that of standards upon which the instrument calibration is based. For this reason, analyses can never be better than the standards from which they are derived.

Acutely aware of this, Bethlehem Steel maintains a company-wide task group to oversee the production of standards. And production it is. Some 35 alloys have been prepared as 1¼" dia. rods, 10 tons to a heat. These are rolled and rerolled to reduce segregation and analyzed and reanalyzed by several techniques and laboratories to certify composition before being released. Enough to last an estimated 10 years, 1-million pins each of several standards have been prepared and cut up into exact one-gram weights as standards for combustion determination of carbon and sulfur.

Although these steel standards are available only within Bethlehem Steel, the company has supplied material for a number of other steel standards for distribution by the National Bureau of Standards. The company also works closely with NBS in the preparation and standardization of iron ores and other materials.

Future

The bulk of production in the Bethlehem Plant is common structural steel—not exotic alloy grades, nodular cast iron, wrought iron or other specialties. But even these so-called common steels are constantly being upgraded and analytical techniques refined to control the properties of the steels more closely. For example, steels with specifications limiting the gas content are becoming important, but the only acceptable techniques for measuring residual hydrogen, nitrogen, or oxygen is by inert gas or vacuum fusion techniques. Wouldn't it be lovely if someone would devise a more rapid spectrometric technique so that gases in steel could be determined on the same sample used to measure alloy content? Wouldn't it be even lovelier if someone devised a rapid, low-cost, portable, accurate, objective method for the determination of carbon in steels when mixups occur? According to Ted Linde there's a bundle of cash awaiting that inventor.

Acknowledgments

I wish to express my sincere thanks to each of the scientists and engineers mentioned in this article who were so helpful in describing the fascinating world of steelmaking at the Bethlehem Steel plant and Homer Research Lab in Bethlehem. Particularly valuable were the tour and interviews arranged by T. R. Linde, Senior Engineer.

—AJM

REFERENCES

1. T. R. Linde, Analysis of Sensor-Lance Samples for BOF Control, paper presented at FACS, Philadelphia, PA, Sept. 1979.
2. T. R. Linde and G. J. Sitek, Portable Manganese Analyzer to Separate Mixed Steel, Materials Evaluation, VOL. XXXiii, No. 11, Nov. 1975.

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View from Behind the Counter

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Listening to a paper presented at the Raman Conference in Bangalore, India, in the late summer of 1978, I was pleasantly surprised to hear a RAMALOG laser-Raman system referred to as a "Spex." A few months later, at the Pittsburgh Conference, a speaker called our Mixer/Mill blender/grinder a "Spex." Again, I beamed. But then I wondered: Here were two scientists, each busily engaged in the rather confined field of optical spectroscopy, yet peculiarly poised worlds apart in their interests. Was the one scientist aware that we manufacture a host of sample-preparation devices that boost productivity? Did the other know that we make high-performance research spectrometers?

So, when your editor invited me to initiate a series of articles profiling the companies in the industry that supplies the products uniquely tailored for you readers, I readily acquiesced. Here was an opportunity to describe who we are, what we produce, where, and how we got there. A good place to begin is to flash back some 30 years.

By 1950 optical emission spectroscopy as an analytical tool had long since emerged from the peek-and-ponder age. Progress had been made to the point where metals and alloys were being analyzed photoelectrically albeit with a considerably relaxed definition of "quantitation" than that demanded today. But quantitation was limited to a relatively few substances. For the vast majority of substances, any spectrochemical technique capable of approaching actual concentration was achieved only with much difficulty.

Yet the allure of spectroscopy—its uncanny ability to untangle the composition of almost anything almost instantly—was so striking to those accustomed to waiting weeks for wet-chemical results that we practitioners of the art could just about write our own analysis ticket.

For materials other than the few alloys for which standards were available, that ticket was indeed a bargain by today's rules. Unapologetically, we would submit a report cluttered with such lucidly explicit terms as "strong," "weak," and "not detected." When pressed by disappointed production people to amplify these terms, to suggest at least approximate concentrations, we would self-righteously refuse, our non-negotiable excuse being that catch-all matrix effect. With then-current methods, sediments, ores, dusts, and the like could not be routinely analyzed more accurately than within a factor of 10 at best.

Unknown to most emission spectrochemists, analysts at Oak Ridge had contrived a better idea, although it would be years later before that technique was declassified and publicized. Fortunately, however, Louis Rogers had independently solved part of the problem in a less sensitive application than atomic energy. His research centered on citrus crops in Florida where trace elements in soils were suspected of affecting the yield. To pinpoint the elemental makeup in soils of widely differing matrices, Rogers formulated a base standard (aptly called Medication) which contained about 10 elements all at identical concentrations. Along with the base, he devised a technique for successively diluting this with graphite

powder to form a series of graded reference standards against which the soils, after similar dilution with graphite, would be compared. Spex Mix and G standards owe their origin to this pioneering procedure.

In 1954 I was the working partner in a newly founded, independent service laboratory cranking out spectrochemical data for a number of paying customers. Naturally, only impossible analyses came our way. All varieties of you-name-its were submitted for next-day results at a minimum charge. And, one by one, clients began balking at our fanciful analytical designations. Fearful about losing hard-earned business, we simply had to find a better method. After many painful months of seeking, I finally learned of and was able to obtain a small amount of Medication from Rogers who, at the time, was employed at Armour Research Foundation (now IITRI) in Chicago, the organization where I had cut my wisdom teeth.

One Saturday morning, I gathered a few NBS standards for a trial of Rogers' dilution technique. Each of the NBS materials was diluted 10-, 100-, and 1000-fold with high-purity graphite powder, a laborious procedure with the hand-operated mortar and pestle. The diluted materials and Medication, similarly prepared, were arced. Many hours later, the still-wet photographic plate was slid into the stage of a comparator and I began visually interpolating and plugging in concentrational estimates. Finally, with much nervousness, I gingerly compared these with certified NBS values. Success! Within a factor of 3, my values matched those of NBS.

That was the inspiration phase. What followed was the incorporation phase. Without benefit of a detailed market survey, a hard-nosed business plan or a realistic cash-flow projection, Spex Industries was launched to sell the standards. To render the procedure more universal and saleable, an expanded base with 43 of the common elements was prepared. To simplify the procedure, this was diluted in graphite in four decades from 0.1% to 0.0001% of each of the elements. A brochure was printed describing the standards and the initial results achieved with the NBS reference materials.

Within 3 weeks after the brochure was mailed to the entire SAS mailing list, a sizable number of orders and inquiries were received, vindicating our belief that other spectrochemists would welcome a better method to cope with semiquants.

But, as any businessman will gladly caution, a single product does not a business make. As orders trickled to a halt, it became financially obvious that additional products would have to be added to Spex' line if it were to remain active.

Consumables proved to be our path to viability. More often than not, prospective customers were reluctant to adopt the proposed semiquantitative technique on a regular basis because the procedure was too lengthy. Our technique entailed first grinding the sample to a fine powder, and next weighing, diluting, and homogenizing it repeatedly, with graphite. Provided productivity was ignored, hand grinding with an agate mortar and pestle was fine. Realistically, however, four successive dilutions

by this technique seldom could be justified in terms of technician hours per analysis. Clearly, a better sample preparation method was called for. To the rescue came the Wig-L-Bug, an electrical shaker that, slightly modified, was the same triturator dentists long depended on to prepare silver-mercury amalgams for filling teeth.

Harold Mullin, since retired from the old AEC laboratory in New Jersey, brought the dental amalgamator to my attention. Although he demonstrated that the gadget could whittle mixing time down to a few seconds, he admitted one serious drawback: the only vials fitting the Wig-L-Bug were of glass. Not only was silicon and calcium introduced during agitation, but the vials, responding antagonistically to their rough treatment, would often fly off the handle and commit suicide. Special, expendable, plastic vials and balls, plus an appropriate restraining harness, proved to be the solution and Spex' next products.

Soon afterwards we introduced the first of our HiPure inorganics: copper hydroxy fluoride and granular silver chloride. Both are buffers, diluents that enhance the determination of one or more elements when the material to be analyzed is arced or sparked. CuOHF is highly selective, improving the detectivity of boron and silicon. AgCl helps to volatilize most impurities present in uranium oxides. Ordinary reagent grade AgCl may be pure enough for the purpose but is so soft that it smears when ground and thus resists mixing with other materials. The granular form is far superior in that respect.

These two buffers spearheaded a list that now totals over 800 high-purity inorganics. They are now produced in a modern facility that went on stream just last July. The Wig-L-Bug, too, became just the first of several sample preparation products that we manufacture to ease the burden and improve the productivity of optical emission spectroscopy, IR and x-ray spectrochemical analysis.

So much for the spectrochemical part of our business. The spectrometer line got off to a different, if equally fortuitous, start.

Princeton University's Plasma Physics Laboratory, one of the world's centers for atomic fusion research, relies on an array of spectroscopic disciplines to study the complex reactions and to probe the enormous temperatures attained in their huge experimental machines. Energized in these machines by temperatures approaching 100 million degrees, most atoms wind up highly ionized. As a result, their spectra are emitted at ultrashort wavelengths, as far out as the soft x-ray region. Needed to record such wavelengths are special grazing incidence spectrometers. Instead of directing the incident radiation on the grating at an angle near normal, the designer strives for angles as high as 88°. The higher the angle the shorter the cut-off wavelength. Thus, with a variable incidence angle to choose from, the researcher has a variable order-sorter filter at his disposal.

When we were approached by Princeton's scientists to design an appropriate instrument, it was as their last resort. By that time, several major firms had already been contacted, but all had failed to propose a solution to the dual requirement for a spectrometer that would scan linearly in wavelength (or frequency) while providing for a variable angle of incidence. Our technical staff

conjured up a way to achieve both. And, after intense scrutiny by a contingent of Princeton's accountants, engineers, attorneys, and scientists, we ultimately negotiated a contract to construct the instrument. Since that time, we have built a dozen or so Grazing Incidence Spectrometer/Monochromators (GISMOs) for institutes here and abroad. Although they have been operating satisfactorily, the market potential has scarcely been a powerful incentive for a company seeking challenge and growth.

Spurred on by that capitalistic instinct, we sought a larger more stable market. An evacuable Czerny-Turner spectrometer framed around the GISMO drive was our next entry. After studying its specifications, Bell Labs friends, particularly physicist James Ferguson, contributed some sound advice that led to the modular-instrument approach we still favor: facilitating attachment of sources and detectors to their respective slits; providing ready interchange of gratings, and a swingaway mirror for rapid switching from photographic to photoelectric detection; offering rigid optical bars to expedite experimental setups. But their best advice was to design a simple nonevacuable model, efficient for infrared, visible, and near UV performance.

Within the year 20 of our 1700-series UVISIR spectrometers were sold to several of the world's blue chip research organizations—including Bell Labs—where versatility was important to scientists stretching the state-of-the-art. Initial applications were often related to the newly discovered laser—then a solution looking for problems—which needed a spectrometer to isolate the array of spectral lines that were emitted.

One of these early experiments was conceived by Bell Labs' Darwin Wood and the late Sergio Porto. Intuitively, they foresaw the laser as a source for Raman spectroscopy. At the time, the only practical source was the Toronto arc—a cumbersome, troublesome, expensive, hazardous, mercury discharge lamp. Thousands of watts of driving energy were needed for it to excite the very feeble lines characteristic of the Raman effect.

Intrigued by the coherent, monochromatic, polarized, narrow pencil of light beamed from a pulsed ruby laser, Wood and Porto rigged up their first experiment. The taut string of red light was directed through a tube of an organic liquid and the 90° scattered light was focused on the entrance slit of a spectrograph loaded with a high-speed photographic plate. Success was immediate: weak frequency-shifted lines appeared on the plate. The efficiency of the laser was shown to be enormously greater than that of a mercury arc in exciting Raman spectra.

A breakthrough without question, yet the Wood-Porto method was far from ideal. It relied on a photographic plate with its poor quantum efficiency and nonlinear response to both wavelength and intensity. Moreover, stray light from the spectrograph itself clouded the distressingly weak Raman spectra.

Characteristically, Porto tackled both problems at once. "Why not couple two spectrometers?" he asked. In this way, he reasoned, photoelectric detection would supplant the photographic plate and thereby generate rapid quantitative information. Secondly, stray light, introduced mainly by the diffraction grating, would be reduced by the square of its intensity relative to the excitation frequency (Rayleigh line).

Porto's idea was intriguing enough for his supervisors to authorize underwriting of Spex' first double spectrometer. It consisted of two, independent, single instruments optically bridged so light from the first was steered through the second for further monochromatizing. Crude though it was, the instrument worked. Soon papers began pouring out of Porto's laboratory to *Physical Review Letters*, experimental documentation of atomic, molecular, and crystal interactions that had been only tenuously theorized until then.

Luckily, one result was never published. Puzzling him and others at Bell Labs for weeks, an effect was observed that was periodic in wavelength. Effects proportional to frequency are obviously energy-dependent and well known, but one proportional to the reciprocal of energy—wavelength—is a rarity and could be quite important. After repeating the experiment over and over and noting the same weird periodic spectral dips on the stripchart recorder, Porto was sure enough to reveal the information cautiously to us. "Had we ever seen such spectra?" he asked. Politely, we inquired about the periodicity. "Fifty Angstroms," was his reply. Instantly, the mystery was solved, for that was the period of the imperfect leadscrew of each spectrometer; when one zigged a bit, the other zagged, modulating the perceived intensity at the photomultiplier. Not for making history was this result of an anomalous instrument! All concerned enjoyed a good laugh and, immediately, Porto dubbed the phony phenomenon the Spex effect while, exerting due modesty—or friendly retaliation—we counter-dubbed it the Porto effect. Those of you who knew this bright, outgoing, jocular person, whose sense of humor rivaled his uncanny mastery of the "quick and dirty" experiment, will appreciate the long-standing joke.

Porto and others have helped and are still helping to guide us in the ongoing quest to optimize Raman instrumentation. For the vanishingly weak intensities typical of Raman spectroscopy, photon counting was found to be the ideal means of measurement. Focusing the laser beam on the sample proved superior to multipassing parallel beams as with older mercury arcs. A GaAs photomultiplier of RCA became *de rigueur*. Spex double spectrometers were subjected to extensive refinements: stepper motors for digital scanning; a cosecant drive for scanning linearly in cm^{-1} rather than nm; holographic gratings and special optics to slash stray light by several more orders of magnitude; computer compatibility to facilitate unscrambling of often confusing, noisy, raw spectra; accessories for working with all types of samples; TV and diode arrays for decreasing analysis time; modifications to permit operation in the UV for resonance Raman with its frequently fulfilled promise of up to 10^6 improvement in signal level.

COMPLAINT DEPARTMENT

The customer may not always be right but rarely are manufacturers granted the opportunity of relating our side. Decide for yourselves after reading the following accounts.

A professor of chemistry at a prestigious mid-Western university phoned one day lodging a bitter complaint. The very first time one of his students pumped up one of our hydraulic presses, the KBr die dug a big dent in the

cheap platen. When queried about the pressure applied, he said, quite casually, "Oh, the maximum, 25 tons." A little mental arithmetic revealed that that pressure exceeded the rated compression strength of steel. Startled, I shouted that his student was darned lucky; the die could have exploded in his face! Naturally, the professor hung up hurriedly. Well, as we manufacturers are fond of saying, it's easy to make something idiot-proof—but student-proof? That's impossible.

Then there was the Physics professor of a prestigious Eastern university who called irately about a "defective" grating he had just mounted in his spectrometer. To check the grating he had set up a tungsten lamp as a source. When scanned spectrometrically, instead of the expected smooth, black-body curve, out emerged a series of sharp absorption bands. So vociferous was this professor that to calm him a salesman was diverted 200 miles to visit the university. What he found was the plastic cover protecting the grating while silently displaying its absorption spectrum!

Mercury lines from overhead fluorescent lamps have erroneously illuminated the literature at least once. That was when a Raman researcher cautioned his peers about "impurities" in glass sample capillaries. While their source remained unknown (rare earths were suspected), they could easily be mistaken for Raman lines, he warned.

We can claim credit for thwarting publication of several other instances of mistaken spectral identity. One is memorable. Two scientists lugged into our application laboratory a van full of huge capacitors and extensive electronic gear in order to pulse a dye laser. Their intention was to obtain Raman spectra for the first time with this new type of laser that was capable of emitting radiation over a wide wavelength range. The first test was photographic. After the bank of capacitors were hooked together, they were fired repeatedly over a period of an hour or so, and the spectra were exposed on high-speed Polaroid film. As soon as the film was developed, it appeared evident that success was at hand. A flock of lines appeared, but the jubilation proved to be fleeting for the lines were not Raman; they were the mercury emission spectrum from the ubiquitous fluorescent lamps above. As bearer of the bad news, luckily we weren't beheaded.

No emission spectrographer is worthy of that designation until he or she 1) double-exposes spectra of two irreplaceable smidgeons of samples or 2) loads a photographic plate in obverse or 3) exposes a one-of-a-kind sample on the leader or trailer instead of the 100-ft stretch of 35-mm film in between or 4) develops a plate in hypo. The no. 2-type candidate pops up about once a year around here. "You sent us a batch of bad plates," he moans, "causing me no end of grief." Of course, when upon questioning, we learn that the spectrum stops abruptly at around 360 nm, the glass cut-off, the cause is embarrassingly obvious.

STATUS LINE

Today, Spex Industries employs 100-odd talented and dedicated people in New Jersey, California, and West Germany. Although our products are now well known in most developed and many developing countries, too, we

still smile quizzically when a university in Algeria orders a UVISIR spectrometer, or a petroleum research institute in the People's Republic of China orders a FLUOROLOG spectrofluorometer, or a Mexican cement factory orders a SHATTERBOX pulverizer, or a space agency in India orders a RAMALOG Raman system.

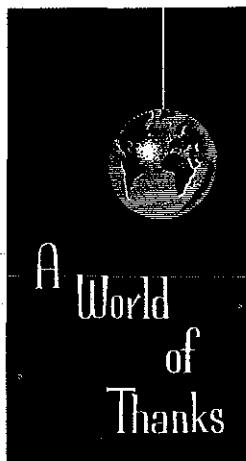
Like other high-technology firms, Spex is top-heavy in research and development personnel whose collective job it is to outmode our own—and competitive—products every few years. And, as technology snowballs along, the mean time between old and new models of instruments is dropping swiftly.

But let's not lose sight of the fact that instruments constitute the message; the medium lies elsewhere. Throughout the world, natural resources have peaked,

making it increasingly difficult to locate ever-dwindling pockets of oil, gas, and other minerals. Unless the dissemination of pollutants and toxic effluents is halted, we will leave a legacy of pervasive fear and danger to future generations. Good health relies on the continuing presence of enzymes, hormones, vitamins, trace elements, etc. and, simultaneously, the absence of a comparable variety of complex substances. The expenditure of energy is shamefully wasteful. Only the surface has been touched in our understanding of basic natural phenomena.

To correctly decipher all of these messages, advanced analytical instrumentation will continue to be the keys. Spex remains dedicated to the task of making, filing, and honing a few selected keys.

—AJM



Season's Greetings



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