

## MICRO AND TRACE ANALYSIS SHIFT INTO HIGH GEAR

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THE squeeze is tightening on emission spectroscopy. X-ray techniques, encroaching on its once-private light element domain, are now within earshot of carbon. Atomic absorption spectroscopy, though requiring that the sample be suitably dissolved, is reliable, turns out to be a considerably simpler technique when large numbers of samples are to be analyzed for a single element, shows limits of detection within one or two decades of that of emission spectroscopy, is exceedingly fast once the sample is dissolved. Of particular significance, is the ease with which comparatively inexperienced personnel can handle routine work.

With all these threats to its very existence, the emission spectrograph, far from being shelved, remains generally strong and in trace and micro analysis unquestionably dominant. As the need grows for purer metals, semiconductors and compounds, limits of detection are somehow lowered. Minute concentrations of elements are less of a challenge and with respect to the number of elements determinable emission still carries the banner.

One area that proliferates without improvement is terminology. Scientists seem to enjoy adding words to their vocabulary. They either coin new ones or, more often, borrow existing ones from associated disciplines after bending meanings just enough to confuse everyone. We are no exception. Although emission spectrochemists are already suffering from a hash of poorly digested terms, we now propose "responsivity" as subtly distinct from "sensitivity," a term—bandied about since the days of Bunsen and Kirchoff—that elicits different meanings from different people. ASTM (1) has, in fact, thrown up its hands in despair, solemnly exiling sensitivity as, "an ambiguous term whose use with or without modifiers . . . is to be avoided." In its place they define "Detection Limit, a stated limiting value which designates the lowest concentration or mass that can be estimated or determined with confidence and which is specific to the analytical procedure used. Note—unless otherwise stated, the detection limit is assumed to have a confidence level of about one standard deviation."

Sensitivity is, nonetheless, pragmatically meaningful and will continue to be part of the trade jargon, furnishing ballpark comparisons of performance. We just know that an arc is more sensitive than a spark, a large spectrograph more sensitive than a small, the 103-0 more sensitive than the SA#1 emulsion, techniques for solids more sensitive than those for solutions, raies ultimes more sensitive than other spectral lines of the same element.

Yet, as we strive to detect elements at ever-decreasing levels, we begin to question, even qualitatively, what is meant by sensitivity and find that at least two distinct meanings are implied. When a sample is excited, the persistent lines of an element may be quite strong but obscured by background and, like the proverbial needle in a haystack, defy finding. On the

other hand, the background may be negligible but the line still does not appear. In both conditions, the limit of detection has been reached. But one circumstance is energy-limited; insufficient energy has impinged on the detector for a positive response to ensue. This state of affairs is referred to as responsivity in infrared technology and we recommend its adoption by emissionists as well.

Thus we might clarify what we think we know is so. An arc is more sensitive than a spark because the spark excites multitudinous "air" lines masking the lines of interest. A large spectrograph is more sensitive than a small one because background spectra are brought up at a slower rate than even a weak line in a large spectrograph. A small spectrograph is generally, however, more responsive; it is optically faster. The 103-0 emulsion is more responsive than SA#1 (i.e., it is faster) yet SA#1 by virtue of its finer grain may under many conditions be the more sensitive. Analysis of a solution is special because so often it contains the element of interest at only a small fraction of that in the solid from which it was prepared. Dilution distorts the responsivity evaluation. Raies ultimes are defined as persistent lines, those last continuing to appear on a photographic plate as less and less sample is consumed. But to detect such lines, the most responsive emulsion at the indicated wavelength must be used.

To be sure, this criterion also distinguishes trace from micro analysis. When a tiny sample is arced energy emitted is often too weak for spectral lines of elements to be detected let alone the background which arises from a variety of causes. Responsivity here may be thought of in terms of the limiting sensitivity of the detector under no-noise conditions. On the other hand, sensitivity, more applicable to trace-element analysis, refers to the limiting concentration of an element such that its most persistent line manages to emerge just a little bit stronger than the background. Responsivity thus pertains to a detector-limited situation; sensitivity, to a method-limited situation. Improvements in the responsivity of detectors, especially photoelectric, are paralleling other aspects of spectroscopy so the distinction between responsivity and sensitivity is hardly academic. Progress appears to be under way in reducing the noise from sources other than the detector in at least one area—gratings—and such sensitivity advances will be discussed as well.

Similar confusion in terminology has been provoked by astronomers, spectrochemists and manufacturers (of infrared detectors and photomultipliers particularly) alike. Unmindful of prior designations elsewhere, self-appointed semanticists establish such a term as noise equivalent power (NEP). Unlike ASTM's admirable attempt to tie in "detection limit" with statistical fluctuations, the definers of NEP merely state—and thereby allow subjective optimism to get into the act—that NEP is the power required at a signal:noise equal to unity.

The wavelength and chopping frequency must be specified but obviously the noise is not going to stand still for its measurement and so must be gestimated. Depite this, NEP as a figure of merit can be approximated with a good deal of certainty for a given detector if not for the generic class of detectors from which it derives. Thus, two otherwise identical S20 photomultipliers with different cathode diameters will show NEP inversely proportional to their diameters. NEP seems to be a favorite with manufacturers of infrared detectors but an almost identical synonym, equivalent noise input (ENI), is often substituted by photomultiplier manufacturers. The only difference between the two is in units. NEP is expressed in watts, ENI in lumens.

Detectivity  $D^*$  (also called Detector  $D^*$  or  $D^*$  alone) is a term introduced to remove the dependence of NEP on the detector sensitive area. It is defined as:

$$\text{Detectivity } D^* = (\text{Detector sensitive area})^{1/2} / \text{NEP.}$$

Since the area of the device is cancelled out,  $D^*$  is helpful in comparing materials rather than specific devices. Presumably, from their  $D^*$  values, one should be able to predict which type of detector would be best suited to a particular application. If you are not already confused, let us bring in detectivity alone (without the  $D^*$ ) which is simply the reciprocal of the NEP. It assuages those thinkers who need the figure of merit to increase with improvement.

Responsivity comes closer to having a single meaning, applicable to any of the photoelectric detectors. To infrared specialists, it is a measure of the signal voltage developed by a photovoltaic device when exposed to a given amount of power and is expressed in volt/watt. Photodiodes—photoconductive devices—are similarly rated in  $\mu\text{amp}/\mu\text{watt}$ . Responsivity of a photomultiplier, however, is given, after internal amplification of  $10^6$  or  $10^7$  at the final anode, in amp/lumen. For consistency, responsivity should refer to the initial stage of the photomultiplier, at its cathode where the energy conversion occurs. Instead, this is usually designated as "cathode luminous sensitivity." Knowing the amplification factor, however, one can readily transpose the two.

If only early photographers had had the foresight to speak of responsivity instead of sensitivity when referring to the speed of their emulsions, terminology might have been surprisingly uniform for both photoelectric and photographic detectors. The photographic emulsion is, unlike most other devices, an integrating detector whose blackening depends on the total amount of energy rather than intensity falling on it. Nevertheless, were its blackening ability called responsivity and framed in units of density/exposure, there would be some degree of consistency in terminology.

So we don't lose track of our goal while wading amidst these semantic obstacles, let us state one of our objectives: to show that modern photomultipliers are better than modern photographic emulsions for the detection of weak signals. They are, in other words, more responsive. To achieve the limit of detection in micro analysis and often in trace analysis, photography should be abandoned in favor of direct-reading photoelectric spectrometers. This does not mean that an ordinary 1P28 tube can be hooked into a direct reader designed for the analysis of steel for one to be rewarded with instant lowering of detection thresholds. It does mean that the best modern photoelectric techniques surpass the best modern photographic techniques for weak-level detection by a factor of about 100\*.

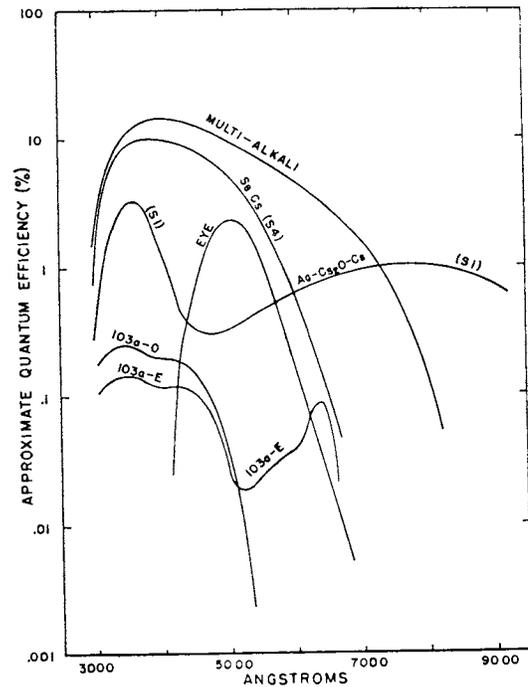


Fig. 1. A comparison of the quantum efficiency of photoemultipliers with different cathodes, various photographic emulsions and the human eye. The "Multi-Alkali" curve refers to an S-20 photocathode which can be extended below 2000Å with a quartz envelope. Some S-20 photomultipliers have a peak QE of 25% at around 4000Å. (Courtesy W. A. Hiltner, *Astronomical Techniques*, U. of Chicago Press, 1962.)

Since it is impossible to convert amp/lumen of a photomultiplier to density/exposure for a photographic emulsion, we shall attempt an alternative approach to compare their responsivity. Their ability to convert a photon of energy into measurable signal, quantum efficiency, can be stipulated for both detectors. A photon at 2000Å ( $50,000 \text{ cm}^{-1}$ ) has 2-1/2 times the energy of one at 5000Å ( $20,000 \text{ cm}^{-1}$ ), however, and, except for thermocouples, linear detectors, equally efficient at converting incoming energy irrespective of wavelength, are not known. But in the ultraviolet through the visible modern photomultipliers exceed their photographic counterparts by a factor of 100. A tube with an S20 cathode has a quantum efficiency as high as 25% while the best photographic plate shows perhaps 0.1 - 0.3%. At least 500 photons at 4000Å must impinge on a photographic emulsion for a single silver grain to darken. Only four such photons suffice for a photomultiplier to emit a recognizable signal that can be positively identified and permanently recorded.

The 16-stage ITT FW 130 stands out among photomultipliers because of its combination of high quantum efficiency, low noise and dark current. It has an S20 coated cathode of 3 mm dia. and dark current, being proportional to the cathode area, is markedly less than in similar tubes. More important, the erratic noise current is reduced by the square

\*A recent ad by Eastman Kodak announcing two experimental emulsions shows that they do not mean to have photography left by the wayside. Type IIIa-J is for long exposures (the "a" stands for astronomical) and "extends the limits of optically observable celestial objects by another magnitude or two." S.O. 166 is for short exposures—micro spectrochemical analysis, photography of phosphor screens and other "fleeting signals."

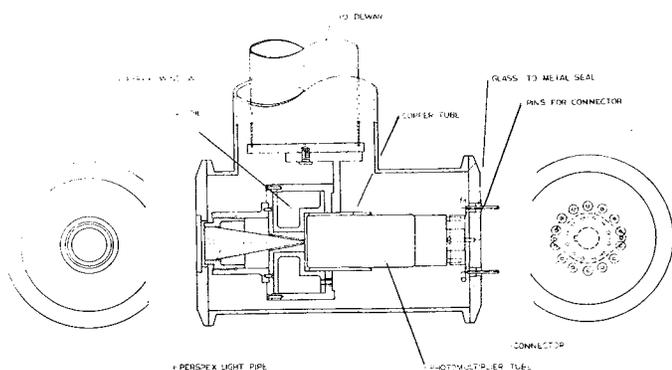


Fig. 2. J. A. Koningstein of Carleton Univ. has utilized this arrangement to effectively reduce the cathode area and thereby the dark current of an EMI 9558 PM tube by introducing a magnetic field. He obtained a 100-fold drop in dark current from the magnetic constriction of the cathode area, estimating as few as 30 electrons/sec. leaving the operative part of the photocathode.

root of this area. For many spectrochemical analyses, merely positioning a condensing lens after the exit slit will tuck a line image inside the cathode face. Cooling to 195K will further reduce noise by a factor of 100, enabling this tube to detect signals so weak that, even given eons of exposure, they could never trace their shadows on a photographic plate. Here the reciprocity law breaks down utterly.

To be most effective for our spectrographic tasks all this responsivity rates top notch amplification. Currently photon counting appears to be optimum. Conceptionally identical with pulse-counting in x-ray analysis this amplification ignores all anode events which do not carry the proper credentials of rise-time and amplitude. At low light levels photoelectrons are emitted in a random fashion from the cathode. Sped through the dynode chain they emerge fully amplified and within a fixed range of energy. A significant portion of noise electrons, on the other hand, originates not from the cathode but between there and the final anode so their amplification is considerably lower. Pulse-height rejection at the low-energy end thus suppresses such dark noise, maximizing detection of weak radiation. At the same time a high-end discriminator rejects electron bursts from radioactive  $K_{40}$  impurities or cosmic rays, forming an effective energy window. (A further discussion of photon counting can be found in THE SPEX SPEAKER, Vol. XI, No. 4.)

**I**F all spectrographic analyses could be conducted under conditions such that the background originated only from the detector (noise and dark current for a photomultiplier, chemical fog for a photographic emulsion), the limit of detection for all elements would be improved by a factor of at least one or two orders of magnitude. Here then lies at least one of the master keys to trace-element analyses in the years ahead. Significant progress has been made, as already stated, in this direction by reducing the scattered light originating from gratings. It has been shown that stray light in properly baffled grating spectrographs originates almost entirely from the grating face and that individual gratings vary in this respect by a factor of 10 to 100. Although all of the causes of such scatter have not been isolated, two are well known

and can be depicted geometrically. Fig. 3A is a cross-section of the rulings of a theoretically perfect grating. No incoming light striking the groove face can be reflected; the grating cannot act as a simple mirror. Fig. 3B is a cross-section of the rulings of a typical grating where some unrulled area, fallow land, remained. This grating acts partially as a mirror, reflecting light to the direct image position thus reducing its diffraction efficiency. More important for trace analyses, such a grating gives rise to scattered light which then interferes with lines being sought. The high intensity continuum of a graphite arc bounces around inside the spectrograph and some of it likely as not will alight in the region of a line of interest.

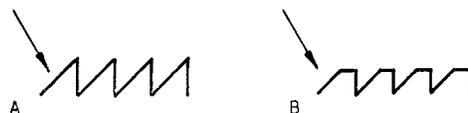


Fig. 3. An ideal grating groove profile is depicted in A. Residual land in B would reflect some of the light thereby introducing scatter and reducing overall efficiency.

A second characteristic is known to influence stray light. When a diamond plows through soft metal to produce a grating groove, debris is deposited on the ridges as well as at the end of the groove. The material on the side is piled up unevenly, leaving reflecting particles of metal pointed every which way. Still further, as the diamond moves across the master blank, it is subject to vibration and chatter. As a result, the groove face is not ideally flat and burnished but is wavy and rough.

The significance of a grating having the least light scattering quality to a spectrochemist interested in pushing the limit of detection of his analyses to its extreme is illustrated in Fig. 4 and 5. What we attempted to do was assure unquestionably reproducible conditions with only the grating a variable. Thus avoiding sparks and arcs, we chose a mercury discharge Pen-lamp, having faint lines of Hg "stand in" for what would normally be faint lines of trace elements. Fig. 4 is a photograph of two sets of three spectra exposed for 3, 10 and 30 seconds on a Spex Model 1700-III spectrometer. The upper set was taken with a grating ruled non-interferometrically; the lower with one ruled interferometrically. While the method of ruling may be incidental, the difference in scattered light between the two gratings is striking. Note that the pair of second-order lines on the right at 3125 and 3131A shows about the same density indicating that the two gratings have about the same efficiency but that the second order 2762A line is more easily observed with the first grating.

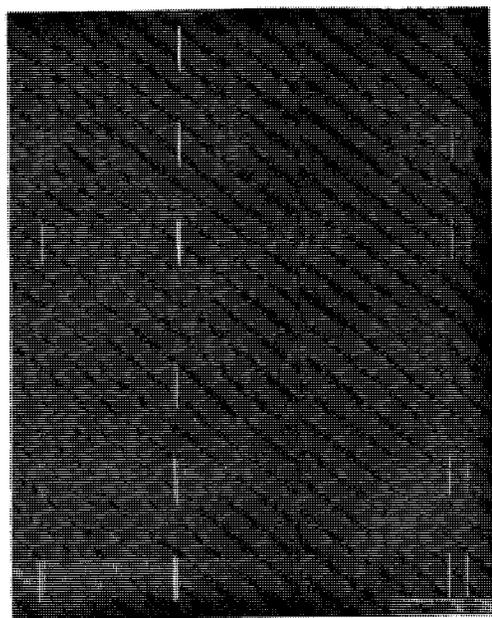
How much more was appraised photoelectrically and illustrated by the tracings in Fig. 5. The 2762A line has a S:N of about 12 for grating A as compared with about 2 for grating B. Merely changing gratings can improve the limit of detection by a factor of 6. And this figure is quite conservative since the scattered light, as can be observed in the tracing, does not consist of a uniform fog but is a series of closely-spaced peaks of differing amplitudes. Should the analytical line of interest happen to lie on a particularly strong scatter peak, the detection limit would be worsened far in excess of 6.

The practical significance of grating scatter is obscured by the fact that relatively few spectrochemists are aware of it or are in a position to compare the performance of their own spectrograph in this regard with others. We are convinced that the wide discrepancy reported in limits of detec-

tion are in large part due to varying stray light. Let anyone attempt to compare from literature references the limit of detection of various methods and he will find himself engulfed with contradictory, inconsistent numbers. It is not uncommon for two authors describing substantially the same technique to furnish limits of detection differing by a factor of 100. Literature inconsistencies are so numerous that one cannot ascribe them simply to subjective differences or "eyeball" optimism.

We are convinced, too, that a majority of spectroscopists would attain an enhancement factor of up to 10 in their limits of detection merely by carefully selecting and substituting a new grating. Strong words, yes, but they are backed by over two years experience with the Spex Model 1400 Double Spectrometer which is applied primarily to detection of Raman lines whose intensity may be as weak as  $10^{-10}$  of the exciting line. Here selection of gratings with low stray light is paramount for observing molecular scatter from phonons, magnons, molecular and elemental species.

Hg 5461



GRATING A

GRATING B

Fig. 4. Grating A and B, equivalent in all other respects, scatter light differently by a factor of 6. Grating A is at least that much better in its limit of detection than Grating B, a Bausch & Lomb reject.

In discussing some causes of grating scatter, we mentioned that poor efficiency often goes hand in hand with high scatter. Today's best commercial replicas show efficiencies in the order of 70-90% at their blaze wavelength, dropping to about half that at 2/3 or twice the peak wavelength. Efficiency is defined in terms of an aluminized reflector: a grating with an efficiency of 80% at 5000A diffracts 80% as much light as is reflected by an aluminized mirror at that wavelength. Early unblazed gratings ruled on speculum or even recently ruled blazed gratings may have an efficiency maximum of as little as 10%. Researchers at Oak Ridge (2) were amazed to find the real speed of their spectrograph improved by a factor of 10 when they switched to a B&L replica. The original grating, itself not more than a few years old, exhibited peak efficiency of 10%.

While it is certainly true that grating scatter is more important than grating efficiency in trace-element analysis, the latter is equally important in micro analysis and in many instances has a strong bearing on the limit of detection in trace analysis. In the analysis of oxygen-free copper for example Publicover (3) recently set down his method which has been extensively applied for at least ten years. A comparatively large sample (2g) of copper is placed inside a tapered graphite crucible and arced for 90 seconds at 15 amp. In this brute-force approach about 80 mg is lost of which most consists of impurities which either volatilize (e.g., As, Cd, Zn, Hg) or oxidize forming a slag on the surface (e.g., Fe, Mn). If Publicover substituted a grating with but 1/10 the efficiency at 2311A, he would require ten times the amount of sample to detect an equal concentration of antimony.

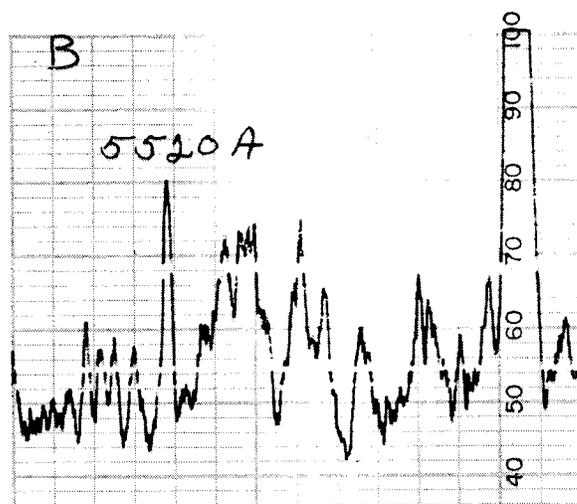
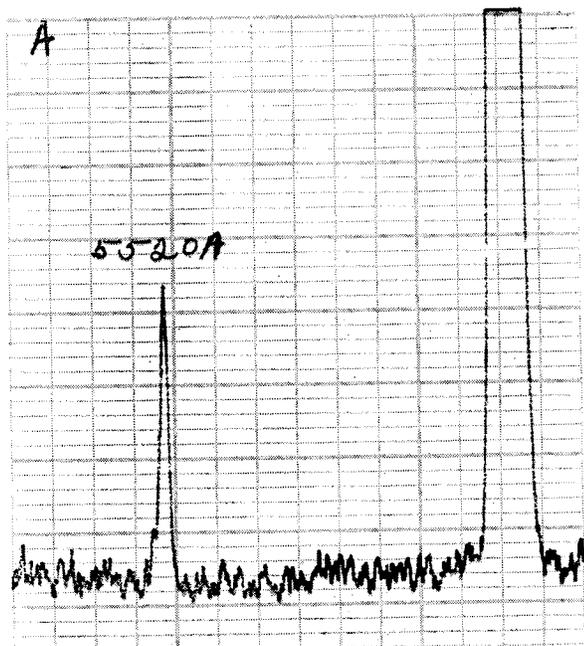


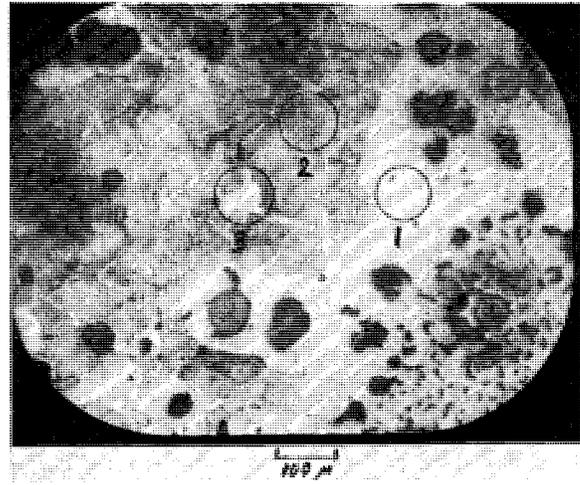
Fig. 5. Comparison of the photoelectric S:N of the second order Hg 2762A line (identified on the raw data charts as 5520A) produced by Grating A and B on the identical spectrometer and under identical conditions. The excessive scatter in the rejected Grating B is seen to fluctuate erratically.

Especially with a plane grating spectrograph, the measurement of grating efficiency is not too difficult. An aluminized mirror is simply taped on top of the grating for the comparison. The source can be a mercury discharge Pen-light covered with an appropriate interference filter to isolate three or four of the principal lines. Of course, photoelectric measurements are best but photographic comparisons may be conducted alternatively. The time-ratio needed to obtain equal densities by the mirror and grating provides a good approximation of efficiency.

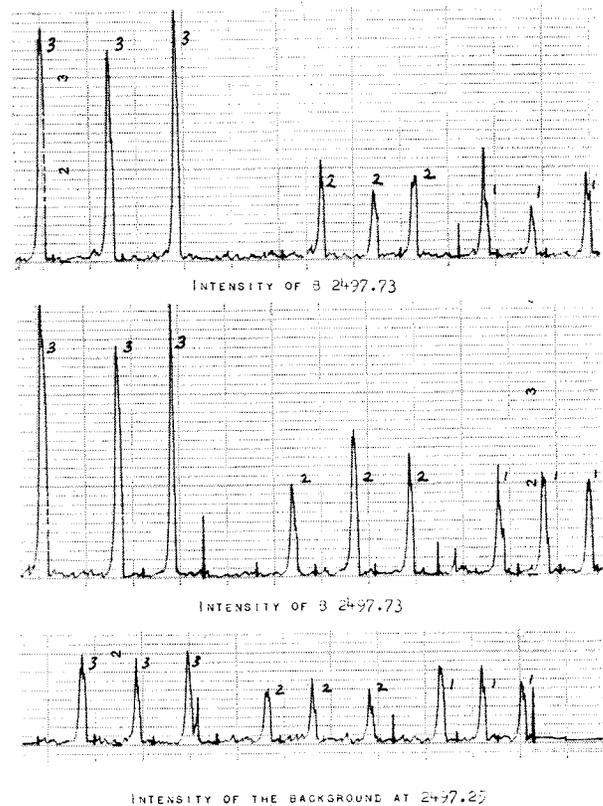
**I**N the past few years, several spectrographic techniques have been developed for micro analysis, either of very small samples or of equally small areas within larger samples. While overlapping broadly, each has its advantages and limitations. The electron microprobe is presently king, capable of many pictorial modes of presenting data, sampling down to around 2 microns and being almost completely non-destructive. Its principal drawbacks are cost and inability to detect the lower atomic number elements. Carbon, for example, escapes identification. X-ray milliprobes are in widespread operation. They have the same low atomic number limitation as the electron probe, have a spatial limitation of around 300 microns, but, as a relatively simple attachment to an ordinary x-ray spectrograph, cost only a few hundred dollars. The laser microprobe is an emission spectrographic device. As such, some 70 metallic elements fall within its scope. Unlike the electron microprobe, the sample need not be electrically conductive enabling the analysis of inclusions in refractory materials. Because of the intense energy density of the pulsed laser source in the laser microprobe, the optics cannot condense the beam to a diameter less than about 50 microns without destroying the glass sets. This then sets the spatial resolution of the instrument. The laser serves only to volatilize the sample; triggered by the ionizing path of the volatilizing elements, a spark excites the spectrum.

Our own contribution to the micro analytical field is the Spex-Mallinckrodt Atomprobe Microspark Analyzer. An emission spectrochemical instrument, it depends on a confined spark alone for excitation. At present only electrically conducting samples can be analyzed. Demonstrated spatial resolution is 5-10 microns. Its ability to detect tiny areas of boron and carbon as well as borides and carbides in alloys marks it as unique among the microprobes. The power of the Atomprobe is evident from the jobs it has already tackled. (See THE SPEX SPEAKER Vol. XI, No. 3 for a fuller account.)

A sample of nodular cast iron to which boron had been added was received for analysis. Comparing this developmental alloy with normal nodular cast iron, the metallurgist found a new phase consisting of triangular components about 60 microns on a side. He assumed that the boron was concentrated in this phase but had no way of proving it with his existing electron microprobe. With the Atomprobe we had no difficulty not only detecting the boron throughout the sample but also showing that the boron had indeed accumulated in the new phase. Fig. 6 is a photomicrograph of the iron alloy in which the new triangular phase is designated as 3. Perlite and ferrite phases in the alloy contain about the same amount of boron as demonstrated by a photoelectric scan of the B2497A line; the new phase was found to contain about four times as much boron (Fig. 7). Sparking for but three seconds and integrating the energy electronically was sufficient to record the boron line on a Spex 3/4-meter Model 1700 Czerny-Turner spectrometer equipped with a 1200 groove/mm grating blazed for 5000A and set to the second order.

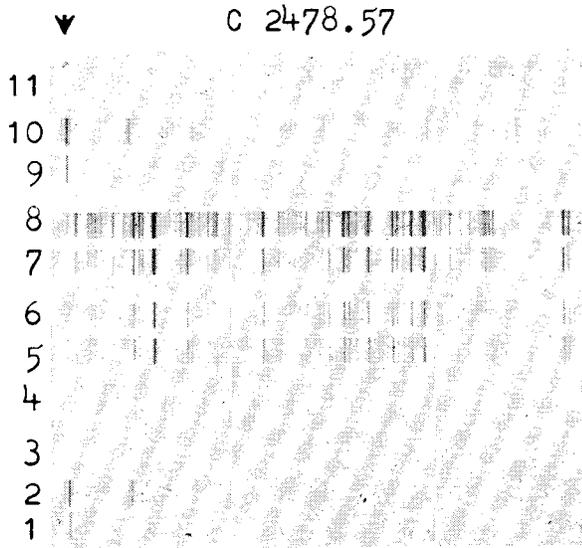


**Fig. 6. Photomicrograph of a nodular cast iron sample. The numbers pertain to the various phases present: 1) is in the ferrite area; 2) in the perlite area; 3) a new triangular phase found when boron was added to the alloy. Atomprobe analysis showed that boron was concentrated in the new phase. The black circular areas are, incidentally, carbon nodules from which the alloy takes its name.**



**Fig. 7. Phototelectric tracings of the boron 2497A line taken at three areas within the nodular cast iron pictured in Fig. 6. Note that although the background at the lines remains relatively constant the net intensity of the boron line is considerably stronger in the triangular phase designated as 3.**

During the course of working with this nodular iron sample, we received a request concerning the possibility of detecting carbon. The graphite spheroids were a natural place to start experimenting. On our very first attempt, depicted in Fig. 8, carbon 2478A poked out in the spectrum of the nodules. Elsewhere in the alloy a line appears at 2478A but at a much lower intensity. It is probably a weak, interfering iron line.



**Fig. 8. Detection of carbon in aluminum and nodular cast iron. Spectra 1 and 2 show carbon specks of about 50 microns diameter in aluminum while 3 and 4 are of the base material exposed for equal intervals of 20 and 40 seconds. Spectra 5 and 6 are of the graphite nodules in cast iron; 7 and 8 show the iron line superimposed on C 2478A. Spectra 9 and 10 are of graphite and 11 of tin as references.**

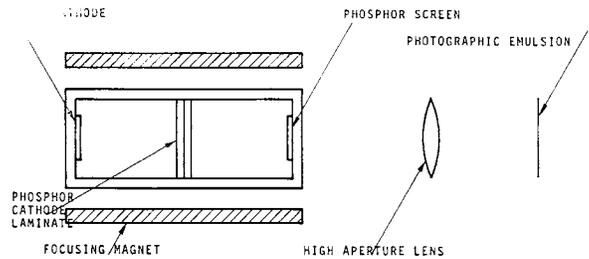
The real problem at hand was the identification of microscopic black dots on the face of an aluminum extrusion. The dots interfered with subsequent anodizing, leaving pit marks which, in turn, reduced the notch strength of the extrusion, a critical aircraft component. When directed to the black inclusions as small as 70 microns in diameter, the Atomprobe readily picked up carbon. Now the story was clear: a graphite lubricant, probably used in the extrusion process, became embedded in the aluminum surface. Aluminum turned out to be an excellent matrix for the carbon determination, incidentally, in that there was no interference at 2478A. The analysis supported our earlier conclusion that what we were seeing in the cast iron ferritic and perlitic phases was not residual carbon but a weak interfering iron line.

**P**HOTOELECTRIC devices exhibit a considerable edge over photographic emulsions with respect to responsivity. Photographic techniques, on the other hand, hold a powerful edge in their ability to display a long spectrum instead of a single line. Unwilling to trade one for the other, astronomers have become marriage brokers successfully wedding the two to obtain devices known as image converters or intensifiers.

Dating from the '30s several types of image converters have been invented. The earliest, the Lallemand Camera Electronique, incorporates a cathode, electrostatic focusing, a transparent fluorescing screen and a photographic plate within the same evacuated housing. While it has produced spectra of excellent quality, the set-up time is objectionably long. A fresh photocathode must be prepared in a sealed capsule, broken by a magnetic hammer, then inserted in the path of the plate each time a new plate is needed. The TV camera

or image orthicon is another type depending on scanning electromagnetically or electrostatically in a raster pattern. A variant of this is the Vidicon. A photomultiplier itself can be used as an image converter by providing it with a parallel magnetic field so that each secondary electron ejected from a focused image on the cathode surface is directed in a straight line in the dynode chain. The Lallemand camera has been improved by strengthening the transparent fluorescent screen to withstand atmospheric pressure. In the resulting Spectracon, a photographic film at ambient pressure is pressed against the evacuated screen.

According to Baum (4), the most promising image converter-intensifier is the so-called cascaded type. Fig. 9 is a diagram of a two-stage cascaded image converter; single and triple stages have been constructed as well. In this device, light is first received on an ordinary tri-alkali S20 cathode surface. For about every seven blue photons impinging on the surface, one photoelectron is ejected from the reverse side of the cathode. Differing from a photomultiplier which employs an unfocused, charged, opaque anode to attract the ejected electrons, the image converter employs a transparent membrane laminate. On the electron side of the membrane is a phosphor which emits about 350 photons for every electron received. On the reverse side is another cathode from which 50 photoelectrons are emitted. Repeating the process, a two-stage cascaded image intensifier will show an overall light gain of about 2500. To prevent light feed-back from one stage to the preceding one, the phosphor coating on the membrane is protected with a thin layer of aluminum, opaque to light but relatively transparent to the electrons which are charged to about 10 kV.



**Fig. 9. A 2-stage cascaded image intensifier. Light entering the photocathode is reimaged at the first phosphor-cathode by means of the focusing magnet and intensified by applied high voltage. The process repeated, a light gain of about 2500 is achieved at the rear phosphor. Transfer optics reimagine the highly-diverging light on a photographic emulsion.**

Most of the light gain of 2500 is empty magnification, however, leaving much room for improvement. What the spectroscopist is seeking is information gain rather than light gain. The light at the final phosphor screen of the converter diverges over a wide solid angle. Even an f/1 transfer lens can reimagine only about 3% of this light on a photographic emulsion. At the same time, the resolution of the imaged light on a photographic emulsion will show about 25 line pairs/mm as compared with three to four times that for the same photographic plate exposed alone. Baum states that, although the blackening of the plate at the phosphor is some 75 times faster than an unaided plate, the degradation of information for spectroscopic purposes is proportional to the factor by which the overall resolution is reduced. Combining the two, a factor of about 11 improvement in information gain is obtained with the cascaded image intensifier over an unaided plate.

To an astronomer this factor of 11 may mean the difference between a three-night vigil under hopefully-clear

skies and a comparatively leisurely two-hour stint to obtain equivalent spectra information about a distant stellar body. Already, distant stars are being photographed with the aid of image intensifiers. Red shifts which more than double the wavelength of the light have been observed from newly-discovered quasars indicating that they are over  $10^9$  light-years from our galaxy, the farthest stellar bodies ever reported.

In the years ahead such spectacular rewards may be reaped by the emission spectrochemist as well as the astronomer. Until now, the former's main tools have been spectrographs with an f/number of about 20. Special-purpose, faster spectrographs have become available but, with few exceptions, even these have not gone beyond about f/6. As the pioneering astronomers proceed to improve that factor of 11, we analytical chemists will be watching closely to upgrade our responsiveness. Right now the factor of 11 may not seem too attractive weighed against the approximately \$5,000. that it represents in electronic and optical gear. However, compare

this with existing spectrographs. The Spex f/6.3 instrument is priced around \$8,000. while a commercial Meinel f/2.8 instrument, with but about a 5-fold speed gain, costs about \$35,000.

Where to start and when to stop in a review paper are always difficult to decide. Many new and promising techniques have been omitted as surely as the fact that some of the methods described will not pass the hardest test of all: time. We promise to reread this paper in a few years and see if we can once again set the record straight. ASTM has had the foresight to prepare our path with a newly-defined term: ultra-trace analysis (under 1 ppm).

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### PELLEMENTS? ELEMENTARY!

Equally in direct reading emission spectroscopy and in x-ray spectroscopy, a need exists for "setting up" standards to maximize the output signal to the detector. In the one a refractor plate is rotated or the individual element exit slit is moved to peak on the line to which the photomultiplier is set. In the other the goniometer is adjusted for maximum response to x-ray spectrographs. Doing this often means scurrying about for a chunk of metal containing the element of interest and, in the likely case that it contains several other unknown elements, running the risk of adjusting an instrument to an interfering line.

So we offer Spex Pellements, pressed pellets of compounds of individual elements at a 1% concentration level, to reduce the scurrying cost, by an amount perhaps equal to several times their modest price. Inside one of our Spec-caps is pressed a mixture containing the element in a matrix of SP-1 high purity graphite powder. The resulting pellet, about 3/16" thick, is flat, smooth, conductive for sparking on a Petrey Stand or can be easily set into the sample compartment of an x-ray spectrograph, vacuum or air. Reinforced by the aluminum Spec-cap, it is strong enough to resist a drop or two from bench to floor.

### SILICON METAL POWDER STANDARDS

Starting with G (graphite base) semi-quantitative standards in 1954, we have built up a library of powder standards specifically applicable to a number of matrices. Finally acknowledging that silicon solid state devices are here to stay, we now prepare a set containing the 49 common elements of Spex Mix in a silicon metal matrix of undoped semiconductor-grade purity, effortlessly pounded to a particle size of -325 mesh by shaking chunks together with Lucite balls in a #8006 Lucite container with the Spex Mixer/Mill. Included are:

Ag Al As B Ba Be Bi Br Ca Cd Ce Cl Co Cr  
Cs Cu F Fe Ga Ge Hg I In K Li Mg Mn Mo Na  
Nb Ni P Pb Rb Sb Se Si Sn Sr Ta Te Th Ti Tl  
U V W Zn Zr

### MORE MANAGEABLE SLIP-RINGS FOR X-RAY CELLS

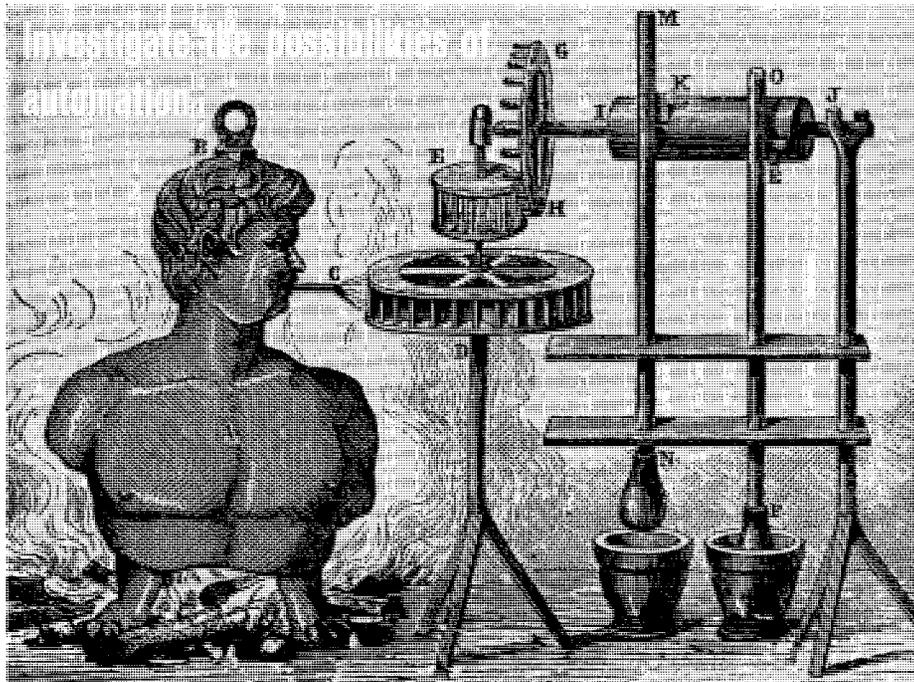
Despite the fact that very few complaints have drifted back to us in the six years since the cells were introduced and the further fact that their rapid rate of sales growth would give them a clean bill of technical health, handling of our X-ray cells (#3515) has been improved to make them even more attractive. Synthetic rubber O-rings (#3519) are being substituted for the Teflon (#3516) and polypropylene (#3514) rings sold previously to hold the Mylar film in place.

To counteract the frustration of having only ten fingers anchored to two hands we also came up with a simple Placement Tool (#3513). Assembling is accomplished by first pushing the O-ring down . . . oh, take our word, it works!

It also seems about time to drop the "Liquid" from their name. Powders and Millipore filter catches, as well, are conveniently held by sandwiching them between two layers of Mylar. For this you'll need two rings per cell.

- |   |      |                 |
|---|------|-----------------|
| <b>1015 Pellement</b> , pressed pellet 1-1/4" o.d. x 3/16" thick, containing 1% of any one of the following elements (specify) in a high-purity graphite base: Ag, Al, As, Au, B, Ba, Be, Bi, Br, C, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr ..... | Each | <b>\$ 15.00</b> |
| <b>1106 Silicon Metal Standards</b> . 0.1%, 0.01%, 0.001%, 0.0001% of 49 elements in Silicon Metal Base (for analysis of silicon solid state materials) set   |      | <b>\$68.00</b>  |
| <b>3513 Placement Tool</b> for slipping O-ring over x-ray cell .....  | Each | <b>\$ 5.00</b>  |
| <b>3515 Expendable x-ray cells</b> , polypropylene .....  | 100  | <b>\$ 9.00</b>  |
|   | 1000 | <b>\$65.00</b>  |
| <b>3517 Mylar</b> , 1/4-mil film, 2-1/2" x 300 ft. ....   | roll | <b>\$10.00</b>  |
| <b>3519 Expendable O-Rings</b> for #3515 cells.....   | 100  | <b>\$ 8.00</b>  |
|   | 1000 | <b>\$56.00</b>  |

Investigate the possibilities of automation.



THESE TYPICAL GRINDING RESULTS MAY UPSET SOME DOINGS WHICH PREDATE THIS PATENT APPLICATION

HARRIS'S STEAM ENGINE, A.D. 1873

| Material           | Form        | Container | Grams | Min.* | Material          | Form   | Container | Grams | Min.* |
|--------------------|-------------|-----------|-------|-------|-------------------|--------|-----------|-------|-------|
| Asbestos           | Fibrous     | 8501      | 20    | 12    | Lime              |        | 8504      | 35    | 2     |
| Boron Carbide      | Chunk       | 8004      | 7     | 15    | Limonite          | Grains | 8001      | 3     | 30    |
| Carbon (Activated) | Chunk       | 8004      | 10    | 10    | Porcelain         | Chunk  | 8004      | 6     | 15    |
| Cement (Portland)  | Powder      | 8003      | 20    | 30    | Potassium Bromide | Powder | 3114      | .2    | <1    |
| Cement (Portland)  | + 60 mesh   | 8501      | 40    | 2.5   | Silica            | Chips  | 8003      | 5     | 20    |
| Cobalt             |             | 8004 (W)  | 10    | 10    | Slag              | Chunk  | 8001      | 3     | 20    |
| Copper             | Shot        | 8004      | 2     | 15    | Slag              | Chunk  | 8501      | 10    | 1     |
| Fiberglas          | Thin Sheets | 8501      | 10    | 2     | Soda Glass        | Chunk  | 5004      | 1     | 6.5   |
| Granite            | Chunk       | 3127      | 5     | 20    | Ti-diborate       |        | 8004      | 5     | 15    |
| Granite            | Chunk       | 8505      | 5     | 3.5   | Transite          | Chunk  | 8501      | 35    | 10    |
| Granite            | Chunk       | 8503      | 5     | 9     | Zirconium Carbide |        | 8003      | 15    | 30    |
| Ilmenite           | Grains      | 8004      | 5     | 10    |                   |        |           |       |       |

- 3114 -- Stainless Steel Vial in 5000 Mixer/Mill
- 3127 -- Tool Steel Vial in 5000 Mixer/Mill
- 5004 -- Tungsten Carbide Vial in 5000 Mixer/Mill
- 8001 -- Tool Steel Vial in 8000 Mixer/Mill
- 8003 -- Alumina Ceramic Vial in 8000 Mixer/Mill

- 8004 -- Tungsten Carbide Vial in 8000 Mixer/Mill
- 8501 -- Tool Steel Dish in 8500 Shatterbox
- 8503 -- Set of 7 Steel Vials in 8500 Shatterbox
- 8504 -- Tungsten Carbide Dish in 8500 Shatterbox
- 8505 -- Alumina Ceramic Dish in 8500 Shatterbox

(W) Wet ground (water or 1,1,1-trichloroethylene slurry)

\*Minutes to produce --325 mesh

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