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ACCURACY IN SPECTROCHEMICAL ANALYSIS

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I. Introduction

A visitor to a large modern plant manufacturing ferro alloys was surprised when taken through the chemical lab. Hundreds of identical flasks were lined up in a long hood, their gayly-colored contents boiling away. Obviously, the time-saving, money-saving spectrograph was being ignored in favor of old-fashioned, wet chemical techniques. Impatient at the thought, the visitor demanded an explanation. The chief chemist seemed enthusiastic.

"What accuracy can we expect from spectrographic techniques?" he asked eagerly.

The visitor fell into the trap.

"It depends on many factors, of course, but a figure of plus or minus 2-4% would be about average."

The chemist reached into his desk, whipped out a slide rule and sprung it into action. After a moment, he remarked quite casually, "If we were wrong by that amount, it would cost our company about \$12,000 every day."

One of the authors was that visitor and the incident left a lasting impression. So many potential applications of spectrographic analysis lie dormant simply because present-day accuracy is not good enough. Not only is this true in industry where improved accuracy would mean superior quality control as well as savings in money, but in biology and medicine better accuracy could result in a new diagnostic tool to tell the researcher why nature goes wrong. Think of the wonderfully delicate metabolic mechanism in our body that maintains constant temperature, respiratory rate, blood pressure, heart-beat and weight through the release of enzymes and hormones. Many of these are now known to be metallo-organic compounds suggesting as a diagnostic means the possibility of spectrographic analysis of blood, the carrier of most enzymes and hormones. But the accuracy limitations of the spectrograph have, thus far, played havoc with diagnostic correlations. If a spectrographer can determine a trace element in the ppm range or below within an accuracy of 50% of the amount present, he is doing real

well. An element off balance in the body by that amount may, indeed, be misbehaving.

II. Sampling

The scapegoat of all analytical techniques is sampling. After a sample is consumed, no one can argue that it once truly represented the average composition of the material being analyzed. The reader is referred to an excellent treatise on the subject (1, p. 51) which discusses the reduction of a production batch to a laboratory size sample. The spectrographic problem really begins at this point, however, because the spectrograph "sees" only a few milligrams of the actual sample and any segregation whatsoever is greatly magnified.

One method of trimming segregation effects in point-to-plane techniques is that of taking multiple, superimposed exposures at different places along the sample. Another, and one that is readily automated, is to move the sample slowly and uniformly during the sparking. Hurwitz (2, 3) showed how traversing segregates aids in obtaining a true determination and, further, that certain elements, which ordinarily spark off at the beginning of the exposure, have a constant intensity with time when new areas of the sample are continuously being sparked. He cited (4) Al and Mg determinations in zinc-base alloys. Ordinarily, spectral line intensity of these elements drops sharply after the first few seconds, but by using a moving specimen, the sparking-off effect is removed. Improved results were confirmed in the analysis of cast irons by Clark (5) who moved the sample linearly during the sparking so that the sparked area was equivalent to eight stationary burnings. As shown in Table I, the technique aids markedly in matching spectrographic with wet chemical determinations.

TABLE I.
SPECTROCHEMICAL ANALYSIS OF CAST IRON
Deviation from Wet Chemical Values, %

Element	Single Determination	Sweep Method	Four Superimposed Spectra
Mo	5	3	2
Cr	6	3	2
Ni	4	2	1
Mn	5	4	3
Si	13	4	5

*Presented at the 10th Annual Symposium on Spectroscopy, Society for Applied Spectroscopy, Chicago, Ill., June, 1959, and at the Denver Conference, Rocky Mountain Spectroscopy Society, August, 1959. Reprinted by permission of "Applied Spectroscopy."

Note in Table I that, although better than individual sparkings, the sweep method is not quite as precise as the multiple exposure method in which four individual burnings are superimposed. The principal reason for this is statistical. Theoretically, any determination can be improved by the square root of n (the number of determinations) by taking the arithmetic mean of n values.

To take advantage of the sweep technique, a Petrey Stand with a slowly rotating table, as pictured below, is manufactured by Spex Industries. The speed of traverse is determined by the choice of motor but about 90° per 30 seconds—the normal sparking time—is suggested.

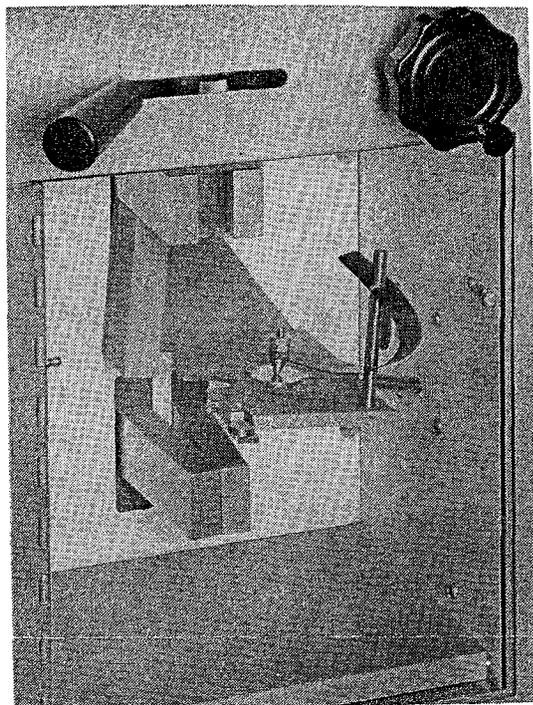


Fig. 1—The Petrey Table (9011) used with the Spex 9010 Arc/Spark Stand. Specimens may be placed on a turntable so that a large area is sampled. A jet (not shown) may be directed at the spark to reduce matrix effects.

For powders the sampling problem has a number of aspects often overlooked: particle size differences, adsorption and absorption of water vapor and atmospheric gases, packing of the powder into the electrode, to name a few. Recognizing these problems, Tingle and Matocha (6), in an excellent piece of work, converted a method normally considered but semi-quantitative into one with quantitative accuracy. Their technique involves fusion of samples with lithium borate serving to homogenize the sample and convert it to a common matrix simultaneously. The sample thus treated is ground and screened so that only a selectively chosen particle range is used in the analysis.

Packing electrodes is a problem neatly handled with the Elpac, a new machine which automatically tamps craters full. An excess of the material is placed in a disposable polyethylene funnel perched snugly around the neck of the electrode. A tamper is lowered into position and a fixed vibration packs the crater in a few seconds.

Both uniformity and tight packing are achieved with the instrument as illustrated in Table II. In three out of four typical samples, the amount of material packed is reproduced within around 1%. Furthermore, the amount packed averages around 50% more than that obtained by hand packing. Note, too, that two of the electrodes chosen were $1/8''$ d. and center-post types which are, of course, extremely difficult to pack by hand.

TABLE II.
"ELPACKED" vs. HAND-PACKED ELECTRODES

Material	Quantity Packed mg (average of 10 runs)		Coef. of Variation %	
	Elpac	Hand	Elpac	Hand
Potassium Carbonate:				
graphite, 1:1	221*	171*	1.2	4.0
Iron Oxide	283*	167*	2.5	4.0
Li_2Co_3 plus graphite, 1:1	82**	66**	1.3	8.1
Li_2Co_3 plus graphite, 1:1	24***	10***	1.0	10.

* $1/4''$ d. electrode with undercut crater

** $1/4''$ d. electrode, crater undercut with center post

*** $1/8''$ d. electrode, crater $1/4''$ deep

Incidentally, Dr. A. Strasheim, the inventor of the Elpac, has stated that much better results are achieved with baked powders, the effects of gas and moisture being exaggerated when automatic packing is used.

Table III, taken from Strasheim's article (7), shows that superior packing with the Elpac does, indeed, result in improved precision. The figures in this table represent the coefficient of variation of intensities of *individual* lines, illustrating the fact that dc arc burnings themselves are more reproducible when the Elpac is used.

TABLE III.
PERCENT STANDARD DEVIATION OF A SERIES OF
RELATIVE INTENSITIES OF ANALYSIS LINES^a

	Fe	Al	Ca	Sn	Na
Operator 1	23.5	17.7	9.7	17.5	13.8
Operator 2	21.7	14.8	16.4	16.9	17.3
Operator 3	21.6	9.5	7.6	7.7	11.1
Machine	19.0	7.4	6.6	7.5	8.3

a—Twenty samples excited

III. The Source

Spark sources have been improved steadily in recent years. The use of an air blast at the auxiliary gap helps stabilize the spark. Controls of the auxiliary gap spacing and oscilloscopic observation of rate of discharge of the spark are helpful in reducing variables. Superior materials and shapes of the auxiliary gap electrodes also aid in maintaining spark stability. While too new to evaluate, the Bardocz electronically controlled spark (8) appears promising.

Feldman and Ellenburg have formulated a procedure (9)† by which, they claim, optimum reproducibility is obtained from their spark source:

- 1) Auxiliary gap opened to 10 mm or wider.
- 2) Autotransformer in primary circuit set at zero.
- 3) Source turned on.
- 4) Autotransformer adjusted to give a predetermined voltage across its variable arm.
- 5) Auxiliary gap narrowed until one breakdown occurred on each half cycle.
- 6) Autotransformer adjusted to give the desired number of breaks per half cycle.

Variables such as cleanliness, smoothness, and shape of the auxiliary electrodes, as well as resistivity of the ambient atmosphere which is temperature and humidity dependent, are

†Reprinted by courtesy of "Analytical Chemistry."

avoided by using this procedure. In the opinion of the authors, it aids in reproducing the curve of current vs. time from one discharge to the next.

Attempts have been made to couple the advantages of the spark's stability with the arc's sensitivity and such hybrid sources may now be obtained commercially. In pure arcs—still the sources of highest sensitivity—several new developments are notable. The constant current dc arc is one. Through electronic control, the dc arc may be maintained within a few percent. Since the drift of an arc as the sample is consumed and the gap widens may amount to 100%, a constant current dc arc should result in superior overall accuracy. A commercial source is not yet available in the U. S. A., but three spectrographers have independently built such units. They are L. E. Owen (10) of Goodyear Atomic Corporation, E. Ziemendorf (unpublished) of the Carborundum Company in Niagara Falls and D. O. Landon (unpublished) of Spex Industries. Incidentally, a bonus gotten with the constant current dc arc is potentiometer control of the current instead of the cumbersome motor-driven heavy iron core reactor. The pot permits accurate settings before a run is made and rapid changes in current without overshooting.

Over the years, there have been many attempts to tame the dc arc through the use of external contrivances. Magnets have been used both to constrain the arc column and to rotate it at fixed speed. Gas jets, double arcs, center-post electrodes are still other innovations aimed at tranquilizing the easily excitable arc.

Of these gadgets, one that has "caught on" is the Stallwood jet (11) now used in dozens of laboratories. With it, an annular curtain of gas is blown upwards around the arc column to restrain arc wander. Compressed air may be used but, to achieve the added benefit of increased sensitivity and suppression of cyanogen bands, mixtures of argon and oxygen (30 to 50% of the former) are recommended. *latter*

The Spex version of the jet is pictured in Fig. 2. The

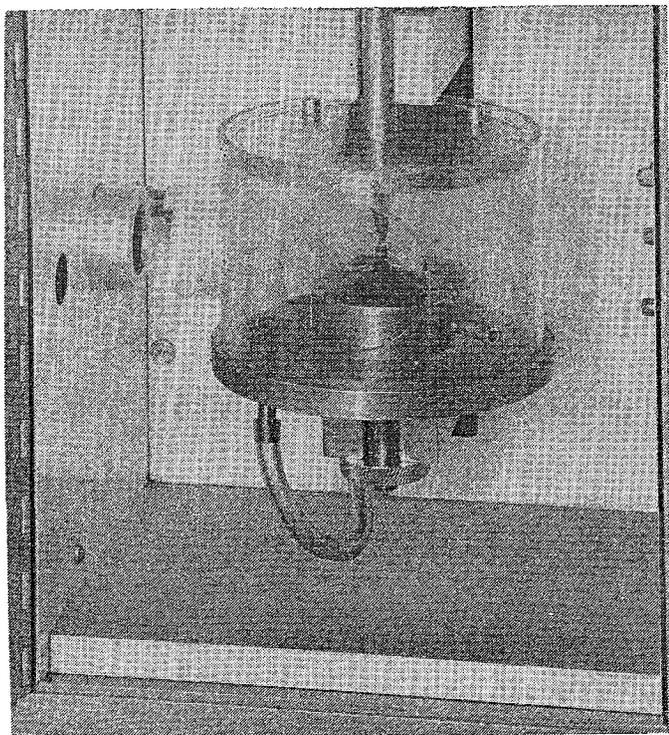


Fig. 2—Stallwood Jet (9014) mounted inside the Enclosed Arc Chamber (9015). A curtain of gas is directed upward around the arm and, in combination, all evidence of atmospheric gases is eliminated.

entire assembly fits in the lower electrode jaws, a feature which automatically centers the electrode with respect to the jet.

Improvement in accuracy through the use of the Stallwood jet has been confirmed by a number of spectrographers since the original article was written in 1954. Joensuu (12), describing its use in the analysis of rare earths on a routine basis, cites the additional advantage that fumes are blown out continuously so there is less self-absorption. The results of our own experiments are shown in Fig. 3 and Table IV. The spectrograms dramatically illustrate the improvement in line-to-background ratio especially in the region of the CN bands.

Other major advantages of the Stallwood jet are reduction of matrix effects and prevention of selective volatilization of low boiling elements. This is accomplished through the use of deep crater electrodes in which successive layers of sample are burned away while lower layers remain cool. The electrode is placed so that it protrudes by 1-2 mm above the jet housing. As it is consumed in the arc, a rod is used to push it upwards through the hollow stud.

Inert gas atmospheres have been the subject of numerous papers and the general opinion seems to be that decided improvement in accuracy and sensitivity may often be achieved. The reader is referred to the article by Thiers and Vallee (13) for detailed information. A recent article by Hammaker and associates (14) illustrated the advantages of using an atmosphere of argon-oxygen in suppressing the cyanogen band intensities. From the viewpoint of accuracy, the result is to remove background almost completely from behind many sensitive spectral lines and so permit their use without having to make inaccurate background corrections.

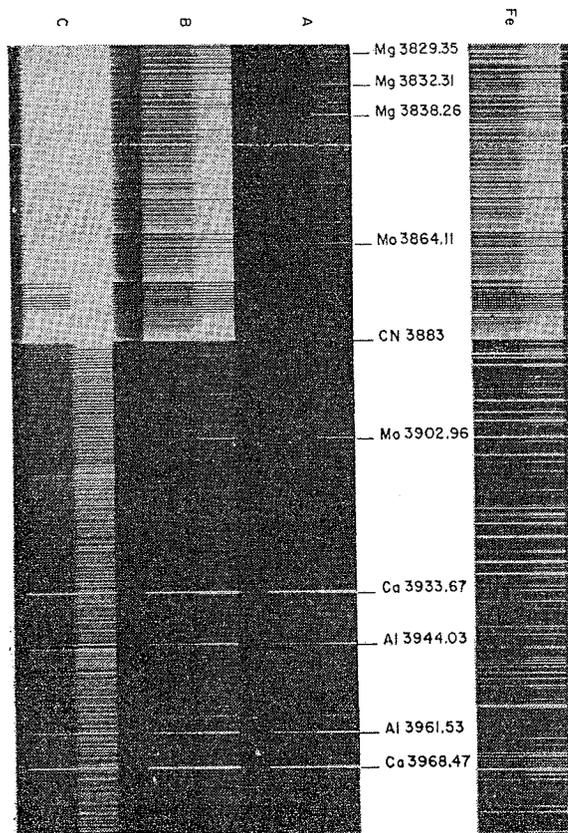


Fig. 3—A, B, and C are three spectrograms taken under almost identical conditions of the Spex G2 standard containing 0.01% of 43 elements. The burning for C was made in an open dc arc; in B a Stallwood Jet was used; in A the combination Stallwood Jet and Enclosed Arc Chamber. Note the enhancement of many lines and freedom from background, making the elements many times more sensitive. Note, too, the reduction in the CN band in B and its complete elimination in A.

TABLE IV.
COMPARISON OF PRECISION OF INTENSITY READINGS
WITH AND WITHOUT STALLWOOD JET

Element	Wavelength A	Coef. of Variation, %	
		With Stallwood Jet	Without Stallwood Jet
Copper	3274	11.5	21.0
Titanium	3235	2.8	13.7
Silver	3280	2.7	13.4
Cadmium	3261	4.6	10.0
Tin	3263	2.7	16.7
Zirconium	3273	3.5	20.0
Average Coef. of Variation		4.6	15.8

Fry and Schreiber demonstrated how analytical accuracy could be improved when miscellaneous samples of steel are run by the use of an air blast (15) directed at the spark gap. Variations in chemical composition, physical size and shape, and metallurgical history affect the analytical curves less when an air blast is used.

IV. Electrodes

An unpublished report by S. R. Wiley illustrated how precision could be materially improved step-wise by going from 1/4" to 3/16" to 1/8" diameter electrodes. With his Wadsworth Spectrograph cylindrical optics were used so that the arc column was focused at the slit in the horizontal plane. Accordingly, wandering of the arc off axis caused large changes in the intensity of the slit. By restricting the wander with a narrow electrode, this effect was strikingly reduced.

While discussing electrodes, the subject of physical properties of graphite should be considered. Taking the electrode for granted, the spectrographer does not often question their uniformity from one to the next. Yet W. R. Kennedy (16), American Cast Iron Pipe Co., discovered some surprising differences (Table V). Using eight types of graphite rods of American and foreign manufacture, he sparked the same sample of cast iron nine times with each rod, machining it after every exposure to a hemispherical tip of 30°. Results for Si and Mn determinations are given in Table VI.

TABLE V.
PHYSICAL PROPERTIES OF GRAPHITE RODS

	Water Absorption %	Hardness (diamond penetration)	Electrical Resistivity ohm. in. x10 ⁻⁴
Nat. AGKSP	—	—	2.7
Nat. AGKS	14.8	6.1	2.6
Nat. SPK	—	—	4.8
Ringsdorff RW I ek	18.6	6.0	3.1
Ringsdorff RW I extra	6.9	9.2	3.2
Ringsdorff RW IV	.27	9.0	3.2
UCP U-1	13.3	8.1	3.6
UCP U-2	15.1	4.2	4.7
UCP UF4	—	—	4.7
UCP UF4S	—	—	4.9
UCP Spectrotech	14.8	7.0	4.5

Kennedy tried to track down the cause of varying reproducibility from one brand or type of electrode to another. Porosity variations seemed to be a logical offender and so he tried to obtain information on this indirectly by measuring the water absorption after boiling. Although quite wide variations were found (.27-19%), he could not correlate them with spectrographic results. Kennedy also found differences in electrical

resistivity and hardness but again could not correlate the results. But he could demonstrate that shifts in working curves and attained precision were directly attributable to the type of electrode employed.

The shape of an electrode is, as can be judged from the tremendous number of preforms now available, meaningful in attaining high accuracy. Selective volatilization is, for example, very directly related to accuracy. If one were running a sample for magnesium and tungsten in a conventional undercut electrode, magnesium would volatilize out during the first few seconds of arcing, tungsten during the last few. Using such electrodes, the determinations of these elements is thus subject to inherent errors. In addition, refractory elements often wind up as beads which drop out of the cup before they are completely consumed. For the determination of many elements of varying volatilization rates, Landon (17) found that a very deep (1/2") crater in a narrow thin-walled electrode produced similar burn-off curves for many elements of varying volatility. As already mentioned, Stallwood (11) used deep, narrow electrodes with his jet to reduce selective volatilization and, consequently, matrix effects.

V. Weather

Spectrographers, too, are bothered by weather's unpredictability, as witnessed by the fact that so many laboratories are air-conditioned. In practice, however, while it is well known that temperature, pressure and humidity variations are factors influencing spectrochemical results, air-conditioning usually means temperature control only.

One effect of weather variations is on a spark source, and this has already been mentioned. The main effect of temperature variation on the spectrograph is to defocus it to a degree which, though visually undetectable, may be enough to change the line widths and, consequently, their density. Here, temperature gradients are particularly troublesome because, by heating parts unequally, they affect different regions on the plate unequally. The slit and optical components may also distort to give rise to changes in line density. Apart from the spectrograph proper, temperature variations change the sensitivity of photographic emulsions and the parameters of electronic components in the source unit and the microphotometer. Humidity affects the sensitivity of photographic emulsions, too, not only by disturbing the formation rate of the latent image but also by absorbing radiation at the shorter wavelengths.

VI. Optics

Considered a permanent fixture aligned, tested and sealed by the manufacturer, the optical system is ignored by spectro-

TABLE VI.
EFFECT OF GRAPHITE COUNTER ELECTRODE
ON PRECISION

Rod Stock	Coefficient of Variation, %	
	Si	Mn
RW I ek (Ringsdorff)	3.90	1.54
RW I extra (Ringsdorff)	2.02	2.72
RW IV (Ringsdorff)	2.79	1.74
UCP U-1	2.57	1.87
UCP U-2	3.20	2.74
UCP UF4	2.71	2.42
UCP UF4S	2.99	3.02
Nat. AGKSP	3.78	2.48
Nat. SPK	1.50	1.90

Material — Steel Std. NBS 1162

Graphite rod — machined to 30° hemispherical tip

No. of determinations — 9 each run

graphers. Periodic checking is, nevertheless, recommended to avoid needless loss of precision. Improperly aligned external and internal optics, poor focusing, spectrographic aberrations, slit eccentricities all may give rise to drifting data.

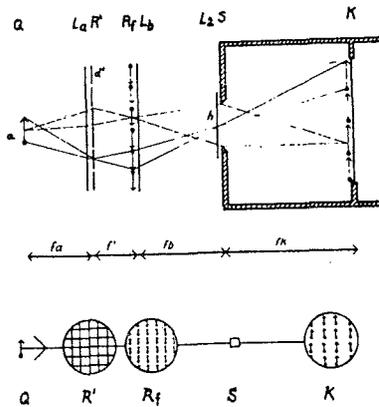


Fig. 4—Ray diagram of the Linsenraster optics used to reduce the effects of arc wander. The source *a* is imaged by a mosaic of lenses on the collimator *k* in such a fashion that, as the arc wanders from one side of an electrode to another, the image moves to a much smaller degree across the face of the collimator.

The purpose of the external optics is to fill the spectrograph aperture with light and so obtain the maximum speed and resolving power. The images should be regularly inspected for vignetting of the source image by some aperture in the spectrograph (commonly the collimator). This is particularly important if a long slit is used (e.g. with a stepped sector or filter) since vignetting results in uneven illumination along the length of a line, affecting arc and spark lines in radically different ways.

Other causes of uneven illumination along the length of the lines are chromatic aberration of the optics and dispersion of any prisms in the optical system. (Here, it is interesting to note that B. & L. has recently changed its bi-prism system of dividing the beam to the gratings of the Dual Grating Spectrograph to a mirror system which eliminates both problems.) In the commonly used three-lens system of illumination, the

first lens, used for producing an intermediate image of the source, should be achromatically corrected to obtain uniform line illumination at all wavelengths (18).

External optics are plagued with still another annoyance—arc wandering—and recently several novel corrective measures were proposed. One is the Linsenraster announced by Steinhil (West Germany), a lens system which produced an array of small intermediate images of the source instead of one as in the conventional three-lens system (Fig. 4). As the arc wanders, each small image wanders but to a correspondingly smaller extent. Excellent control of arc wandering is said to be achieved in this fashion although at the expense of some loss of speed. A second system of correcting arc wandering is the use of a bi-prism as suggested by L. J. Linder (unpublished) of the Alcoa Research Laboratories in E. St. Louis (Fig. 5, 6). An aperture is placed at the intermediate image position so that the image here is focused on the collimator. The apex angle of the bi-prism is so chosen that the image of the source, which would ordinarily fill the aperture in the screen, is split into two adjacent images with only half of each image falling in the aperture. When, as a result of arc wandering, one image moves out of the aperture, its twin moves into it from the other side. Light from all parts of the source is thus always entering the spectrograph but the intensity of illumination is, of course, reduced by a factor of two. The Linsenraster has the disadvantage of chromatic aberration; the bi-prism, chromatic dispersion.

As has been mentioned under the heading of "Weather", improper focusing and changes in slit width disrupt relative intensities. They also adversely affect the sensitivity limit of the spectrograph because the maximum line-to-background ratio is reached only when the slit is made narrow enough to allow the natural line breadth to be recorded. Again the necessity of maintaining constant and optimum positioning of the optics is emphasized.

Astigmatism and coma are two more optical imperfections which take their toll in accuracy. These are generally greater off axis: lines at the end of the plate are affected more than at the center. Astigmatism changes the intensity of a line by discarding some of the light vertically. Coma, on the other hand, widens a line asymmetrically. Accordingly, it is good practice for the spectrographer to maintain the same wavelength coverage on a plate for a given procedure to assure that

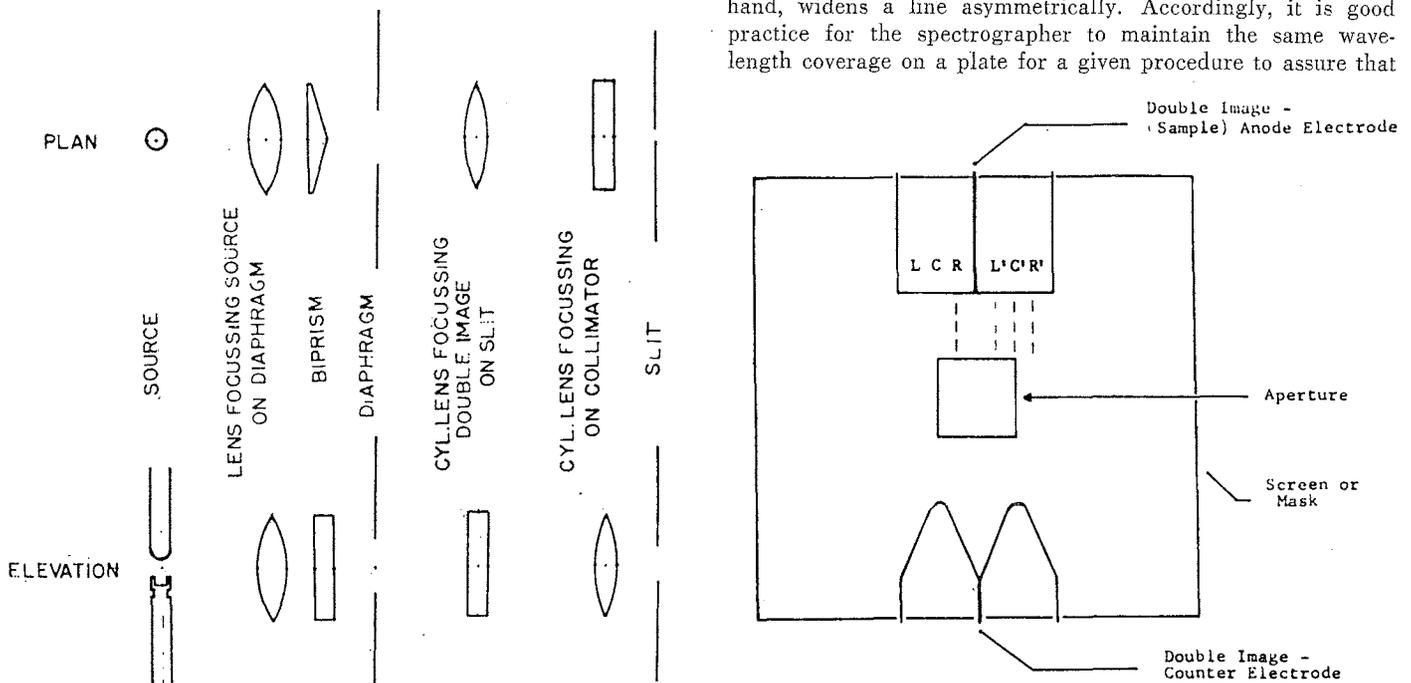


Fig. 5 & 6—Side-by-side images produced by bi-prism on aperture. As one image moves off axis, its twin returns thus increasing sensitivity as well as accuracy

all aberrations act on a particular line in the same way each time.

VII. Calculations

Evaluations of errors due to calculations made at various steps leading to the final % concentration in spectroscopy are, necessarily, indeterminate because so many calculations are graphical and, therefore, subjective. Reading and preparing a graph as well as the choice of scale, the thickness and closeness of fit of the line all depend on the skill of the operator. Here a recent trend is quite helpful. It is to convert scales wherever possible, to straight line graphs. Thus, the familiar S-shaped H&D curve appears on many calculating boards today as a straight line through the simple expedient of using a Seidel, or similar, transformation. Incidentally, such a transformation corrects only for the toe of the curve. The shoulder—at low transmittance values—results partially from scattered light in the microphotometer which enters the slit from portions of the spectrogram around the line itself. It is best for the spectrographer to steer clear of this region of high density in his work.

Analytical curves are normally straight but background may introduce a curved portion at values where the line and background begin to merge. To straighten out this region, background corrections are advisable and several have been proposed (1, p. 79). Analytical curves are dependent on the presence of a third element and this effect can be minimized through the use of calculations involving ratios of concentrations rather than the calculations themselves. This, too, is explained by ASTM (1, p. 74).

VIII. Photometry

Since quantitative spectrochemical analysis depends upon the evaluation of relative line intensities which, in turn, are obtained through photographic density measurements, its accuracy depends upon the methods used for calibrating emulsions and interpreting the data. From the standpoint of accuracy, a calibration procedure using two lines, two steps of a sector or filter is the best practical choice. The use of several steps requires a slit too long for uniform illumination. Other methods are hard to set up.

Under Section VII, the value of using linear plots of the calibration data was stressed. With a modern microphotometer, Seidel coordinate paper should yield a reasonably linear graph from about 4-90% T.,* the lower limit being set by the scattered light in the instrument. The scattered light originates largely from field illumination which, in modern instruments, allows the spectrographer the decided advantage of watching the line as it is being measured. Some designs will, however, scatter more light than others. There are two effects of this scatter: 1) the observed gamma will be lower than the true gamma; 2) at very low transmittance values, the H&D characteristic curve will deviate from a straight line. For accurate work, no transmittance readings should be taken below that where the H&D curve is no longer straight.

The linearity of a microphotometer is another pertinent variable. By linearity is meant the ability of a microphotometer to reproduce the transmittance value of a spectral line regardless of its sensitivity setting. A simple test may be performed as follows:

Set the background reading in a clear portion of the plate at 100% T. and read the transmittances of several lines at levels of about 5%, 30% and 70% T. Next, reduce the

*The Seidel function suffers as the gamma departs from 2. At high and low contrast, the Kaiser function is preferable.

overall light to the detector in some manner, by using a dimmer switch often provided on microphotometers or with a neutral filter (uniformly fogged film or smoked glass) taped to the condenser lens. Two or three such filters should be used having transmittances of about 25%, 50% and 75%. Take readings of the spectral lines 1) without resetting the background at 100% T; 2) after setting the background at 100%. In all instances, the relative amount of light transmitted by the lines should be the same.

In practice, of course, variations are obtained when the above procedure is followed. A study of these will set practical limitations of the microphotometer for the spectrographer. Periodic checks are suggested as electronic components age.

Analogous to this electronic check is one which should be performed on the optics, especially with regard to focus. On many microphotometers the focus setting is much more critical than can be detected by the eye. In fact the best way of focusing the instrument is by setting it to the maximum effective density of a line:

Choose a line of around 30% T. in the middle of a plate. The width of the line should be at least three times the width of the scanning slit. Take several readings of the line at different focus settings and pencil a marking on the lens in the position of maximum density (best focus). Repeat for lines near the four edges of the plate. The optimum focus should be the same provided the carriage moves in a plane perpendicular to the optical components.

IX. Conclusions

After a few months indoctrination, a freshman spectrographer will often wonder why all of his analyses are not perfectly accurate. With all the precautions he is taught to take and with the wonderful, expensive equipment at his disposal, he cannot imagine anything less than perfection. Some of the reasons for loss of accuracy are contained in this report. Some, like "matrix effect" have been largely ignored because they are too involved to be described in generalities. Still others are sure to have escaped us altogether and we shall welcome their being brought to our attention. Through such exchanges of information, it is hoped that present accuracy limitations can be continually extended to make the emission spectrograph an increasingly useful tool in industry and science.

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tricks of the trade

THE POROUS CUP TECHNIQUE

Ever since Cyrus Feldman of the Oak Ridge National Laboratory devised the porous cup technique, it has been the subject of controversy, some claiming that it is the best answer to many of their problems, others complaining of inherent difficulties. Taking the middle ground, the vast majority of spectrographers have reported that usually the method works well but, at times, perhaps because of variations in preformed electrodes, results are under par.

We won't purport to be able to straighten you out completely but we'd like to pass on a few bits of information that have come our way. First of all, there seems to be no question that part of the trouble is in the electrodes which vary in some mysterious property that no independent test has, as yet, uncovered. Call the property porosity, if you will, but tests designed to correlate this with spectrochemical results have been fruitless.

Morris Slavin of Brookhaven National Laboratory thought he could pin down intensity variations in the porous cup technique by measuring the air permeability of a number of electrodes both before and after a burning. What he did was to use a vacuum desiccator with a pressure gauge hooked to it to determine the time for a fixed air pressure to build up through the electrode. He obtained varying results all right but could not tie these in with the intensity variations.

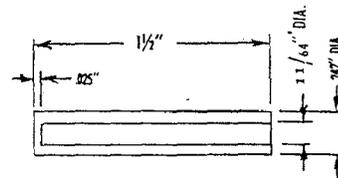
Not being able to predict variations by indirect techniques, Slavin now resorts to sampling several electrodes from a particular batch and accepting or rejecting the batch accordingly. This would be fine except that, on one occasion, a batch rejected by another spectrographer as completely unusable (the solution would simply not flow) was found to be the best Dr. Slavin had ever used. Here one clue was immediately evident: Slavin uses nitric acid solutions, the other sulfuric.

Consulted on the problem, Mr. Feldman reported that he has experimented with several mineral acids and that, at concentrations of less than 1%, the particular acid has no effect on analytical curves. Higher concentrations of perchloric or sulfuric acids were found to affect the intensity ratios of certain lines. As for the electrodes themselves, he checks each batch for "free flow" by which is meant that a pronounced pink color appears in 3-5 seconds in a spark at a power level of about 2.5 rf amperes.

Feldman has adopted the following rules for his porous cup work:

1. Use only free-flowing electrodes.
2. Maintain acid strengths of 1% or less if possible.
3. If an acid strength in excess of 1% must be used, prepare analytical curves with synthetics matching in both acid concentration and matrix.
4. Use flat-ended 1/8" d. counter electrodes.
5. Monitor the spark with the procedure quoted on p. 2 of this journal.
6. For the highest precision, use a low-powered (less than 5 rf amperes) spark. Three independent laboratories reported coefficients of variations of less than 3% using weak sparks.

Which of the dozens of porous cup preforms should be used? A number of spectrographers have adopted the one sketched below.



POROUS CUP ELECTRODE

This electrode has a .025" thick floor as compared with .040" in many others. In addition, the capacity of the cup is large, minimizing the possibility of the solution drying out during the exposure. If this occurs, results are bound to suffer. Depending on the solution, it may be necessary to seal the electrode beforehand to prevent seepage from the sidewalls which may damage the jaws of the arc/spark stand. One sealing treatment is to bathe the electrodes in a 2% solution of Plicene (Cenco) in benzene or Fisher's Label Glaze dissolved in alcohol. The spray which often corrodes other metal parts can be confined with a Plexiglas shield such as the one we supply with our 9010 Arc/Spark Stand.

Returning to the electrode itself, National Carbon recently announced a new grade of graphite stock called SPK which is claimed to have a more uniform physical structure than other grades. Several spectrographers have tried using the Spex 4037 electrodes machined from SPK rods and have reported that it appears quite promising for porous cup work. Accordingly, we are stocking these and they may be ordered by specifying:

4037 Porous Cup Electrodes, National SPK
Per hundred\$ 22.00

★ ★ ★

FUSION TECHNIQUE FOR X-RAY SPECTROSCOPY

A rapid technique that greatly reduces matrix effects has been devised by T. J. Cullen of United States Metals Refining Co., Carteret, N. J. The sample is fused with potassium pyrosulfate, the cooled material then ground and briquetted. Specifically, 200 mg of the sample and 10.00 g of potassium pyrosulfate are fused using an ordinary Meeker burner and a platinum crucible. The melt is poured into a beaker to cool and then ground to -200 mesh after which it is pressed to 12,000 psi to form a 1-1/2" d. briquet.

Direct analysis on the briquet has produced excellent results for the common metals present in a wide range of concentrations and matrices. Straight line calibration curves have been obtained for some elements in the range of 0.1 to 100%.

Potassium pyrosulfate has the advantages of fusing at moderate temperatures, forming stable briquets and, since it is water soluble, cleaning of crucibles and grinding containers is facilitated. Standards can readily be prepared from metals or metal oxides. Mr. Cullen, incidentally, used the Loomis 20-ton Hydraulic Press and 1-1/4" die (Spex cat. no. 3620 and 3621) for pelletizing and the Spex Mixer/Mill with a tool steel vial for grinding the materials.

KEEPING UP WITH THE DOCUMENTATION OF MOLECULAR SPECTROSCOPY

In talking to DMS Subscribers at Spectroscopy conferences, we have been pleased to learn that their enthusiasm for the DMS Current Literature List matches our own. This publication is the outgrowth of the literature survey that is continually going on for the preparation of the DMS bibliography cards. It averages seven to nine pages every six weeks, a typical issue containing references to 227 articles from 64 journals. This list calls recent publications to the attention of subscribers more quickly than the completed bibliography cards can be made available. Its coverage is also far broader than the number of articles selected for the bibliography cards.

Every effort has been made to let the reader know at a glance whether or not he wants to follow up a given reference. Each item contains the literature reference, names of the authors, title of the article and the language in which it appears. In addition, for those items which will not later appear on literature cards, the following information on spectroscopic content is noted:

- Complete spectral diagrams
- Partial spectral diagrams
- Band tables
- Some bands mentioned
- Discussion of spectroscopic results
- Analytical applications

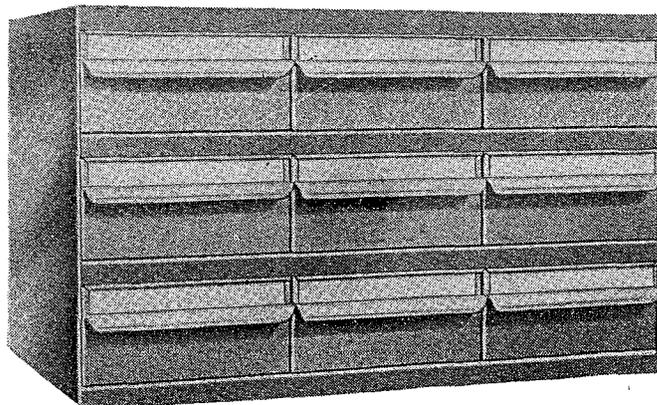
We have all had the growing conviction that keeping abreast of the literature is an impossible task for the practicing spectroscopist. It looks as though this new service may be well on its way toward keeping us all better informed.

★ ★ ★

LAST MINUTE TRICK OF THE TRADE

Lou Casper demonstrated a neat way of cleaning fixed slits originally suggested to him by Francis Leisey, both of the

PLATE STORAGE CABINET



By commercial standards, the ordinary 4" x 10" spectrographic plates are an odd size and do not fit office file cabinets. The pictured unit is ideal for the purpose. It contains 9 drawers, each 11-1/4" x 4-5/8" x 12" deep and equipped with two separators per drawer. About 1000 plates in envelopes can be stored in the unit. The separators as well as the front of the drawers may be labeled for reference.

3820 Plate Storage Cabinet, with nine drawers for 4" x 10" plates. Overall dimensions 19-3/4" high x 34" wide by 12" deep. Steel, welded frame construction, finished in grey, ivory, brown or tan **\$46.00**

Kawecki Chemical Co., Boyertown, Pa. He uses cellophane wrapping from a package of cigarettes, which, conveniently, turns out to have a thickness of about 25 microns (.001"). Yes, cleaning smaller slits can still be frustrating.



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