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## A VISIT TO KODAK

THE last article devoted to photographic emulsions to appear in the SPEX SPEAKER was published back in June, 1963. Recently, I reread it and found, much to my surprise, that it seemed remarkably current. The types of emulsions recommended, calibration techniques and processing conditions have hardly changed.

Or have they? The practicing spectrochemist, concerned mainly with obtaining reliable analytical figures, tends to ignore the photographic end of things. He has enough trouble tracking down and overcoming variables elsewhere in his operations. So perhaps there have been developments about which he is unaware. The thought persisted and, finally, I decided to update my own knowledge. What better way to do this than to visit Eastman Kodak? Arrangements were made through Ed Hahn who associates with Bill Swann in that homey department at Kodak dealing with the strange requests made by curious scientists. Over two days Mr. Hahn led me on whirlwind and often impromptu visits to laboratories and offices of theoreticians in all four corners of Rochester as I made determined attempts to find out what's new.

First stop was with Don Anderson in the Industrial Laboratory at Kodak Park where a spectrochemical system was installed in 1954. Prior to that time, the Research Laboratories shared with the Film Testing Division a prism spectrograph and the responsibility for the development and control of spectrographic products.

Over the past 16 years the production-oriented, well-equipped emission laboratory has contributed immeasurably in controlling the quality of standard photographic products, working daily with those that most spectrographers have come to rely upon to help solve their problems.

Today, the Industrial Laboratory operates on two shifts with a Baird 3-meter photographic spectrograph as well as a Baird direct reader, the latter handling the standard method analysis. Integrated with other sophisticated pieces of analytical apparatus, the spectrograph polices the raw materials going into Kodak products. The composition of zinc and aluminum castings for cameras and projectors, of film bases, of photographic paper, of silver nitrate and alkali halides and gelatine for emulsions—all these and many more—is controlled through rigorous, routine testing.

Cleanliness is the master key to quality control of photographic plates. Particulates in the air wind up as obtrusive white or black spots on the emulsion. Atmospheric impurities of many kinds sensitize or desensitize plates, upsetting their uniformity. A few ppb of mercury in the atmosphere can ruin an emulsion because it is such an excellent hypersensitizer or fogging agent. And mercury salts are of course

prevalent in skin medications. It takes a good deal of detective work to keep employees from inadvertently bringing into production areas not only mercury salts but any of hundreds of salves, hair tonics and cosmetics which can raise havoc with the properties of emulsions. Kodak maintains a list of materials that are considered safe for use with photographic materials. The list is constantly revised and expanded.

The enviably high uniformity of Kodak's plates and films has been achieved by the joint efforts of many Kodak people. An increasing appreciation of the spectrochemist's needs developed with the uses of these products in its own quality control operations. Before Kodak spectrochemists worked regularly with their own products, production could not be expected to appreciate the importance of a burr on the edge of a plate which would ultimately prevent it from sliding into a microphotometer plate holder. Or that a plate thicker than the nominal 0.040" might break when bent to conform to the radius of the camera in a 1-meter spectrograph. Or that it really was important to perpetually maintain the H&D curve from batch to batch to a degree beyond that required for amateur and professional films. Or that the curling of a film could put sections of it out of focus in the camera or microphotometer. When the significance of all of these properties was brought home by direct experience of lab personnel, their control during production was demanded. All of us have benefitted thereby.

EMISSION SPECTROSCOPY is, as all veteran practitioners are well aware, more of an art than a science. How reliable the final results are and how fast they are transmitted to the customer depend on the overall efficiency of the operation. It is therefore of particular interest to note Kodak's operation, what analytical methods they settle on, how they process, calibrate and measure their own plates.

It turns out that, like other industrial concerns which manufacture a multitude of products, the bulk of Industrial Lab's photographic spectrographic work is semiquantitative; geared to obtain rapid, reliable analytical figures within  $\pm 25\%$  of the actual concentration for the myriad diverse samples received every day. On the other hand, some materials have to be controlled within closer concentration limits. These analytical objectives became the basis for establishing the ground rules for the operation of the spectrographic laboratory.

Semiquantitative analysis immediately suggests dc arcing of the sample to attain the necessary limits of detection. For the analysis of powders in ordinary cratered electrodes an automated procedure has been instituted whereby the arc is programmed to switch from 5 to 15 amperes

after a predetermined time. The entire sample is burned to completion at the higher current. Other excitation techniques depend on the particular type of sample. The graphite spark technique is depended on for the analysis of organic liquids. They are first ashed, taken up in acid and dropped onto the flat ends of 1/4" diameter graphite electrodes which have been presealed with methyl cellulose.

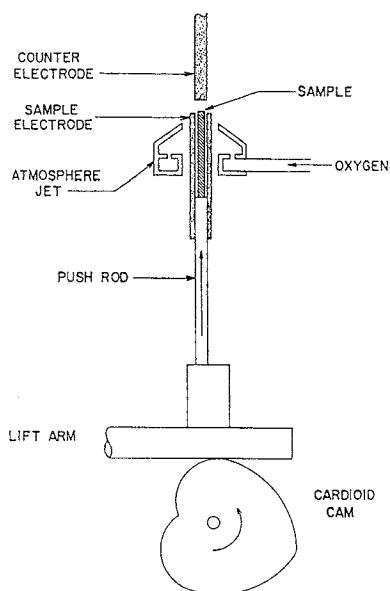


Fig. 1 System for advancing electrodes.

The importance of airborne dirt in the quality control of emulsions can be gauged by the size of the effort devoted to its analysis. The work load of the direct reader on two shifts is largely concentrated on dust samples. A unique analytical method has even been devised for the purpose (1). At stations scattered throughout production areas, small exhaust blowers suck air against filter paper discs about one-inch in diameter. Collected daily, the discs are rolled into tight cylinders and arced in a push-up electrode system shown in Fig. 1. When the analytical results emerge from the computer, the level of dirt and its trend, upward or downward, can be followed methodically. The build-up of a particular element can be watched, hopefully soon to be correlated with something going haywire. Through special computer-generated charts, lab personnel can actually tell when cleaning personnel have been in. Immediately afterward the dirt level rises as some of the fixed dirt is stirred into the air.

Although arcing and preparation techniques are straightforward, several aspects of the photographic process are not. First of all, Kodak spectrochemists expose most of their samples through a 4-step rotating sector. Though wasteful of plate space this technique may constitute the main reason why they are able to achieve excellent accuracy so consistently. Only those steps falling in the straight-line portion of the H&D curve are measured, the proper step for that spectral line selected for measurement by the operator. Should he choose the wrong step, the ever-alert computer flags the analytical result, cautioning that its accuracy may stray outside of preselected requirements.

The Industrial Laboratory does most of its semiquantitative work on the SA#1 emulsion. The first step in working with it is calibration. Only one calibration curve is established covering the region 2800-3400A. Forty-eight iron

lines are measured in two steps each and, based on the two-step method, a calibration curve is drawn. The result is a sort of grand-average curve applicable over the entire wavelength range selected. Over this 600A interval, although the contrast sags from around 1.3 to 1.2 and then sweeps upward to about 1.6, interpolations on a single calibration curve are capable of achieving  $\pm 5\%$  precision. Furthermore, the curve is rarely redrawn. Enough SA#1 plates are stored in a refrigerator to last about six months, the one curve serving all that time. When switching to a new batch, Kodak's spectrochemists usually do not find enough of a change to warrant changing the calibration curve. Part of the secret for obtaining such enviable day-to-day precision is to follow the Industrial Lab's lead by staying clear of the toe and shoulder of the H&D curve.

A secondary secret may be involved in the plate processing operation. Following its own company's suggestions for developing plates, the Industrial Laboratory has installed a nitrogen burst agitator with a Kodak Intermittent Gaseous Burst Valve, Model 90A and the gas distributed in the processor by a custom-made tube. Nitrogen burst agitation boasts undisputed advantages over the ordinary reciprocating approach. Nitrogen keeps the developing solution from oxidizing; its action is random, excluding the possibility of standing waves; vigorous bubbles flush away depleted developer near strong lines to minimize the so-called adjacency effect in which weak lines bordering on strong ones are denied their just share of developer.

Nitrogen burst agitation can easily be installed in a commercial reciprocating processing unit by making suitable modifications to it and purchasing components from Kodak (2). The Industrial Laboratory started with a commercial unit. Its mechanism was detached from the first (developing) tank and in its place was inserted a perforated stainless-steel distributor. This tube lies on the bottom of the tank permitting the plate to be held in the standard rack. The Gaseous Burst Valve is set to cycle about one second on, 8 seconds off. During the one-second agitation period, the liquid level in the tank first rises in a piston action. Then, as the bubbles stampede to the surface, they thoroughly stir up the developer. A 227 cu. ft. tank of nitrogen lasts about four months.

The Industrial Laboratory processes at 21.5 C, develops for 3 minutes, allows 2 minutes for fixing and a 10-minute wash. Twice a week, half the developer is replaced so it always hovers within complacent middle age.

All plates are manually microphotometered. Whether the required results are semiquantitative or quantitative, intensity ratios are taken and interpolated among standards. The sheer volume of samples, however, has prompted the Industrial Laboratory to develop a data handling system utilizing an IBM 360 computer. As the operator lets the microphotometer sweep over the spectral line of interest, a "track and hold" circuit accessory remembers the peak density of the line. After judging from the meter reading that the peak was properly read, the operator presses a foot switch which, in turn, punches the density value on an IBM card. In general background corrections are next made but care is taken to expose the plate so that the background is less than 80% T, i.e., above the non-linear toe of the calibration curve. The computer, into which a stack of cards representing the particular sample is fed, has been programmed to convert transmittance values to intensity through its stored calibration curve. It next subtracts the background from the element line, ratios the resulting value against the internal standard and types out the concentration value for the particular element.

Among the raw materials routinely analyzed by the Industrial Laboratory are batches of gelatine, silver nitrate and alkali halides for trace elements. These of course comprise the principal components of photographic emulsions. In addition, the lab keeps tabs on the heavy metals in the food additives and vitamin concentrates made by Kodak's Distillation Products Industries Division. The lab also operates in conjunction with production of textile fibres manufactured by the Tennessee Eastman Company Division in Kingsport, Tennessee.

All of this trace work is done by the emission spectrograph and photographic techniques. Shortcomings are exhibited only in the analysis of micro samples. Although bulk dust can be analyzed by gathering enough of it on a filter, individual specks do not give rise to sufficient intensity for their emission analysis. Instead, such micro analysis is handled by spark-source mass spectroscopy. Kodak's lab, like most other mass spectrometry laboratories, has found the Ilford Q-2 plate best suited to this work. Ask why Kodak SWR plates are being slighted and it turns out that there is a good reason: outgassing. In mass spectroscopy, the threshold of sensitivity depends on the quality of the vacuum inside of the instrument. At  $10^{-6}$  torr — the limit imposed by outgassing of an SWR plate — this detection threshold is several orders of magnitude poorer than at  $10^{-8}$  torr. This pressure, which can be reached in about 2 hours in the presence of a Q-2 plate, takes the mass spectrometer out to the ppb ballpark.

This brings up the far and vacuum ultraviolet, the region for which Schumann plates such as Q and SWR were originally designed. The range between 2000A and 2500A harbors a number of spectral lines unreachable with ordinary emulsions. Although these lines may actually appear, absorption by the gelatine eats into their intensity; washed out, weak lines are the result.

Several new developments have recently been made in emulsions of the so-called Schumann type. The problems associated with emulsions for this region have been twofold: poor speed and extreme susceptibility to scratching even in normal processing. Some years ago Kodak Pathe in France developed two emulsions, SC-5 and SC-7, which are sold in 35-mm film strips abroad. These emulsions, about ten times faster than SWR, are difficult to obtain here.

Not to be outdone, Kodak Rochester recently announced (3) a similar film, type 101-01, which has neatly mitigated the scratching and marking problem. Along both sides of the unperforated 35mm film, a raised track composed of tiny balls of polystyrene imbedded in gelatine keeps the wound film from contacting itself. The material was originally developed for NASA. Its price of \$46 per 25 feet will, unfortunately, continue to constrain most of its applications to outer space.

### Choosing an emulsion

Reviewing the recommendations made by Spex in 1963 and in 1968 by Eastman Kodak (4), we find a consistent inconsistency. For work in the ultraviolet SA#1 and SA#3, with their relatively high contrast and low speed, were singled out; for the visible and infrared, high speed, low contrast 103-O, 103-F and IN were suggested. Obviously, there's a contradiction here: both cannot be optimum for similar analyses. Assuming that silicon and cesium at the same concentration levels are to be determined in a certain sample, one would expect to be advised to expose analagous rather than antithetical emulsions in the ultraviolet (Si 2881A) and near infrared (Cs 8521A), respectively.

Before attempting to resolve the confusion, one should remember that there are two distinct types of analyses encountered in spectrochemistry. The first and much more common is of a sample representing a large batch of material. Because such a sample could conceivably be as large as the batch itself, the spectrochemist never has to be concerned that it is too small for optimum exposure. In fact, a mistake is easily rectified by rerunning the sample. This "unlimited" sample can be diluted with buffers such as high-purity graphite to reduce the intensity of strong lines down to density values where they can be accurately measured with a microphotometer. For this unlimited sample, the spectrochemist is expected to report semiquantitative or quantitative figures over concentration ranges extending from parts-per-billion traces up to 99%.

At the other extreme is the micro sample, often so small that the analyst must take its spectrographic picture in a second or so before it is puffed away into oblivion. Its spectrum should obviously be recorded on a fast emulsion for, whatever the side effects, the overriding consideration is to get any exposure whatsoever on the plate. Intuitively, then, the unlimited and limited samples call for emulsions of diametrically opposing properties. As we hope to show later, however, intuition may have to be tempered somewhat.

Both intuition and reason tell us that the best emulsion for the unlimited sample is one with high contrast (but, because of the unremitting nature of photographic emulsions, low speed). Whether the work to be done is qualitative or quantitative, for traces or minor constituents, the spectrochemist brackets the intensity of a particular line in the sample inside those of standards. High contrast facilitates and permits accurate comparisons of lines. The most popular ultraviolet emulsion for the purpose is SA#1, combining just the right amount of contrast and speed to optimize crude visual comparisons or rigorous densitometric treatment. The counterpart emulsion to SA#1 in the visible is IV-F; in the near infrared, IV-N. Differing primarily in their wavelength regions of sensitivity, these emulsions are all quite similar in other parameters: contrast, speed and granularity.

But, despite their similarity to SA#1, IV-F and IV-N are rarities. If they are optimum for determining such elements as the heavy alkalis and alkali metals in unlimited samples, why do most spectrochemists seem to prefer 103-O and IN? The answer is inherent in the blaze of gratings. Usually the spectrograph at his disposal incorporates a single grating blazed at around 3000A. Out at 8000A the efficiency of this grating drops to one-quarter or less. Compensating for the loss, most spectrochemists prefer the expedient of switching to a faster emulsion. In so doing, however, they sacrifice the contrast and granularity considerations so desirable in SA#1. They would do far better to expose on slower emulsions, burning their samples four times as long to compensate for the loss in grating efficiency.

Now let's turn to the micro sample for a moment and ponder over the ideal emulsion for its analysis. In general, what is needed is an emulsion maximizing signal-to-noise. Though noise — background — may be essentially absent because the exposure of a micro sample is so weak, it is still necessary to find a wisp of a line above that background. The inquiry then boils down to relating this well known electronic concept of S/N to photographic emulsions. One would think that the photographic counterpart is by this time well established, unambiguously defined, measured and handbook-listed for every emulsion with a scientific application. But the reverse is true. Not only is it

notably missing from the handbooks but photographic experts themselves do not agree on how to define this evasive parameter. No official name has been assigned, although in deference to photoelectric terminology some Kodak physicists are beginning to refer to it as "detectivity."

The parameter that seems closest to pinning down detectivity is a little hard to understand. At least two Kodak physicists — J. H. Altman and A. G. Millikan — define it as the ratio of the change in density of an emulsion to its rms granularity. The numerator and denominator will be discussed separately to show that the neglected ratio promises to be of prime significance to every spectrochemist.

Taking first the denominator — rms granularity. Analogous to the dark current of a photomultiplier, a certain level of background is present in all photographic emulsions. On a *macroscopic* scale, this background appears uniformly grey; like dark current, it may simply be subtracted or biased out. On a *microscopic* scale, however, this is not so. When measured on a microphotometer — the slit size of which is much smaller than that of a normal densitometer — the background fluctuates randomly. It is true noise, statistically varying with the size of the developed silver grains. Like all random noise, rms granularity cannot be biased out, setting the density limit below which a spectral line cannot be detected.

How does Eastman Kodak measure rms granularity? First, the emulsion is exposed to an overall density of 1.0. Then, with a circular aperture 48 microns in diameter, a densitometric tracing is taken. In numerical terms, the published granularity value is a number equal to 1000 times the standard deviation of the fluctuation of the density around the mean of 1.0; that is,  $1000 \sigma (D)$ . For spectrographic measurements, a slit rather than a circular aperture is needed. But the size of the aperture selected is comparable to microphotometer slits in spectroscopy and the numbers obtained are thus significant. SA#1 and IV-series of emulsions exhibit a granularity of .20 or so; 103-F rates twice as poor at .40; the I-series of emulsions are about twice as poor again. Everything else being equal, one can thus expect to detect  $\frac{1}{4}$  the concentration of an element on IV-N as compared with I-N.\*

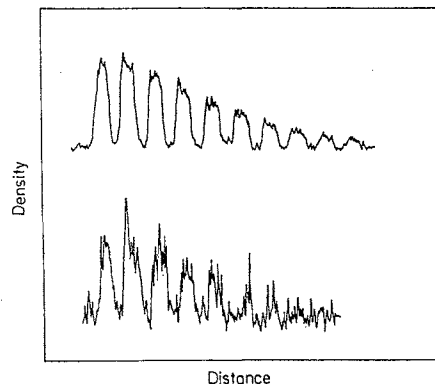
Fig. 2A illustrates the role of rms granularity in S/N. An identical test pattern was photographed (5) on two emulsions in such a way that the ratio of line density to average background intensity is identical. Yet it is apparent that the emulsion with the finer grain structure or superior rms granularity results in the better detectivity. Fig. 2B shows the effect quantitatively through densitometric tracings.



**Fig. 2A** Identical test patterns were photographed first on a grainy plate then on one considerably less grainy. Despite the fact that the line-to-background ratios are similar, the detectivity of lines in the less grainy emulsion is obviously superior.

\*It should be pointed out that at a density of 1.0, background is pretty high for much spectrographic work. The rms granularity of a plate decreases with background level. The argument, however, still holds because the decrease is roughly at the same rate for each type of emulsion.

**Fig. 2B** Densitometric tracings of the lines and background of the exposures of 2A convince one that the effect of enhanced detectivity is not simply an optical illusion.



Now let's return to the numerator in the definition of detectivity: the contrast of the emulsion. Clearly, if the contrast of a plate were zero, no amount of exposure would result in a developable image. At the other extreme, a very contrasty emulsion would favor bringing up a line above its background. Admittedly, the inherent slow speed of the contrasty emulsion impedes the process — it might take an inordinately long exposure to have the line appear — but, once exposed adequately, the contrasty emulsion will result in greater visibility of the line than an emulsion with lesser contrast.

The contrast of an emulsion is of course non-linear. Expressed as density vs. log exposure, it is the familiar S-shaped curve. The "toe" of this curve becomes asymptotic with the base line. This is another way of saying that the contrast of the emulsion approaches zero at low exposure levels. Detectivity is poor in the toe region, and increases to a constant value above the inertia point, corresponding to the inflection in the curve.

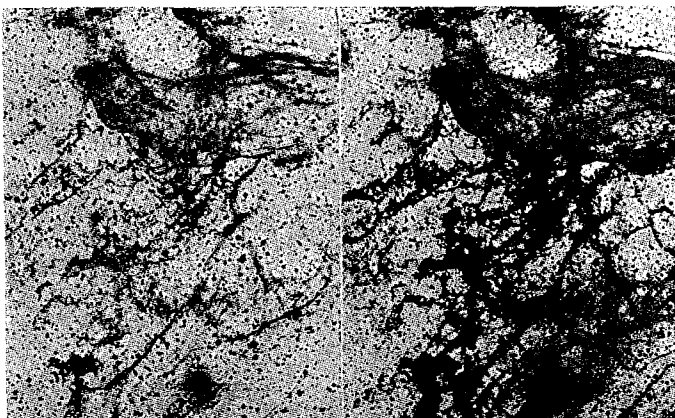
Above the inflection point, the numerator becomes the gradient ( $\gamma$ ) of the emulsion times the difference in log exposure. For a given value of  $\Delta \log E$ , therefore, detectivity reduces to  $\gamma/\sigma_D$ . "Gamma over sigma<sub>D</sub>" is thus identical with detectivity provided the exposure is long enough.

Astronomers were clued in on the importance of detectivity through a paper published in 1965 by Kodak's J. C. Marchant and A. G. Millikan (6). Until that time, one of the favorite astronomical emulsions was 103a-0\*. Marchant and Millikan showed (Fig. 3) that a then-new emulsion, IIIa-J, though less than half the speed of 103a-0, yielded much more information, picking up features which could not be detected irrespective of how long 103a-0 was exposed. (J and O have almost identical spectral response, J extending 500A further to 5500A.) The III-type emulsion is both more contrasty and less grainy than the 103-type and consequently detectivity of the former is doubly better.

A counterpart experiment in spectrochemistry awaits the researcher with time and interest in the problem. Anticipating those results, we do not feel it premature to conclude that SA#1 is an excellent choice for trace-element work in the ultraviolet. What is optimum for micro analysis is not so clear.

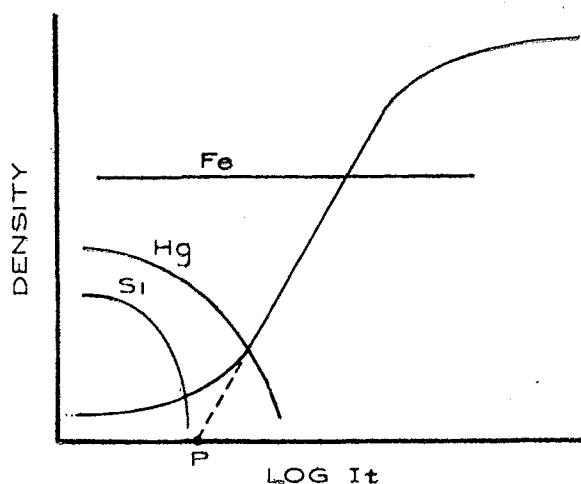
Fig. 4 summarizes idealized trace and micro analytical curves. Burn-off curves for three elements under different conditions are superimposed on a typical H&D curve with its troublesome toe and shoulder. (Normally, the shoulder

\*The "a" designates a modified emulsion with characteristics optimized for long exposures. Anything beyond 2 minutes is considered long so such emulsions might prove beneficial to spectrochemists, too.



**Fig. 3** The detection of weak stellar features is analogous to trace element analysis. A slower but less grainy emulsion on the right, 111a-J, reveals more than the faster but grainier and less contrasty emulsion, 103-O on the left. Exposure time was doubled for the slower emulsion.

is ignored because such high density levels are never measured.) P is the inertia point, the minimum exposure necessary to rise into the region of best detectivity of the emulsion. For the determination of iron in an unlimited sample, the curve labeled "Fe" is drawn. Iron will volatilize more or less uniformly during the entire exposure and the intensity of a selected Fe line will thus remain constant. Burned long enough, the arc will result in enough background behind the Fe line to reach the straight-line or gamma portion of the H&D curve. Under such conditions, artificial prefogging of the plate is unnecessary. Now let's look at mercury in an unlimited sample. Unlike Fe, Hg volatilizes within a few seconds at arc temperatures and, as shown, most of its intensity is lost before the contrast of the plate has had a chance to rise into the gamma region. Prefogging of the plate under such circumstances would then be extremely helpful in lowering the threshold of detectivity of Hg. Note that this is true regardless of whether Hg is present as a trace constituent in an unlimited sample or as a major constituent in a micro sample. Under both conditions, prefogging will optimize detectivity. Finally, let's examine silicon in a fleck of dust. Unvolatile, Si would be expected to burn off uniformly as long as the sample remains in its electrode crater. Within just



**Fig. 4** Idealized burn-off tracings for 1) Fe in an unlimited sample; 2) Hg in trace concentrations in an unlimited sample or as a major constituent in a micro sample; 3) Si as a major constituent in a micro sample. Ordinary SA#1 would be best for case #1. Prefogged SA#1 would be best for case #2. The optimum emulsion for case #3 is not clear.

a few seconds, the entire sample is consumed and the intensity of Si along with all other lines plunges precipitously. The inertia point never having been reached, chances are that Si will not be detected in an unfogged plate. Again, prefogging the plate can help improve detectivity.

Summarizing, it is clear that prefogged SA#1 plates should become off-the-shelf items for a good many spectrochemical problems. Enhancing detectivity of trace elements by possibly an order of magnitude, prefogged SA#1 plates would help edge spectrochemistry closer to those factors known to affect the properties of electronic devices and so simplify many metallurgical, geological and pollution measurements. Not yet clear is what emulsion to recommend for the analysis of micro samples. When a sample can be burned for 5 seconds or so, does the same definition of detectivity apply? If so, would prefogged SA#1 be the optimum emulsion once more? An affirmative conclusion seems to run counter to experience. The analysis of micro samples remains an area where much more photographic research must be done.

Would it not be nice if Kodak offered prefogged SA#1 plates? The subject evokes a unanimous—and understandable—hesitation. For years their goal has been to minimize fog level and extend shelf life against the tolls of time and temperature; fast plates are stored and shipped under refrigeration. Having reached a considerable pinnacle of quality EK's reluctance to reverse itself must be expected to be substantial.

Although prefogging of plates is almost never considered by spectrochemists, astronomers have long practiced the art (7, 8, 9, 10). The trick, of course, is to lift the plate off its toe and take it into the straight line region of the H&D curve where contrast is much higher and uniform. Prefogging is simple. In the darkroom, at some distance from the plate, a lamp is flashed several times to bring the density of the plate up by 0.1 to 0.3 units.

#### XR film for the ultimate dynamic range

Were spectrochemists to be polled concerning what they wanted to improve in the photographic process, high on any list would be the task of expanding the concentration range for any one element when a single line of that element is measured. Right now, the limiting factor is the microphotometer. The transmittance range of commercial comparator-microphotometers is about 2 to 93% (density 1.7 to 0.3). This defines the effective overall concentration range. Assuming a gamma above unity, quantitative measurements are restricted to a range of about 50 times. Si 2881A, for instance, can be measured in samples from, say, 0.001% to 0.05%. For greater concentrations, another silicon line must be selected. Alternatively, through a stepped filter or stepped sector, the concentration range can be extended by choosing the steps appropriate to the density range. But either technique translates into additional analytical time. In the latter, furthermore the number of exposures per plate—the number of samples that can be analyzed on a single plate—is cut drastically.

One way to expand the concentration range is to improve the microphotometer so it accommodates a greater density range. And, as a matter of fact, some commercial microphotometers (without the comparator feature) do indeed cover densities of 5 or 6. Plus-X Pan film developed for 10 minutes in D-76 has this hidden talent of recording over six decades (11). When dense narrow lines are measured with a comparator-microphotometer, however, instrumental scatter rears its ubiquitous head. At a slit width of

50 microns to measure a line of density 0.1 submerged in a background of density 4 requires an instrument that, to my knowledge, has never been constructed.

Let's back up for a moment to a related measurement task in a field that at first glance appears to be far removed. When atomic explosions were first studied, no one could predict within many orders of magnitude the expected intensity of the emitted light. Trouble was there would be only one chance to record the light. Charles Wyckoff, then of EG&G, devised a solution: an emulsion now known as XR for extended range.

XR Film contains three panchromatically sensitized layers. At the top is a fast layer (ASA 400); in the middle, a medium-speed layer (ASA 10); at the bottom a slow layer (ASA 0.004). In other words, the overall speed range of the multiplexed emulsion is  $10^6$ , the latitude around  $10^8$ . The three layers develop into separate colors although, as will be discussed, they bear no relation to the exposure. Through dye forming couplers, the top layer develops a yellow color, the middle magenta and the bottom cyan. As in some kinds of color films, each of the layers simultaneously develops a silver image. This, however, is bleached out in processing.

The XR negative can be measured in a standard microphotometer provided only that its detector is panchromatically sensitive. With a blue filter, the top yellow layer alone is seen and measured. Similarly, a green and a red filter are inserted to measure the other two layers. H&D curves of the three emulsions overlap one another to permit measurements of a single line over at least  $10^8$  density values.

That XR film remains unknown to most spectrochemists is not mysterious. There is a dollar sign to contend with. Processing of XR film requires the elaborate, automated apparatus designed for color film. Elapsed time is around 50 minutes in the Kodacolor C-22 process as the film is rolled through 14 separate solutions. Although this time has been reduced to 15 minutes in at least one special processor operating at 95°F, its cost (above \$50K) would deter most laboratories from further investigation.

The special processor was constructed for MIT's Lincoln Laboratory where reentry phenomena are studied. In a recent telephone conversation, Dr. David Kocher of that

organization, waxed enthusiastic about XR film in their application. From special air-borne spectrographs, spectra are obtained of space vehicles as they plunge their fiery way back into the atmosphere. The intensity of the emitted light starts from zero and rapidly becomes exceedingly bright. XR film is able to record the entire event spectrographically, faithfully following the wide intensity fluctuations. In the MIT work, 3200A is about the lower wavelength cut-off. This may, however, be due to an optical element in the system rather than the film.

AT PRESENT, XR film is not the total answer to a spectrochemist's prayer. One of these days, perhaps Kodak researchers will provide us with an emulsion which we once fancifully called Panutopian-X. The emulsion would be grainless, would exhibit uniform and high detectivity from 2000A to 9000A, would have a toe-less H&D curve with a uniform gamma of around 1.5 irrespective of wavelength, and would be processed in a single solution, automatically stopped when "done." Along with that emulsion, the manufacturer would supply a set of 1000A bandpass filters squarely cutting off high and low ends to block overlapping orders. While we're at it, we might just as well ask that the price be kept down to the equivalent of less than 5 cents per spectrum.

— AJM

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## SPECTROCHEMICAL MANAGER

If you would like to exchange your present laboratory atmosphere for one primarily sales-oriented, you will want to contact us about a position at Spex. You must have the desire and knowledge to converse with your peers, advising them on technical aspects of spectroscopy, especially emission. You must be innovative, technically competent, able to manage this department of our company. Development and sales of new products, maintaining quality, writing literature and articles will all be part of the challenge. Write or phone Harriet Mitteldorf.

# PICOGRAM SODIUM DEFINITION WITH THE ATOMPROBE

**R. E. Rainford**

IBM Burlington, Components Division  
Essex Junction, Vermont 05452

In the manufacture of microelectronic circuits, the presence of even picogram quantities of sodium can cause deleterious effects. Sodium, at this level, can be detected with a Spex-Mallinckrodt Atomprobe.

Two and one-half mg of deionized water that contained three picograms of sodium, which were established by concentration techniques and emission spectroscopy, were placed on a metallurgically prepared aluminum slug. After drying, a  $\phi$  3-mm discernible ring remained.

Before and after deposition of the water, an analysis of the surface of the slug was made with the Atomprobe using sodium lines 5896 and 5990A. No sodium was detected on the slug before the water addition, but it was detected in the ring deposit.

Observed by microscope, the spark was guided, by continuous adjustment of the x-y position of the stage, to follow the sodium deposit. A 15 micron wide track was traversed over 0.5 mm of the ring during a 6-second exposure on Polaroid 52 film (ASA speed = 3000). Both yellow lines appeared. The procedure has proved helpful in examining actual conductive sections of microelectric circuitry for low picogram quantities of sodium.

# MEGGERS AWARD WINNER

The 1969 William F. Meggers award will be presented to Dr. John P. Walters at the Society for Applied Spectroscopy awards luncheon, October 7, 1970 during the Ninth National Meeting of SAS in New Orleans.



Administered by the Society and sponsored by Spex Industries, Inc., this honorarium is offered annually to the author of the most significant paper published in APPLIED SPECTROSCOPY. Dr. Walters' subject "Historical Advances in Spark Emission Spectroscopy," appeared in APPLIED SPECTROSCOPY **23**, 317 (1969) and APPLIED SPECTROSCOPY Selected Reprints and Review Articles **1**, 9 (1970) and represents one of his principal scientific endeavors.

Each winner renews our pride in being associated with the Meggers Award; our heartiest congratulations go to Dr. Walters.

SA #1	P L A T E S			F I L M	
	/doz.	/3 doz.	/case**	/roll (35mm x 100')	over 6 rolls
	—	\$14.60	\$208.00		
	\$ 8.40	22.70	172.50		
	SA421	daylight		\$13.25	\$11.30
	SA413	darkroom		14.00	12.25
SA #3	4"X10"	9.00	25.30	192.30	
	SP413	daylight		14.00	12.25
#33	2"X10"	—	18.00	243.00	
	4"X10"	—	27.00	194.00	
103-O*)	SP417	daylight		25.25	21.50
103-F*)	2"X10"	14.20	42.60	573.75	
IV-F )	4"X10"	21.50	64.50	464.40	
I-N* )					
IV-N* )					
Ilford Q-2	4"X10"	30.40			

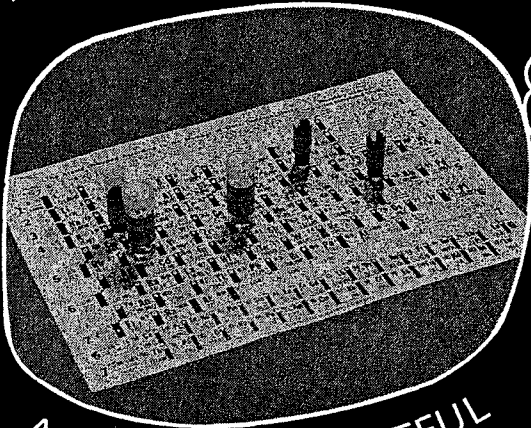
ONLY 103-O is available in single rolls. A 16-roll minimum is required by EK for 103-O, 103-F, IV-F, I-N and IV-N films.

\*Since the manufacturer recommends keeping these emulsions at temperatures under 55°F shipments are normally packaged with dry ice and sent via the fastest means on Tuesdays and Wednesdays. The cost of premium transportation plus a \$6.00 packaging charge is additional. All other prices include delivery by surface transportation.

\*\*2" x 10" plates come 15 dozen per case  
4" x 10" plates come 8 dozen per case

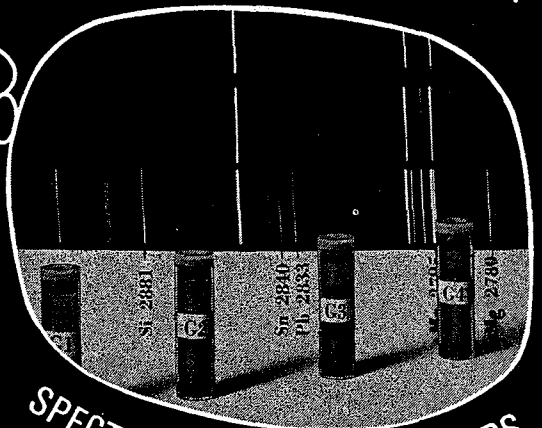
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