

# The

# SPEX

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# Speaker

## SPECTROSCOPIC PHOTOGRAPHY

**E**NOUGH has been said about the photographic emulsion. Its calibration, its storage qualities and idiosyncrasies to fill many a volume. But, despite the sheer mass of literature, authors have been hesitant to put forth rules-of-thumb to steer the novice spectrochemist along the channel of compromise and shortcuts dredged for him by his predecessors. It makes one a bit uneasy to set down in writing that, disregarding the admonitions of the instruction manuals to fix plates for 5-10 minutes, many of us unhesitatingly dunk plates in hypo for just 20 seconds or so. And, to advise that there is one calibration procedure that has it all over most others is the kind of neck sticking out that most authors would happily leave to the other fellow. So this paper is dedicated to the newcomer who, possibly overwhelmed by the confusing statements and apparent contradictions he will inevitably have come across, may be curious to learn how one veteran, having faced the same obstacles, somehow managed to tame the photographic emulsion.

In its spectrochemical applications, a photographic plate is expected to behave as a simple, inexpensive energy integrator. The spectrophysicist, as distinguished from the spectrochemist, is often more concerned with the resolving power and the dimensional stability of the emulsion so he can attain the highest accuracy in wavelength measurements. The interest of the spectro-astronomer is in emulsions whose speed is great at exposure times equalling an all-night vigil. But whatever the other limitations of an emulsion, the spectrochemist needs assurance first of all of some definite proportionality between the spectral light exposure and the blackness of the spectral line. If this can be established, predicted and maintained, he can devote more of his time to the relationship between % concentration and exposure. For, at the risk of being too obvious, the fundamental "flow diagram" exploited in spectrochemistry is:

spectral density  $\rightsquigarrow$  exposure  $\rightsquigarrow$  % concentration.

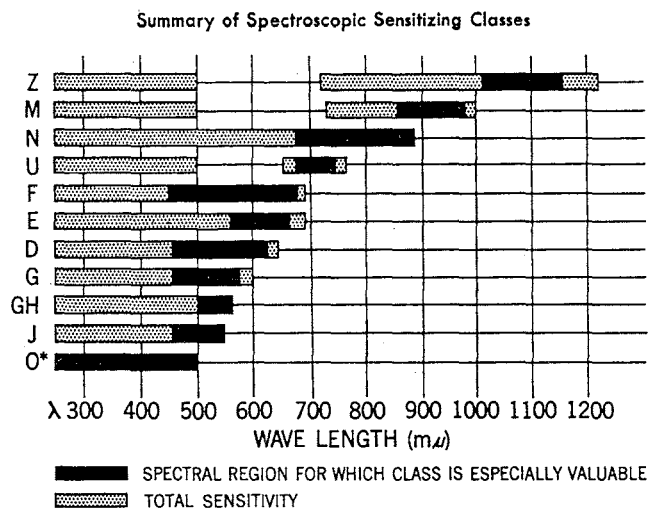
The spectrochemist soon finds to his dismay that the photographic plate is not a perfect integrator of exposure. For a particular emulsion, the density, blackness or transmittance of a spectral line is dependent on the exposure level, the wavelength of light, the "shelf age" of the plate, the development procedure and, to a lesser extent, a host of obstacles glorified by naming them "effects" after their respective discoverers. Then the emulsion's density will apparently vary with the measuring microphotometer, sometimes even with the spectrograph itself. Finally, the emulsion is grainy, the developed image consisting of a series of microscopic black splotches of varying sizes rather than a continuous tone of greys.

Perfect energy integration is not the only emulsion characteristic desired by the spectrochemist. Another is high contrast, a small change in concentration giving rise to a measurable change in line density. Technology, however, limits the choice between high contrast and low speed, on the one hand, and high speed, low contrast and bothersome graininess, on the other. An ideal emulsion would have a high, uniform contrast over an extended wavelength region, but the best manufacturers are able to achieve is a series of emulsions more or less uniformly sensitive over short intervals and so treated that their contrast is relatively constant.

For each job at hand, then, the spectrochemist is called upon to pick the most appropriate emulsion. If his problem is to analyze a sample qualitatively, to search out its complete elemental composition, he may have to expose two or even three plates to record the sensitive lines of all of the elements. More realistically, he is asked to determine only a long list of common elements whose sensitive lines, fortunately, fall in the ultraviolet. For such work, a good choice is the SA #3 emulsion, the sensitivity of which extends to about 5200A. Its contrast is reasonably uniform over the range 2500-5200A. This facilitates interpretation of stepped exposures taken over a broad wavelength interval. For quantitative determinations of the common elements, SA #1 is the likely choice. Its high contrast, crispness of image and freedom from graininess all contribute to good accuracy.

Since SA #1 represents at least 70% of all spectroscopic emulsions purchased in this country, it might be well to dwell on the compromises settled on by manufacturer and user alike in their quest for a generally acceptable quantitative plate. SA #1 has a usable range from around 2300-4400A. Very few elements have uniquely sensitive lines below 2300A (notably selenium, arsenic, antimony) and to determine these at trace levels requires an essentially gelatin-free emulsion such as Ilford Q-2. At the upper end, the 4400A cut-off of SA #1 is a boon with modern grating spectrographs, permitting their use at higher orders without confusing overlapping spectra. When a line appears at what would be measured as 8000A, it must be either 4000A in order II or 2666A in order III. To decide which, the technician merely tracks down the corresponding first order line. Often, in complex spectra it is advantageous to record lines in their higher orders both to separate otherwise interfering lines and to enhance the line-to-background ratio. Since the dispersion of a spectrograph is three times as great in the third order as in the first, interference is correspondingly reduced, and sensitivity boosted by almost that factor.

THE chart below, appearing in many Kodak publications, frequently confuses the intelligent novice. It seems to tell him that if he wants to determine traces of sodium at the yellow doublet (5890A) and calcium at its most persistent doublet (3933A), he should choose an "F" sensitized emulsion for the one and "O" for the other. Yet, and in all fairness most Kodak booklets are careful to emphasize this in the text, all emulsions respond to ultraviolet. Special sensitizing necessary to extend the wavelength coverage does not ordinarily affect the low wavelength end. In our example then, 103-F would be the sensible choice for determining both sodium and calcium, the F and O sensitivities being roughly equal at 3900A although the F reaches out to 6800A while the O cuts off at



5000A. Unfortunately, speed designations can be equally confusing and must be considered in accordance with the speed characteristics of the spectrograph itself.

Most modern grating instruments employ gratings blazed for the ultraviolet, where the bulk of work is done. To longer wavelengths the spectrograph is thus relatively slow. For all regions above 5000A therefore, it is a good plan to use the fastest emulsion, cutting speed where necessary with selective or neutral filters. This is designated 103 and, in decreasing order of speed are I, II, III and IV. The 103 is available only in D, O and F sensitizations while I is available for all sensitizations.

With the foregoing in mind, what should the well equipped laboratory keep on hand to anticipate almost any spectrochemical problem? Obviously, to stock some 30-odd emulsions would be an unwarranted expense in view of their limited shelf-life. Further, to calibrate and learn how to expose each would be a formidable burden.

From a practical standpoint much qualitative work is done with SA #1 because the spectrochemist gets to know the products with which his company deals and can make the necessary adjustments and compensations. When sodium is to be determined either in trace or micro samples, the 103-F emulsion is a common choice. When low potassium, too, is required, I-N is needed. But to determine either sodium or potassium at, say, the 1% level, SA #1 is suitable since ultraviolet lines of these elements may be measured.

The following table comprises a listing of recommended emulsions to be stocked by a well-equipped laboratory engaged in non-routine work. Also given are filters to reduce or remove interferences from overlapping orders.

## RECOMMENDED EMULSIONS

Type	<i>Suitable W.L. Region, A</i>	<i>Typical Uses</i>
Ilford Q-2	50-2500	Qualitative and quantitative
SA #1	2300-4000	Quantitative and trace analysis
SA #3	2300-5000	Qualitative surveys
103-O	2300-5000	Qual. & quan. of micro samples
103-F	2300-6800	Qual. & quan. for Na & Li particularly
I-N	2300-8800	Qual. & quan. for K, Rb & Cs particularly

## RECOMMENDED FILTERS

<i>Spex Cat. No.</i>	<i>Transmittance</i>	<i>Use</i>
9023-C	above 3000A	Eliminating higher orders when photographing 2nd order above 3000A; used with SA #1, SA #3 and O-sensitive emulsions.
9023-UV	2350-4000A	Photographing 2350-3500A in 2nd order without overlapping 1st order; used with SA #3 and other emulsions sensitive in visible region.
9023-Y	above 4500A	Photographing above 4500A in 1st order while eliminating 2nd and higher orders (Na & Li determinations.)
9023-R	above 6000A	Photographing above 6000A in 1st order while eliminating 2nd and higher orders (K, Rb & Cs determinations.)

**E**ASTMAN Kodak recommends D-19 to process all types of spectroscopic films and plates. Rapid acting, and offering high contrast, it has the further advantage of not deteriorating unduly in open trays. Achieving uniformity in processing from plate to plate and over the entire plate is quite another challenge, however. The responsibility here is shared by the fellow in the darkroom and the manufacturer of photo processing units.

Of the many intermeshed facets relating to the uniform development of a latent image, the four most important are strength of solution, time, temperature and agitation. The strength of a developing solution changes in two ways: overall and locally. Periodic replenishment is necessary to maintain the overall strength while agitation of some sort replaces the locally depleted solution as it reacts with the silver grains.

How to maintain the overall strength of a developing solution is not quite a settled matter. Some spectrographers prefer the routine of starting fresh each morning, dumping out and replacing all old solutions. An intuitively more sensible procedure and one used by perhaps the majority of experienced spectrochemists is to replace but half of the solution at regular intervals. The reason is that the reactivity of a chemical is greatest when freshest but it changes most rapidly at its freshest, too. As a solution ages it goes through a period of slow change. By sustaining a developer in a state of "middle age" its reactivity, it is reasoned, is kept most uniform.

I do not recall having seen any data to substantiate either the new or half-new approach and would welcome any information along these lines. Advocates of both methods, however, make it a practice of storing developer in small, completely filled containers to reduce air oxidation. So important is this factor that Eastman Kodak, going a step further, recommends nitrogen burst agitation rather than the traditional approach of rocking either the tray or the plate during development. In the nitrogen burst method (to our knowledge no commercial instrument is available), an inert gas is blown through the developing solution at regular intervals. The random character and great number of tiny bubbles so produced help develop the plate uniformly. If the bursts were continuous a flow pattern could conceivably be produced which would develop the suspended plate unevenly. Typically, a burst of 1 second and a rest interval of 10 seconds are suggested.

Commercial developing units use neither the gas burst nor brush techniques but a regular rocking motion which seemingly could cause local wave patterns and uneven developing. Nevertheless, in practice, these machines operate quite satisfactorily, identical exposures yielding essentially constant transmission of a given measured line. It should be pointed out in this regard that the shape and size of the trays are important; they should be deep and narrow allowing a small surface area to reduce air oxidation. Modern units are so designed.

That time and temperature are essential parameters in all chemical reactions is too obvious to be dwelled upon. Yet, it is not so well known that the mechanical timers provided on many commercial processors are far from reproducible and that the method of regulating temperature through a thermostatically controlled water bath but without forced circulation may be less than adequate especially if the darkroom itself is not air-conditioned. It would be well for the spectrochemist whose management is continually prodding him for better accuracy—and whose isn't—to look into such easily measured sources of error.

Nor is the density of a spectral line determined only by its development. Strict compliance with a schedule of washing and fixing will reduce errors. Equally essential is attention

to the drying cycle which, by affecting the shrinkage of the wet emulsion, indirectly affects the final density of spectral lines. The greater the shrinkage, the greater the measured density and, once more, this is indeed demonstrable with a single test. Let one plate air dry and force dry a second in a photo processor and compare identically exposed spectra.

Plates or film strips are conveniently dried in a modern photo processor. Hot air is blown over the emulsion as it is held on a heated stage. To speed up the drying operation and to prevent stains, it is a good idea first to dip the plate in a detergent solution then sponge it off. While fine-grained photographic sponges are available, ordinary household cleaning sponges have been found to be equally suitable and are much less expensive.

Understandably, Eastman Kodak's literature recommends processing conditions designed to achieve a permanent plate, one not subject to fading or staining even over periods of several years. Most people discard their plates after perhaps a year and might willingly sacrifice a little shelf life for a lot more speed in plate processing. The following table compares the times used by many experienced spectrochemists under pressure of production schedules with those suggested by Eastman Kodak.

	<i>Eastman Kodak Suggestions</i>	<i>In use by many spectrochemists</i>
Temp. of developer, F	68°	70°
Developing time		
thin emulsions		
(e.g. SA #1)	5 minutes	3 minutes
thick emulsions		
(e.g. 103-O)	4 minutes	4 minutes
Fixing time in Rapid		
Fixer with hardener		
(SA #1)	3-5 minutes	30 seconds
(103-O)	2-4 minutes	1 minute
Washing time	20-30 minutes	1-2 minutes

#### Calibration of Emulsions

**H**INGING on the relationship between exposure and density of spectral lines, quantitative spectrochemistry depends on the accuracy with which that relationship can be calculated in each individual laboratory. The relationship, non-linear and affected by a number of instrumental parameters, must be verified frequently and remeasured with every new emulsion batch.

One of the oldest and still surviving emulsion calibration methods entails the stepped sector, a rotating wheel designed to control exposure (the product of time and intensity) by varying time in a predictable way.\* In the stepped sector method, the vertical aperture in front of the slit or camera is opened to record a line of 6-10 mm high. At the source, a stepped disc is so positioned that, when rotated, intensity steps 1-3 mm high are produced. By cutting the notches carefully, the intensity ratio between steps can be made constant, typically between 1.4 and 2.0. In calibrating with a sector wheel, the spectrographer takes several photos of a Pfund iron arc,

\* Time turns out to be easier to alter absolutely than intensity. The accepted but cumbersome procedure for varying the latter is to change the distance between source and slit which, of course, is a function of the square root of the intensity at the slit.

exposing for 5-30 seconds. He then measures the density of successive steps of a chosen iron line and plots these values against the sector ratio.

One serious drawback of the stepped-sector is its tacit, yet questionable, assumption that the line photographed without the sector would be uniformly illuminated along its length. While the criterion might seem trivially easy to meet, in practice quite the opposite is true. Indeed, producing spectral lines of even density along their length does not seem possible on a commercial spectrograph. Often the optics are so set that lines will taper in one direction at the low wavelength end of the spectrum, become more or less uniform in the middle of the plate and develop a wedge in the other direction further up the plate. Even in the center, lines will be found to vary about 10% in relative transmittance along a 10 mm length. To add further confusion, neighboring lines may taper in opposite directions.

Explanations for the tapers can be found, first of all since chromatically corrected lenses are rarely utilized. Expensive and fragile, achromatized lithium fluoride-quartz doublets offer little to help most spectrochemical problems. With an ordinary uncorrected lens, the focusing conditions for visible light are far from those required at 2000 or 4000Å. In some spectrographs, variable astigmatism with wavelength is another disrupting influence on spectral line uniformity. Thirdly, spectral lines themselves may vary in intensity especially when the analytical gap is small.

Having thus recognized the limitations of the stepped sector (and stepped filter by implication), let's get on to another, once popular calibration procedure, that making use of pre-calibrated iron lines. During World War II, Dr. Dieke and co-workers at Johns Hopkins did a commendable job in establishing the intensity ratio of a number of groups of iron lines. Through meticulous measurements and by taking careful grip on all known variables, they hoped to arrive at relative values which could be readily transferred to other laboratories. Unfortunately, results elsewhere failed to confirm those obtained at Hopkins. Without going into all details, suffice it to point out several, then unforeseen, variables and complications: differences in grating blaze, Littrow fog and other scattered radiation, basic differences in microphotometer performance.

Sidestepping the problem, some spectrographers have set up their own relative values for neighboring iron lines. Carefully and painstakingly done, a calibration scheme based on such work becomes perfectly valid for that laboratory. As will be pointed out later, however, the two-line method still boasts one decided advantage: its ease in laying down points on the calibration curve, evenly distributed along the length of the curve. By adjusting the exposure, ten or so readings will give points equi-distant all along the curve. By contrast, it is almost impossible to find ten nearby iron lines with exactly the desired transmittance relationships. This, in turn, limits the accuracy with which a curve can be drawn through the points.

Despite the defects in both the stepped-sector and iron lines methods of plate calibration, spectrochemists, able to live with small errors, often stick with them. The logic of this cannot always be denied. Often, particularly in so-called go-no-go methods, the job is to control production on the basis of broad concentration limits. But the trend today is changing toward tighter specifications on chemical composition and the spectrographer must take precautions to minimize all sources of error including the worst potential one, the photographic plate. When a stainless steel calls for 8% nickel, putting in 8.1% is both wasteful and expensive. When two supposedly identical batches of aluminum alloy rod require different feed-rates on an automatic screw machine, the customer is apt to complain.

More than once such a difference has been traced to the concentration of a particular constituent which had strayed to the high end in one batch and the low end in another.

From the standpoints of both practicality and accuracy, the method of plate calibration most often used today is the two-line or its close relative, the two-step method. Described almost simultaneously in 1944 by Levy of U. S. Steel and Churchill of Alcoa, this method assigns an intensity ratio between two closely spaced spectral lines of the same element. To expand the versatility of the procedure, the lines should be ones differing considerably in their origins; i.e., a change in excitation conditions should give rise to a marked change in the measured intensity ratio. This provides a ready check on the excitation conditions when routine plates are run later. The lines chosen are measured and their approximate intensity ratio determined either through a previously used calibration technique or by assuming a gamma value. In any event, it is important to point out, as did Churchill, that the assigned intensity ratio, which can be a nice round figure such as 1.500, need only approximate the actual value. No error is introduced and a great deal of computational inconvenience is avoided by assigning a value differing somewhat from the actual one.

In running the two-line method, a series of exposures is taken with different times or, with the help of stepped neutral filters or sieve screens, at different intensities with the time held constant.\* The resulting plate will contain two lines at different density levels. For convenience, let us call them two Al lines. The % transmittance values at each step are then plotted, one Al line *vs.* the other in a preliminary curve on linear paper. A smooth curve will result, two "free" points at 0-0 and 100-100 permitting extrapolation to the very highest and lowest density readings beyond the accurate measuring ability of the microphotometer. To obtain the final characteristic curve, values are read off the preliminary curve in an x-y progression, plotted against the assigned intensity ratio taken to the nth power.

Some of the advantages of the two-line method have already been detailed. A tabulation follows:

- 1) No external contrivances are required. Exposure time is the only parameter.
- 2) By properly choosing exposure times, well scattered points can be readily obtained. A smooth curve best fitting the points and extending to the 0-0% and 100-100% transmittance values is easily drawn.
- 3) The method is applicable equally to stigmatic and astigmatic spectrographs and does not assume uniform intensity over the length of a long line.
- 4) A built-in check system, probably the most important advantage, furnishes the spectrographer with a "warning light" should anything go wrong. Suppose he is running a series of aluminum samples at the beginning of the work day and wants to make sure that all conditions—the source parameters, the developing bath temperature, the slit width, etc.—are proper. On his first plate, and on every succeeding one if necessary, he sparks his calibration chunk of aluminum, a piece of metal reserved for just that purpose. Later in the microphotometer he measures the intensity ratio of the two chosen aluminum lines. If the figure 1.500 turns up, everything is ideal (a source of immediate suspicion!). If, as is much

\* I will but mention then dismiss the reciprocity law, assuming as does the experienced spectrochemist that, over the comparatively small exposure ranges used in his work, it stands up without meaningful deviation. That is, errors introduced by varying the time of an exposure are too small to be of concern.

more likely, the measured ratio falls within 1.48-1.53, he is reassured that no "dial twiddlers" were at work during the night, that the thermostat on the developing tank did not go haywire, and that his technician put the customary SA #3 not SA #1 in the camera.

### Background Correction

Often a statement appears in the literature like this: "Lines were not corrected for background which was too high to be considered important." Frequently an area of considerable error is thus tersely dismissed. The problem of background is that it is hardest to measure exactly when its measurement is most needed, i.e., in trace-element work. Here a line may have a transmittance value of 90% while background is 95%. Yet, because of the inertia of the plate as represented by the so-called knee of the characteristic curve, the intensity value as measured using 90% and 95% is indeed significantly different as compared with measuring 90% and 100%.

It is not easy to formulate a rule dictating when to make and when not to make background corrections. A few people deliberately expose plates so that the background falls in the region 70% rather than 95%, thus forcing themselves to correct for background. Others set the 100% transmittance of the microphotometer at the background and thus compensate for changes. The former has merit and is especially valuable in arc work where variations in background between exposures are notably greater than in spark analysis. Setting the background at 100%, on the other hand, is theoretically unsound and may not improve results at all.

How to measure background apart from microphotometer compensation is another matter. Slavin recently pointed out that the characteristic curve as calculated from measurements of spectral lines is different from that obtained when diffuse areas, such as background, are measured. This, however, probably represents a secondary source of error, one well beyond the scope of normal spectrochemical needs. Apart from this, the advantage of a recording microphotometer over a non-recording instrument should not be overlooked. By graphically depicting the variations in the background, the "true" %T can be measured much more accurately on a recording instrument.

### Seidel Function

As normally plotted on log-log coordinates, the characteristic curve of an emulsion is a long sweeping "S", a knee and shoulder separating the central section where density and exposure have a straight line relationship. Put in terms of accuracy, this means that at very low densities (the very high densities are ordinarily avoided in spectrochemical work), accuracy must suffer as it does any time interpolations are made on other than a straight line. The Seidel function simply and almost empirically corrects this situation by expanding the %T scale in such a fashion that the result is an almost straight line. Every spectrochemist will find it to his advantage to switch to Seidel coordinates. No matter what calculating board is used, the Seidel function can be applied to it. (SPEX supplies Seidel graph paper.)

### Error Reduction

THE fact that direct reading spectrochemical analysis is consistently more accurate than photographic techniques indicts the photographic plate as a large source of error. Apart from the need for careful calibration, densitometry and interpretation, quantitative spectrochemical analysis can be improved through an understanding and limitation of still other variables. To begin with, the plate itself should not be con-

sidered a static device with unchanging properties. On the contrary, its emulsion consists of unstable chemical constituents subject to all of the chemical laws. Heat and time are the most destructive factors, eventually causing the emulsion to fog and lose sensitivity. All plates should, for this reason, be stored in a deep freeze if they are to be kept for more than a few months. Those of high speed (103 and I designations), the Schumann (Ilford Q, Eastman SWR) and ones sensitive to long wave excitation (M, N, Z) should always be kept in a deep freeze.

You, the spectrographer, also have control to a large extent over the storage and shipment of plates. All dealers should have provisions to store sensitive plates in a deep freeze and insist that, despite necessary additional charges plates be shipped by fast transportation and, where necessary, packed in dry ice. Even then, you should anticipate your summer needs for "bread-and-butter" plates and order these well in advance of the warm weather. Shipping a case of SA #1 plates by air across the country is expensive but may be necessary in the summer when temperatures inside a truck or on a loading platform may reach 120°F. Special plates should be purchased only from dealers whose turnover is rapid and who care and know enough about the problem to want to protect the ultimate user.

When one thinks of a photographic emulsion as the ingredients in a continuing chemical reaction, he realizes, too, that it is easier to obtain uniformity within a particular batch than batch-to-batch uniformity. Accordingly, for his routine work, the experienced spectrographer often specifies a number of boxes of plates all with the same emulsion number. In a recent publication, Eastman Kodak has decoded the number appearing on all spectroscopic plates. To take their example, in the number BMC3D2, BMC indicates the type of emulsion (in this case SA #3) 3D2 indicates the third coating in the fourth month of 1962. Any remaining numbers are internal control numbers, according to Eastman Kodak, "and bear no relationship to the coating time of the emulsion." It is thus possible to find in an unopened case of plates with the same emulsion number, boxes with different control numbers. Similarly, with films only the first six numbers comprise the emulsion number.

Lastly, the effects of ambient humidity and temperature on a photographic plate during exposure have not been fully explored, to my knowledge. It is well known that moisture absorbs radiation preferentially with wavelength. Temperature, as it does in any chemical reaction, affects the emulsion, too. Temperature and air pressure also affect the focus of a spectrograph, perhaps not visually but to an extent which can be measured densitometrically. A defocused line is broadened and its density decreases.\*

While it is not convenient to maintain the pressure in the laboratory constant, temperature and humidity control are mandatory. Furthermore, frequent focus checks should be made preferably objectively by using the method proposed by Arrak. By taping a narrow vertical mask down the center of the grating, defocusing of the spectrograph results in doubled lines. The distance between the lines, a function of the distance that the slit is out of focus, is extrapolated to zero to obtain true focus. The Arrak technique, incidentally, will indicate whether or not the entire plate is uniformly in focus. If not, it points up the necessity of using the same setting on a wavelength adjustable spectrograph for accurate work.

\* This is another reason photoelectric spectroscopy is inherently more accurate. A photomultiplier reads the total light received. Provided its exit slit is wide enough, a line slightly out of focus will read the same as one in focus. Not so with the photographic plate where *maximum* densities are read.

SINCE a good deal of literature is devoted to the spectrographic plate, much of this paper is either knowing or unwitting plagiarism. To furnish a complete list of references would be a monumental task of questionable value. Yet, without any intention of disparaging or underestimating the importance of many additional excellent papers in the literature, I feel it important to mention a few which would be helpful to the novice.

1) Churchill, J. R., *Ind. and Eng. Chem., Anal. Ed.*, 16, 653 (1944).

This paper outlines the two-line method in sufficient

detail so it may be followed by the novice.

2) "Methods for Emission Spectrochemical Analysis," ASTM, 1960.

A description of the Pfund Arc is presented as accepted methods of plate calibration.

3) Arrak, Arno, *Spec. Acta.*, 12, 1003, 1959.

Presented is a method for objectively and quantitatively focusing a spectrograph, as well as a means for checking the focal plane of the instrument.

—AJM  
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## Spectroscopic Plates and Film, Delivered Prices

4" x 10" Plates	Per Case (24 doz.)		Per Package		2" x 10" Plates	Per Case (45 doz.)		Per Package	
	East*	West*	East*	West*		East*	West*	East*	West*
SA #1 3 doz. pkge.	142.50	152.50	19.20	20.70	SA #1 3 doz. pkge.	180.00	190.00	12.85	14.35
1 doz. pkge.	167.40	177.40	7.75	7.75	1 doz. pkge.	210.60	220.60	5.20	5.20
SA #3 3 doz. pkge.	158.00	168.00	21.20	22.70	SA #3 3 doz. pkge.	198.00	208.00	14.20	15.70
1 doz. pkge.	198.00	208.00	8.50	8.50	1 doz. pkge.	230.00	240.00	5.70	5.70
Kodak #33 3 doz. pkge.	194.00	204.00	27.00	27.00	Kodak #33 3 doz. pkge.	243.00	253.00	18.00	18.00
103-F, 103-O, 1-N** 1 doz. pkge.	415.00	425.00	19.88	19.88	103-F, 103-O, 1-N** 1 doz. pkge.	495.00	505.00	12.65	12.65
Q-2 Ilford Plates** 1 doz. pkge.	.....	.....	15.20	15.20					

### Photographic Chemicals

D-19 Developer	one gallon	\$1.10
Kodak Fixer	one gallon	.75
Kodak Rapid Fixer	one gallon	1.60
Kodak Rapid Fixer	five gallons	5.65
Indicator Stop Bath	16 oz. btl.	1.20

### Delivery Schedules

All sizes and emulsions listed above are normally in stock so that most shipments are made within 24 hours. Those requiring dry ice packaging are shipped on Tuesdays and Wednesdays. Additional emulsions and sizes of Kodak Spectroscopic Products, not listed here, are available for 30-60 days delivery.

### Kodak No. 33 Plates Reinstated

A number of spectrographers have found that SA #3 plates do not adequately substitute for the discontinued SA #2 plates. Graininess and fog level are both somewhat greater in the new emulsion, sometimes interfering with trace-element determinations.

The old No. 33 plate, a closer substitute for SA #2 for such measurements, is being made once more by Eastman Kodak as a special item on a minimum order basis. Since the minimum is quite high for any one laboratory (180 dozen 2" x 10" or 90 dozen 4" x 10"), we have agreed to stock this emulsion and make it available to spectrographers in the individual 36-plate packages.

SA #1 Film (35mm x 100')	Daylight SA 413	Darkroom SA 421/1
Individual Rolls	12.90	12.15
6 Rolls or more, East*	11.22	10.57
West*	11.42	10.77

SA #3 Film	Daylight SP 413	Darkroom SP 421/1
Individual Rolls	14.00	13.25
6 Rolls or more, East*	12.18	11.53
West*	12.38	11.73

103-O, 103-F, 1-N** Film	Daylight SP 702	Darkroom SP 421
Individual Rolls	23.30	22.55
6 Rolls or more, East*	20.25	19.55
West*	20.45	19.75

\*East or west of the Mississippi River.

\*\*Since Eastman Kodak recommends keeping these emulsions at temperatures no higher than 55°F, shipments are normally made via the fastest means and are packaged with dry ice. The cost of premium transportation plus a \$5.00 packaging charge is additional in such cases.

# SHATTERBOX NEWS

Extremely fast, efficient grinder, the Shatterbox spins a hardened concentric puck and ring around the inside of a closed, removable dish at 900 rpm. Although ball-bearing steel is the most popular material for a grinding container, tungsten carbide and high-alumina ceramic have their place, too. Typically, 10 ml of a sample may be ground in 3 minutes to -325 mesh. With reasonable precautions, the particle size distribution from sample to sample may be maintained remarkably constant.

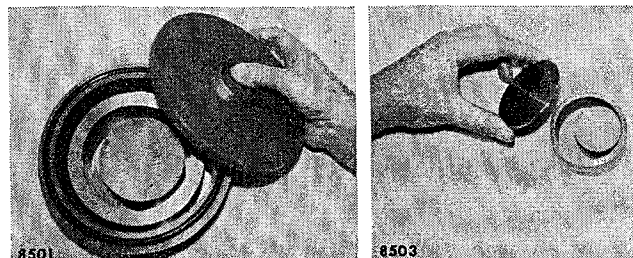
A quick scan of the materials listed below will reveal how universal the Shatterbox is turning out as a tool for grinding production samples quickly and reproducibly prior to x-ray and emission spectrochemical analysis. From the standpoint of sales, probably the most interesting, if unexpected, use of the instrument is in grinding Portland cements and intermediate raw mixes. Scattered throughout the country, many Shatterboxes are now whirling away on a 24-hour-a-day, 7-day-a-week basis busily engaged in the control of uniform, high-quality concrete.

Although many variations are possible, one method of preparing samples of cement was recently described by Mr. O. Brown, Marquette Cement Research Laboratories, Chicago, Ill. at the ASTM meeting in Atlantic City. To a 2.00g portion of cement or 6.00g of raw mix is added 0.10g of sodium lauryl sulfate (Fisher S-329) as a grinding aid to reduce packing and sticking. (Some spectrographers substitute ordinary household detergents such as "Tide" at 5-10% for the sodium lauryl sulfate.) The sample is ground in a hardened steel container for six minutes to reduce the particle size to under 20 microns. It is then pressed at 8000 psi (10,000 pounds in a 1-1/4" dia. die) after a quantity of cellulose powder is added as a backing for ease in handling. When internal standardization is required, 0.040g of V<sub>2</sub>O<sub>5</sub> and 0.040g of NaCl are added before grinding.

In the metals industries, the Shatterbox is helping to stabilize the composition of slags, raw materials and master

alloys. Other customers are manufacturers of welding fluxes, fertilizers, pesticides, inorganic chemicals as well as research laboratories in the geological and mining fields.

May we test grind some of your samples? No obligation, naturally.



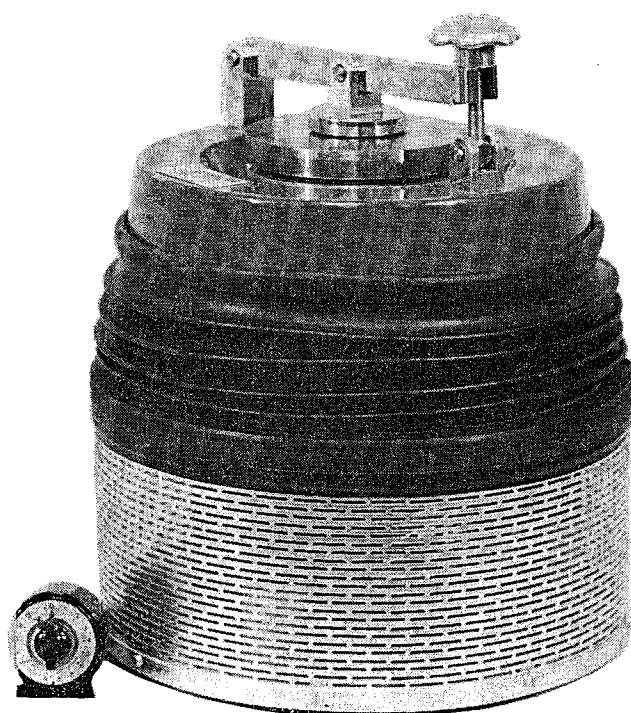
- 8500 Shatterbox, grinder and blender, 1/3 hp motor 50-60 cy., 115v or 230v (specify), 0-15 min. timer .....Each \$925.00
- 8501 Grinding Container, hardened steel, 100 ml capacity .....Each \$200.00
- 8502 Grinding Container, hardened steel, with provision for filling with inert gas; gasketed and held closed with 4 thumb screws, 100 ml capacity .....Each \$245.00
- 8503 Grinding Vial, hardened steel, for multiple sample handling, 15 ml capacity, the Shatterbox will hold 7 of these vials (requires 8503R rack) .....Each \$ 42.00  
Set of 7 \$275.00
- 8503R Rack, for holding up to 7 8503 vials .....Each \$ 55.00
- 8505 Alumina Ceramic Grinding Container.....Each \$310.00

## Grinding Tests Using 8501 Hardened Steel Container

Material	Form as received	Time, min.	Amount grams	% Passing 325 mesh
Asbestos	Fibrous	12	20	100
Cement, Portland				
raw mix	+60 mesh	2½	40*	100
Ferro-chromium	+100 mesh	5	25	100
Ferro-manganese	+200 mesh	3	25	100
Ferro-molybdenum	-80 mesh	4	25	100
Ferro-niobium	-80 mesh	3	25	100
Ferro-silicon	-80 mesh	4	25	100
Ferro-titanium	-80 mesh	6	25	100
Ferro-vanadium	-80 mesh	7	25	100
Fiberglas	thin sheets	2	10	100
Fluorspar	+100 mesh	3	50	100
Pesticide	-100 mesh	15	50	100
Phosphate, raw mix	+60	2½	40	100
Iron powder	-80	6	5	68
and	-10	10	100	100
Slag, blast furnace	chunks	1	10**	100
Slag, open hearth	chunks	1	20	76
Slag, site	chunks	10	35	100

\* sodium alkylarylsulfonate added, 5%

\*\* Household detergent (Tide) added, 10%





Return Requested

Metuchen, New Jersey

3880 Park Avenue

INDUSTRIES INC.

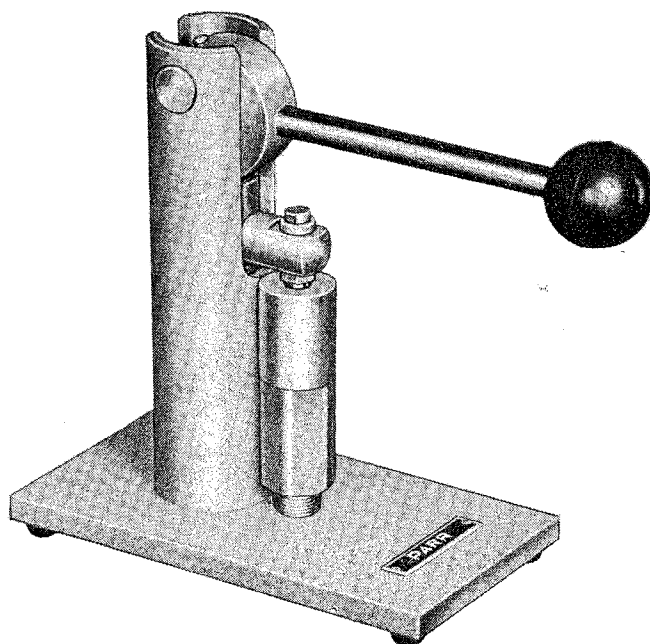


## HAND PRESSING OF EMISSION POWDERS

Instead of packing electrodes with a powder, many spectrographers make it a practice of pelletizing the sample with conducting grade graphite (SP-1) and dropping the pellet into the cup of an electrode. By helping remove an operator variable, this promotes precision. The trouble with the technique has been the incompatibility of available electrode diameters and commercial die sizes. Thus the National L-3906, L-3909, L-4000 and L-4006 preforms have cavity diameters just enough under 1/8" to prevent such a standard pellet from fitting. Similarly, preforms L-3900, L-4012, L-4018, have diameters under 3/16".

Rather than advance a new set of electrodes with the proper cavity diameters, it seems wiser to manufacture suitable equipment for preparing pellets. The basic unit is already well known in many spectrographic laboratories. It is the Parr Pellet Press, a hand operated instrument capable of providing enough force against a small area to prepare a suitable tablet from powder. To the basic unit is added plunger and die sets of 0.118" and 0.178" dia. respectively.

The compressive force in the press is developed by hand on a 7-inch lever attached to a large steel cam. The punch is attached to a spring loaded ram which bears against the cam and automatically moves up and down with the operating lever. The mechanical advantage of the system increases continuously as the punch descends, practically approaching 50:1. A force of 40 pounds on the lever thus develops about 75000 psi on the 1/8" plunger, 25000 psi on the 3/16" plunger. Plunger and die sets are all interchangeable including standard diameters of 1/2", 3/8" and 1/4".



- |      |   |          |
|------|---|----------|
| 3625 | Pellet Press, hand operated, without plunger and die .....                        | \$ 72.00 |
| 3626 | Plunger and Die, for preparing pellets 0.118" dia., fill height of die 3/4" ..... | \$ 60.00 |
| 3627 | Plunger and Die, for preparing pellets 0.178" dia., fill height of die 3/4" ..... | \$ 46.00 |