

**The****SPEX****INDUSTRIES, INC. • 3880 PARK AVENUE • METUCHEN, N. J. • ☎ 201-549-7144****Speaker****A SPECTROCHEMICAL PRIMER**

by

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**D**URING the 19th Century, America, the land of opportunity, proudly rejected the old world apprentice system in its energetic burst of enthusiasm to industrialize. If a young man was to work at a trade, he was to be paid while he learned. In sharp contrast to his European contemporaries, held to menial tasks for years by masters, Americans had the choice to stay at a job, to quit, move up, laterally or down.

The philosophy drew hard-working, spirited young people to our shores to share in our economic successes. While European craftsmen remained strapped to their inefficient traditions, we constantly sought and found cheaper means to produce better products. Mass production became the keyword. No longer was it necessary to train a cobbler to make a pair of shoes from the ground up. Instead, shoe manufacture was divided into as many parts as its economics dictated.

The result a century later is the Age of Specialization with its benefits as well as drawbacks. To the individual, mainly during early adulthood, the system is often baffling. Desperately needing to specialize but denied apprenticeships, many youngsters are trapped in the middle void.

To a large extent, this training hiatus has carried through to our own field of spectrochemistry, a discipline requiring two distinct backgrounds. The theoretical foundation, best acquired in college, enables the practicing spectrochemist to develop his methodology with a minimum of cutting and trying. But spectrochemistry is an art as well as a science and here is where experience is essential. No course can be expected to tell the newcomer that a buffer consisting of equal parts of lithium carbonate, graphite and silver nitrate enhances the sensitivity for certain tramp elements to a level below which they are not detrimental in a certain alloy.

Under the apprentice system, the novice would systematically assimilate such information during his years of training. Without it, he must rely on the literature and on formal and informal sessions with his fellow compatriots during which "tricks of the trade" can be shared. Yet for want of constant instruction, he must expect to make errors which have been made and corrected by others many times in the past.

It is the purpose of this paper to attempt to bring together some of the practical ideas that the seasoned, well-rounded

spectrochemist has acquired over the years. If we can save time for just a few of the new spectrochemists, we shall have fulfilled our mission.

Unhesitatingly, our first suggestion is to purchase and digest the latest edition of ASTM's "Methods for Emission Spectrochemical Analysis," Amer. Soc. for Testing Materials, Philadelphia 3, Pa., 1964. The book represents the combined efforts of hundreds of pioneers who, with full knowledge that their work would remain largely anonymous, were, nonetheless, impelled by their desire to set a course for succeeding generations of spectrochemists. The initial sections, "General Practices," are particularly to be recommended because they bear the stamp of approval of American industry as a whole. While shortcuts are in constant use in most laboratories, they frequently entail compromises acceptable only for a specific application. By contrast, ASTM presents the broad, unabridged picture to enable the spectrochemist to achieve results acceptable to all, within the organization where the work is done and outside as well.

**Preparation of Standards**

Unlike traditional wet chemical quantitative procedures, spectrochemical analysis is not a primary method. Measurements are taken of the density of spectral lines not of the weight of a separated element. Standards form the backbone of any method. Without them no spectrochemist, whatever his experience, would hazard a guess better than a "ballpark" figure.

Standards should, on the one hand, be compositionally identical with the unknown and, on the other, cover a composition range to bracket the expected analyses. Obviously, the two requirements are self-contradictory and compromises must be worked out. A common compromise is to keep the major element at a fixed level while varying the lower concentration constituents. Thus, the Bureau of Analysed Samples series of eight low alloy steel standards all contain around 94% iron; the concentration of alloying elements is balanced so they total 6%.

In choosing the concentrations of elements added to a standard, a good rule to follow is to vary the levels by a constant factor. This will result in equally spaced points on the concentration axis of the analytical curves and so optimize calculation precision.

\* Now at International Nickel Company Research Laboratories, Sterling Forest, Suffern, N. Y.

TABLE I

## Ideal Set of Hypothetical PbO Standards

Std. No.	Concentration, %				
	Bi	Sn	Cd	Zn	PbO
1	0.10	1.0	0.0032	0.032	98.9
2	0.032	0.32	0.010	0.10	99.6
3	0.010	0.10	0.032	0.32	99.6
4	0.0032	0.032	0.10	1.0	98.9

In this set of standards, the matrix of lead oxide remains essentially constant while the constituent elements vary. By setting the dilution factor equal to the square root of ten, equally spaced points over a logarithmic cycle will result.

## Sample Preparation—Powders

ASTM's book devotes three whole chapters to sampling, denoting its importance. In spectrochemistry, where samples are exceedingly small, getting a representative amount of material into an electrode may mean the difference between a genuine and a meaningless analysis. Sample and standards must be closely matched in such things as particle size distribution, acid concentration, metallurgical history. The preparation area must be kept scrupulously clean. What would be considered slight contamination in a typical wet chemical procedure might well be catastrophic in a spectrochemical procedure where 10-50 mg of material is arced. The room should be kept clear of smoke, dusts, and fumes. Glassware, spatulas, and balance pans should be free of etch marks and corrosion.

Fine powders, the type of sample frequently employed, can easily be spread. Electrostatic charges developed in a plastic vial may tickle a non-conducting powder so it flies off the spatula. To prevent cross-contamination, plan to cover the working area with fresh tissue. Kleenex has been found to be free of most trace elements including titanium which frequently is added to paper products as a whitening agent.

Manipulation, transfer and arcing of powders are all facilitated when the particle size is kept reasonably large to maintain a proportionally high bulk density. Graphite powder, the most common diluent, can be purchased in a -100 mesh cut by specifying SP-2X.

While it is both costly and impractical to maintain complete sets of spatulas, funnels, balance pans, etc., for each type of material, it is a good plan to keep at least one reserved for critical trace-element work. Incidentally, the balance found best for most spectrochemical applications is not the analytical but the torsion types. Particularly well suited to repetitive weighings, their speed rivals that of the most expensive single pan balance. The sample pan is quite small, facilitating the transfer of material, and one balance (Sauter) features a pan in which the material can be weighed directly into a plastic vial in which it is later mixed.

One of the advantages of a powdered sample is that it can be buffered or diluted readily. Mixing and grinding, once a tedious hand chore varying in efficacy and particle size among operators and their moods, has been made much more consistent with the mechanical devices on the market for the past several years. Of the many suggestions applicable to their efficiency, the following are general:

- In dry weather, static electricity can interfere with mixing. "Rinse" the plastic vial and ball with a little graphite beforehand.
- A drop or two of alcohol will aid in mixing small amounts of some materials. But too much alcohol will attack the plastic!

- Many hard, brittle substances such as quartz, silicon, glass, antimony or platinum sponge can be ground without metallic contamination in a plastic vial with several plastic balls. For protracted grinding, a good precaution is to tape the outside of the vial. In grinding metals, an exothermic or pyrophoric reaction can occur. Feel the plastic container frequently to forestall a temperature rise which can melt the vial.
- Always mix for a minimum length of time—under 30 seconds generally—to retain a fairly large particle size.
- Addition of a dye such as gentian violet will indicate mixing completeness.
- 1/8" balls are often preferred to larger ones for mixing although they are harder to retrieve.
- When a Wig-L-Bug is used only with 1" long plastic vials, special arms (not commercially available) can be made to speed changing of vials. Attached to the spring steel arms are two aluminum cups facing inwards to hold the vials.

Some miscellaneous suggestions for handling powders are:

- When large amounts of a powder are to be "quartered" to obtain a representative sample, the NSL all-plastic micro-riffle works well.
- Plastic vials are readily marked with a lacquer or felt marking pen.
- One simple way to remove any dust from inside a vial is with clean, oil and moisture-free compressed air. If this is unavailable, canned Freon may be substituted. Marketed as the "Effa Duster" by Ernest Fullam Co., P.O. Box 444, Schenectady, N. Y., it is also helpful in cleaning slits and optical surfaces.
- The Spex electrode funnels are designed to facilitate loading vials as well. For many samples, however, a larger funnel easily fabricated from Lucite has been found helpful. A rack to hold a number of vials can be simply made by drilling blind holes in a 1/2" thick plastic sheet.
- Although mechanical electrode loaders have not proved universally acceptable, a simple vibrator acts as an excellent aid in transferring powders to an electrode crater. One employing a self-interrupting bell relay is easily made.
- Even though it is almost obvious, for the sake of completeness, it should be mentioned that filled electrodes should be stored in a covered rack, that they should be handled only with clean tweezers and that, when burning a group of standards, the order should be from most dilute to most concentrated.

The bulk of powder procedures call for either a weighed or packed sample depending on the accuracy required, but often a pelletized sample is advisable especially if the excitation calls for sparking. The Parr hand press with dies matching the inside diameter of many electrode craters offers a convenient and inexpensive method of preparing such pellets.

## Sample Preparation—Fusion

The accepted definition of semiquantitative analysis is a procedure which gives concentration values within 2/3 and 3/2 of the correct value. Methods of poorer accuracy are termed qualitative; better, quantitative. Probably the most commonly employed methods of semiquantitative analysis are those where the sample in powder form is diluted with a pure matrix and then compared with a group of standards based

on the same matrix (11). Graphite, lithium carbonate and silica are typical matrices. Depending on the need, such semi-quantitative methods can approach quantitative accuracy provided intermediate standards are prepared, densitometric measurements are made and the matrix is carefully chosen to match that of the unknown.

But we always return to the matrix and, of course, it is not always known and may, in fact, be a mixture almost defying analysis. For the quantitative analysis of such materials, the best methods involve fusion techniques. Better than any other methods, fusion converts samples to a common form, chemically as well as physically. Probably the most careful work on fusion methods has been developed at the Alcoa Research Laboratories by Tingle and Matocha (10). In this, the sample is fused with a mixture of lithium carbonate and boric oxide. Carefully ground to attain a uniform particle size distribution, the fused bead is mixed with graphite powder, pelletized and sparked in a direct reader. Precision in the order of 2% reported by the authors has been matched in other laboratories. One disadvantage of the method is its comparative poor sensitivity (around 0.01% for most elements) but, by arcing and switching to an ordinary spectrograph, sensitivity can easily be improved at some sacrifice of accuracy.

#### Sample Preparation—Metals

Casting a disc around 1-1/4" in diameter is usually the first step in preparing a metal sample. The size has been standardized by the National Bureau of Standards and, on special order, they will upset-forged their rod standards to this shape. Sample molds of many varieties have been proposed. One type, described by W. R. Kennedy in the new ASTM book previously mentioned, is particularly well suited to ferrous materials. With it, a two part necked casting is formed. The bottom is quick-chilled against a copper plate to produce a hard, uniformly dense metallurgical structure while the top, cast in sand, cools slowly and is soft enough to drill for subsequent wet-chemical determinations. Another, in which the disc cavity is held horizontal and is bottomed with copper, produces a uniform sample for sparking.

Metal samples can be surfaced either with a lathe or a belt sander. With the former, especially with metals that machine poorly, the surface may vary considerably from the inside to the outside as the linear speed of the lathe tool varies. Care should be taken to spark to the same annular portion of such samples and standards. With a sanding belt, hills and valleys are gouged out in parallel grooves. Sanded samples should be so mounted on the Petrey stand that the grooves are at right angles to the optical path. From the standpoint of convenience, the sanding belt is advantageous over the lathe but there is a greater danger of cross-contamination with the former. To avoid this, it is a good plan to keep and mark belts for each alloy.

Sparking to wires or foils frequently taxes even the experienced person. Wires can be wrapped around mandrels which, in turn, are placed on the rotating shaft of a solution analyzer. Foils can be cemented to a copper block to dissipate the heat generated by the spark. A word of caution: because of large thermal and surface differences between such samples and massive standards, concentration figures are often subject to large errors.

#### Sample Preparation—Solutions

Solutions offer a means of bypassing the metallurgical history of metal samples. Inhomogeneity and particle size—potential sources of error with powders—are skirted with solution methods. Of the techniques proposed over the years for

sparking solutions, the porous cup, once popular, has fallen into disfavor. To be exploited successfully, it is necessary to maintain the porosity and the floor thickness of electrodes beyond the normal tolerances of the manufacturers.\* The rotating disc is probably still the workhorse of most solution methods.

Before the advent of the plasma jet, Baer and Hodge (1) wrote an excellent summary of various solution methods detailing their pros and cons. Advantages of the plasma jet are extremely high sensitivity—higher by at least a factor of 10 over other methods—capability of determining any element amenable to spark or arc methods, convenience of operation, high precision and accuracy, applicability to flammable liquids (13).

Storage of solutions, especially dilute ones, presents some difficulties. Adsorption on the walls of a container may make an appreciable change in the concentration of metals. Polyethylene bottles may be porous (12). A tightly capped polyethylene bottle which has collapsed after a period of time has lost some of its solution. Despite its reputed inertness, polyethylene is attacked by acetone and other solvents. Blanks should be run.

Acids and other liquid reagents should be screened for trace-element impurities and purified, if necessary.

For a number of years the Russians (7) have employed an evaporation method for the analysis of refractory materials. With their method, the sample is heated in a graphite cup by resistance heating. As volatile elements vaporize, they are condensed on a chilled collector electrode—normally a copper or graphite flat end electrode—held about 1-2 mm above the heated sample. This collector electrode is then handled by more conventional means using arc or spark excitation. Vaporizations may be carried out in vacuum, air or other gas. With the evaporation method, extreme sensitivities have been reported.

#### Sample Excitation

In general, high voltage spark excitation affords better precision but less sensitivity than arc sources. Newer combination sources offer intermediate compromises and some advantages of both. Too frequently, however, the novice expects small miracles from small adjustments in one or more of the electrical parameters in his source unit. The stability of the discharge, the amount of heat generated in the sample, the exposure time all have to be compromised. Doubling the RF current or the capacitance of a spark source may not significantly affect the line-to-background ratio of an element being measured.

When a sample is arced, however, a few simple precautions may improve results significantly. With powders, the spark igniter may jolt a good portion of the sample out of the crater. One way to reducing this amount is by keeping the particle size of the sample and graphite fairly high. Another way is to decrease the arc gap before the arc is struck. The inlet of air to an arc stand should not be overlooked. If asymmetric, the air may have a tendency to bow the arc. For similar reasons, the draft should be carefully controlled.

\* What to do with unused porous cup electrodes? Mr. S. Weisberger of General Telephone and Electronics Research Laboratories, Bayside, L. I., find them excellent for a gas transport electrode (3) when sparking in an inert atmosphere. A small hole is drilled laterally all the way through the hollow porous cup electrode. Gas is then blown through the top of the electrode and out this hole. Samples are sparked inside of a quartz cylinder.

Water-cooled electrode clamps are the rule rather than the exception in modern arc stands but the degree of cooling can vary markedly even with a recirculating system. Enough distilled water is needed in the reservoir to maintain the temperature reasonably constant. A small amount of algicide (available during the summer at stores that sell kiddie wading pools) will prevent the formation of slime in the water.

Depending on the composition of the condensed vapors, water, alcohol or alcohol-acid mixtures can be used to wash the inside of an arc stand. Deposits on lens elements can also be removed with solvents or with lens paper. Be wary of treated eyeglass papers as the silicone may have unwanted absorption bands. Molten particles will pit a lens but its transmittance is not seriously affected until the scarring is considerable. It is preferable to load the upper electrode first to cut the likelihood of knocking any unnoticed material from the electrode jaw into a sample cup below.

### Electrodes

Just as small changes in electrical parameters have no real bearing on an analysis, so small dimensional differences in electrodes are of little significance. Whenever a new method is to be developed, we strongly urge that one of the ASTM electrode shapes be chosen.

In the past few years, manufacturers have announced several new grades of graphite varying in density, electrical and thermal conductivity. While there is no doubt that these grades are not strictly interchangeable, i.e., small biases may be evident in analytical curves or the transmittances of lines, few rules of thumb to guide the spectrochemist are known as of this writing (2). One important, though unpublicized, improvement was made recently in the National AGKSP grade. Grain and pore sizes are much more uniform in the newer material.

The sale of carbon electrodes is given a shot in the arm occasionally with the publication of a pertinent paper. The truth of the matter seems to be that increased sensitivity does, indeed, result with carbon electrodes; however, because they are so expensive and brittle, many spectrochemists find it expedient to seek greater sensitivity elsewhere.

### The Spectrograph

Too often, the heart of a spectrographic laboratory—its big spectrograph—is ignored, its focus and alignment allowed to drift with the whims of changing ambient temperature or pressure, vibration, “settling” of the metal framework or hardy gremlins. The spectrograph, like a piano, must be tuned regularly. Like a piano, too, there are “chords” to which the tuner can refer as a performance check.

One well-known “chord” is the four-line iron “triplet.” Immediately after the spectrograph is set up by the manufacturer, the iron triplet should be recorded under optimum conditions: slit width, 10-microns or narrower; current, 3 amps or less with a Pfund or iron globule arc (see ASTM book previously referenced, p. 68); emulsion, SA#1 or similar fine-grain plate. A series of graded exposures should then be made and kept for future comparisons. If a recording microphotometer is available, tracings of the lines will offer the best means of future reference. Alternatively, the spectrochemist can resort to visual observations of line shape, resolution and focus. With other than fixed position instruments, the iron triplet should be recorded in the center of the plate, and at both ends in the first and higher orders. This will permit alignment tests over the whole plate.

Another important check is of intensity. Modern aluminizing results in exceedingly stable reflecting surfaces and any abrupt loss of optical speed probably means dirt, dust or corrosion on the mirrors or grating. A clean camel's hair brush or the Effa duster will remove loose dust. More stringent cleaning, best reserved for an experienced person, may be accomplished by floating a layer of collodion on the surface and, after it hardens to just the right consistency, stripping it off. With luck and skill, the aluminizing stays intact.

Entrance slits must be cleaned with great care. The old whittled matchstick is still an acceptable tool for the purpose. Newer ones include 1/4-mil Mylar film (used for x-ray liquid cell windows) and canned Freon.

If the room can be darkened, light leaks in the spectrograph can be found simply by placing a lamp inside the instrument. Soft, black Apiezon W, a common high-vacuum sealant, is excellent for stuffing light leaks. Inside seals, where practical, are preferable.

Regardless of the care taken in maintaining the alignment of a spectrograph, the intensity, shape and appearance of spectral lines will vary depending on the lateral position of the plate in which they are photographed. Coma, astigmatism and other aberrations are present in all spectrographs, their degree depending largely on the lateral position of the image. It is therefore essential that the same wavelength setting be maintained for a particular method. Do not, for example, expect to squeeze the low wavelength boron lines in by displacing the spectrum and have the analytical curves for the other elements remain invariant. “Curve shifts” are not always explainable but they can be artificially produced by moving the wavelength setting in just this way.

Curve shifts can result because of changing humidity or aging plates. Storage of plates in either a deep-freeze or refrigerator, depending on their rated shelf life, will reduce a well-known source of error.

### Bookkeeping

The term is somewhat facetious yet bookkeeping is a good word to describe the task of turning out the daily work efficiently. The spectrochemical process is multi-stepped and, like getting a big jet plane off the ground, demands a check list as a reminder of every minor, though vital, link in the chain. A convenient way of setting up such a check list is by having a rubber stamp made up with information such as that in Table 2 and stamping it on each plate envelope. By filling in an appropriate space, the operator indicates that he has checked that parameter.

TABLE II  
Typical Checklist

Plate No. ....	Date.....		
Plate type .....	Method No. ....		
Slit Ht. ....mm	Slit W.....	Wavelength.....	
Filter .....	Starting Rack No.....		
Source No. ....	Pretimer...sec.	Exp. Timer...sec.	
Power setting.....	L....C....R....	Breaks/hf cycle.....	
Powerstat.....	Aux. gap.....	Current.....dc Amp.	
Electrodes	Upper.....	Lower.....	Gap.....mm
Sample Preparation .....	(Method No.) .....		

It is a good plan to summarize every method developed and keep this information in a looseleaf notebook. In addition to the details in Table 2, the summary should reference analytical curves for each element (each on a separate page), and the standards designated for the method.

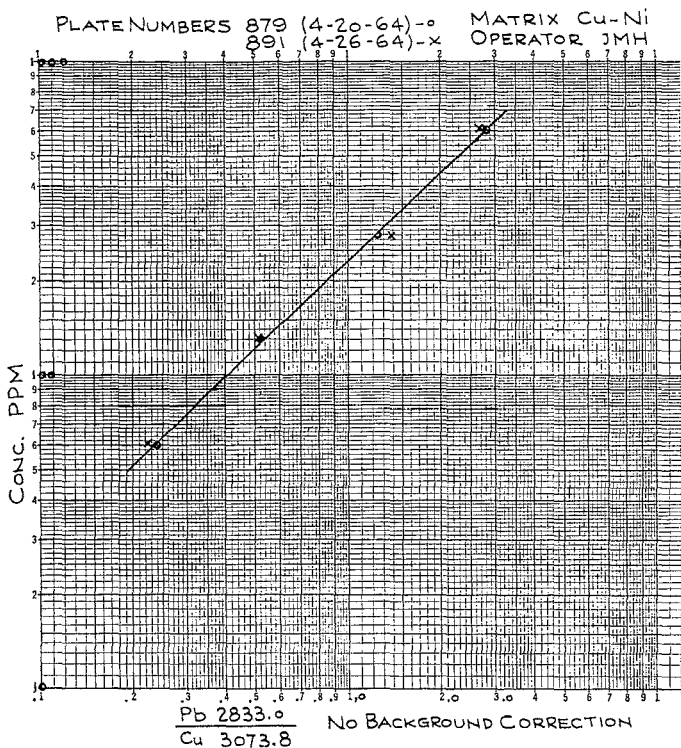


Fig. 1—Typical Analytical Curve

An analytical curve like this reveals much more than slope and displacement. Note: 1) the plate number for reference; 2) the concentration range covered; 3) a rough precision guide in the form of repeated plates and their keyed designations; 4) line pairs together with an abbreviated notation telling whether background corrections have been made.

Another aspect of bookkeeping is the photographic record itself. Each plate should be numbered in the same relative position (the photographic numbering devices on the market are excellent for the purpose) to save time later by indicating the high and low wavelength ends of the plate. As for the spectra themselves, we would caution the operator against crowding the plate. There are several reasons for this. First of all, emulsions on plates are not as uniform as those coated on film. Thus, a space every 6-8 spectra permits checking the 0 and 100% transmittance close to the lines being measured. Secondly, an accidentally broken plate containing a great deal of information takes an inordinately long time to reproduce. A reference spectrum of iron should appear on each plate. While this is not always necessary for routine operations, many "routine" samples are later subject to further scrutinizing for elements not originally sought.

Because of the great many parameters and variables involved in his method, the spectrochemist frequently needs a short cut to ascertain whether he or his technicians have not made one or more mistakes somewhere along the line. A common way of doing this is to run a particular standard under fixed conditions on each and every plate.\* The intensity ratio of a chosen pair of lines is measured and if it falls within preset limits, everything is "go." Should it stray from these bounds, an error or problem somewhere along the way is indicated and has to be tracked down. Incidentally, the choice of line pair is important. They should differ widely in excitation potential in order to emphasize any difference in source settings. They should be free of interference and close together in wavelengths.

\* This could well be the reference spectrum used as a wavelength guide on all plates.

## Excitation in Controlled Atmospheres

Air, though unchallenged as a convenient atmosphere for excitation, does have limitations. In recent years, the advantages of other gases and mixtures have prompted many to re-vamp their procedures. By eliminating nitrogen from the arc, the buildup of dense cyanogen bands is overcome thus opening large wavelength regions for measurement. Rates of sample vaporization may be controlled by variations of the atmosphere and this, in turn, enhances sensitivity for desired elements.

Of the many methods devised for controlling the atmosphere around an arc, probably the most popular is the Enclosed Stallwood Jet, in which the sample is excited in an atmosphere of 30:70 oxygen:argon. With this mixture, the cyanogen bands can be virtually eliminated. If they persist, two sources of trouble are likely. One is the purity of the gas itself. Unless the gas cylinder is properly purged, it may contain residual nitrogen. The second potential source is aspiration of atmospheric air caused by a gas flow rate greater than that needed to minimize the cyanogen band intensity. For the most critical work (where nitrogen is to be determined, for example) the Spex Stallwood Jet should be mounted in the jaws of the arc stand rather than on a side post. So mounted in the jaws, the Jet excludes air altogether.

## Spectrum Evaluation

The ease of interpretation of a spectrographic plate is greatly dependent on the amount of preparatory work done in the lab. The more varied the sample load, the more complete the reference plate library need be. In addition to a good reference book listing spectrum lines (14), it is a good plan to have on hand the following plates:

- 1) Fe arc and spark plates with wavelengths marked every 5-10A.
- 2) A set of qualitative plates with principal lines of a large number of elements.
- 3) Arc and spark spectra of individual pure elements.
- 4) A set of semiquantitative plates.

Lettering a reference plate should not be hurried since it will be a constant source of information for many years. One method is to intersperse between the plate and the viewing box a piece of thin graph paper. A pen such as the Kohinor No. 00 or the Lithographic No. 62 (available from local stationers) produces very fine lines. To facilitate marking, Mr. Raymond Vogel of Mallinckrodt Chemical Company's Weldon Springs, Missouri plant, has cut a wedge out of the bottom of a viewing lens. Laid on the plate, the lens furnishes an enlarged image while permitting the penpoint to be moved right inside the field.

An unusual, though highly effective gadget for interpolating wavelength is the Spex Spacing Divider. This has eleven teeth, equally spaced but so adjustable that the divider can be used to sub-divide a fixed distance in uniform increments of 1/10.

Microphotometry of lines is subject to a number of errors which may not be suspected. First and foremost is focus, the importance of which cannot be overemphasized. Modern instruments, with their 15-20X magnification, have a short depth of focus and any temperature change may very well disrupt measurement accuracy. Plates are fairly flat and present little change in focus over their area but film, especially in dry weather, may buckle to affect transmittance readings seriously. Comparator-microphotometers, with their convenience in seeing while measuring, are subject to scattered light errors arising from the field light in the detector path. Dust on the optical elements increases the scattering power and therefore reading errors.

A rule of thumb in microphotometer measurements is that the slit width of the instrument should be less than one-half that of the line width. This condition satisfied, the peak density will be measured. One way of testing this condition is at the time the emulsion is being calibrated. Take two sets of spectra, the spectrographic slit width doubled for the second set. Within the error of measurement, identical calibration curves should result; a marked difference may indicate that the microphotometer slit width is higher than specified by the manufacturer.

Conversion from transmittance to percent concentration—the climaxing step in the spectrochemical procedure—gives the enterprising analyst his rein. With little exaggeration, there are probably as many different calculating boards and slide rules as there are laboratories. These vary in complexity from the simple vertical and horizontal log-log sliding scales to the computers on which several laboratories have programmed their emulsion calibration curves. On one point, however, nearly all seasoned spectrochemists are agreed: reliance on Seidel rather than logarithmic coordinates for the transmittance axis. Measurements in high transmittance regions, subject to huge errors on log or linear coordinates, are made much more exacting with Seidel paper.

Collecting and keeping tabs on the data and calculations is another non-standardized area. Fig. 2 depicts a portion of a typical data sheet.

**S**PETROCHEMICAL analysis does not end in the laboratory with a concentration figure. No matter how accurate and sensitive the method, improvements will be made in the years ahead. The new spectrochemist should join and become active in his local SAS and ASTM's committee E-2. As infor-

mation exchanges, these organizations help everyone not only by giving individuals the welcome opportunity of contacting associates and peers to keep abreast of what's new but also by furnishing data for that yet unpublished "Journal of Negative Results."

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Cu-Ni                      QUANTITATIVE COMPARISON     4-20-64     JMH                      FILM NO. 879

SAMPLE	Std 101			Std 102			Std 103			Std 104			SAMPLE A692		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Cu 3013.8	21.2		25.9	23.4		26.8	24.6								
Pb 2833.0	85.8 24	60	62.2 52	130	16.3 125	280	4.2 2.8	600	26.5 95	210					
Sn 2839.9	81.8 27	30	60.9 48	65	27.0 91	140	11.8 1.65	300	30.6 86	93					
Fe 3021.0	90.7 20	10	59.0 50	22	18.6 1.15	46	3.3 3.2	100	6.7 2.06	80					
Cr 3132.1	38.9 15	80	36.6 25	120	32 40	200	0	300	35 11	<80					
SAMPLE	9	10	11	12	13	14	15	16							

COL. 1 % TRANSMISSION  
 COL. 2 INTENSITY RATIO TO MATRIX LINE  
 COL. 3 % CONCENTRATION

SPEX  
 Instrument, Inc.

CALIBRATION CURVE  
 γ =

Fig. 2—Typical Data Sheet

In this data sheet, each spectrum is represented by three vertical columns. In the first, transmittance values of the internal standard and unknown lines are recorded. (This box is suffi-

ciently tall to permit recording background transmittance values beneath.) On an 8-1/2" by 11" sheet of paper, sixteen samples with up to 15 elements can be handled legibly.

# STEEL and CAST IRON STANDARDS

## NEW B.A.S. MILD STEEL RESIDUAL STANDARDS

When the original set of mild steel standards was issued by the British Bureau of Analysed Samples, certificates were supplied for 11 elements. Four other elements—Ti, Zr, Ta, Nb—were assigned approximate values. In the latest series, 15 elements have been certified but, because of the difficulty involved in homogeneously distributing so many elements, they have been divided into two groups. Each of the groups may be purchased separately.

The standards, in the form of discs 1-1/2" dia. x 3/4" thick, are equally suitable as emission and x-ray spectrochemical references. As in all other standards issued by the Bureau, the analytical values are weighed averages of figures determined by several laboratories representing British industry, government, research associations and the Bureau itself. All figures as well as pertinent procedural information appear in the individual certificates.

**BSS 21-24 Low Tungsten Steel Standards**, rods, 3/4" dia. x 3" long; Tungsten 0.70%, 1.29%, 2.16%, 3.41%. Each contains about 0.02% C, 0.13% Si, 0.036% S, 0.014% P, 0.07% Mn, 0.02% Mo and 0.01% V .....Set of 4 \$ 67.00

**BSS 281-284 Low Tungsten Steel Standards**, granules, 100g each, analysis as above.....Set of 4 \$ 45.00

**BSS 31-35 Carbon Steel Standards**, discs 1/2" thick x 1-3/4" dia., .07-.47% C, .06-55% Si, .01-.08% S, .004-.067% P, 14.72% Mn, .003-.11% As. ....Set of 5 \$ 82.00

**BSS 41-46 Nodular Cast Iron Standards**, rods, 1-3/16" dia. x 1-1/2" long; 0.012-0.128% Mg, 0.32-1.42% Ni, 0.01% S, 3.3% C, 0.02% P  
Set of 6 \$115.00

**BSS 50-55 Mild Steel Residual Series, Group A**,  
Set of 6 \$ 96.00

**BSS 56-60 Mild Steel Residual Series, Group B**,  
Set of 5 \$ 80.00

**1200 Low Alloy Steel Standards**, blocks 1" x 1" x 1-1/2" for use both in x-ray and optical spectroscopy. Elements vary in such a fashion that the iron remainder is kept constant at around 94% to minimize matrix effects. Element ranges are Si 0.10-0.96; Mn 0.16-1.54; Ni 0.19-4.98; Cr 0.19-2.97; Mo 0.17-1.51; V 0.12-0.65; Cu 0.13-0.55 percents .....set of 8 \$124.00

**1202 Low Alloy Steel Standards**, same as above but granules for photometric and solution analysis.  
set of 8, 100g each \$104.00

### MILD STEEL RESIDUAL SERIES GROUP 'A'

Ni %	Cr %	Mo %	W %	Ti %	As %	Sn %
0.022	0.131	0.22-	0.17-	0.022	0.031	0.085
0.099	0.106	0.068	0.077	0.13-	0.003	0.014
0.194	0.039	0.045	0.048	0.043	0.012	0.24-
0.172	0.22-	0.100	0.25-	0.018	0.058	0.024
0.050	0.077	0.17-	0.106	0.034	0.084	0.13-
0.23-	0.22-	0.16-	0.12-	0.013	0.013	0.046

### GROUP 'B'

Mn %	Cu %	V %	Co %	Al %	Pb %	B %	Sb %
0.32	0.36	0.060	0.023	0.006	0.014	0.001	0.006
0.16	0.16	0.13-	0.006	0.020	0.011	0.003	0.033
0.43	0.08	0.18-	0.17-	0.050	0.016	0.004	0.025
0.12	0.07	0.08-	0.070	0.058	0.051	0.008	0.019
0.45	0.05	0.026	0.020	0.020	0.003	0.007	0.018

### LOW TUNGSTEN STEEL SERIES

W %	C %	Si %	S %	P %	Mn %	Mo %	V %
0.70	0.02	0.13	0.036	0.014	0.07	0.02	<0.01
1.30	0.02	0.13	0.038	0.014	0.05	0.02	0.02
2.16	0.18	0.21	0.036	0.018	0.07	0.04	<0.01
3.41	0.18	0.22	0.036	0.018	0.07	0.02	0.03

### NODULAR IRON SERIES

Mg %	Ni %	C %	Si %	Mn %	S %	P %
0.012	0.32	3.24	2.2	0.39	0.011	0.025
0.024	0.39	3.26	2.1	0.39	0.010	0.022
0.039	0.52	3.31	2.1	0.37	0.009	0.022
0.053	0.64	3.32	2.1	0.41	0.009	0.020
0.078	0.96	3.26	2.0	0.36	0.008	0.020
0.128	1.42	3.39	2.1	0.39	0.007	0.020

### LOW ALLOY STEEL SERIES

Si %	Mn %	Ni %	Cr %	Mo %	V %	Cu %
0.41	1.54	1.24	0.51	1.51	0.65	0.55
0.28	0.34	2.23	0.42	1.05	0.23	0.20
0.65	0.84	1.00	0.99	0.67	0.51	0.39
0.22	0.26	3.26	0.27	0.23	0.15	0.34
0.15	0.16	4.98	0.19	0.30	0.21	0.25
0.23	1.02	0.19	2.33	0.53	0.18	0.16
0.10	0.56	0.27	2.97	0.17	0.12	0.13
0.96	0.40	0.55	1.29	0.83	0.35	0.15

### PLAIN CARBON STEELS

C %	Si %	S %	P %	Mn %	As %	Ni %	Cr %	Mo %	Cu %	V %
0.47-	0.55	0.029	0.044	0.36	0.113	0.05	0.12	0.02	0.07	0.08
0.07 <sub>0</sub>	0.06	0.010	0.019	1.14	0.003	0.04	0.15	0.02	0.01	0.02
0.63-	0.25	0.090	0.067	0.62	0.070	0.04	0.11	<0.01	0.05	0.10
0.14 <sub>5</sub>	0.36	0.012	0.004	1.47	<0.002	0.01	0.02	0.01	0.01	0.02
0.26 <sub>5</sub>	0.54	0.055	0.036	0.72	0.024	0.04	0.20	0.01	0.06	0.08



Return Requested

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### JOURNAL AWARD FOR 1963

Presentation of the annual Society for Applied Spectroscopy Journal Award for 1963 was made at the SAS general membership meeting March 5, 1964, during the Pittsburgh Conference. Mr. F. D. Leipziger of Sperry Rand Research Center, Sudbury, Mass., the recipient, was honored for his paper "Some New Upper Limits of Isotopic Abundance by Mass Spectrometry" (*Applied Spectroscopy*, 17, 6, 158-160, 1963).

Initiated in 1960 and sponsored each year by Spex Industries, Inc., Metuchen, New Jersey, the award carries a prize of \$100.00 for the paper selected by the Journal Award Committee as most outstanding for the year.

Through a misunderstanding the committee decided on a winner for 1963 before one was chosen for 1962. This oversight is currently being remedied.

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### NEW "National Carbon" CATALOG

Union Carbide's Carbon Products Division has published a new catalog on its National graphite and carbon materials. In attractive loose-leaf form to permit updating and additions, the booklet already contains a wealth of technical information for a practicing spectrochemist. Particularly helpful are the sections cross-referencing ASTM and National numbers and

those furnishing tables and photomicrographs on the various grades of graphite. Suggestions for which preforms and materials to use where, are also offered.

A copy of the catalog will be sent free of charge if requested from us. Please furnish your professional rather than residence address.