

SPECTROSCOPIC ELECTRODES

WHEN, in July 1957, a SPEAKER article was published on electrodes, we hoped it would serve as an everlasting guide, advising novice and veteran alike of the types of preforms on the market and laying down ground rules for their proper choice and application. Scientific progress being what it is, the article is long since outdated. In the interim, purity has surged steadily ahead to the point where, today, the best graphite rods boast impurity contents about 1/10 of what they were then. Many different types and shapes of preforms have been added, a few abandoned. With greater understanding and experience, the spectrochemist can now more intelligently pick an electrode to optimize the data.

All considered, we once again find it timely to review the subject and, because the older article is out of print, it seems best to start, as we did then, with a review of those properties of graphite which make it so attractive for at least 95% of all spectrochemical work.

T A B L E I

Advantages of Graphite for Spectrochemical Analysis

- 1) It is available in high-purity form at a reasonable cost.
- 2) It is easily machinable.
- 3) It has fair electrical and thermal conductivity.
- 4) It does not absorb appreciable moisture.
- 5) It provides a chemically reducing atmosphere to an arc discharge.
- 6) It is non-toxic either cold or in an arc.
- 7) It emits few spectral lines or bands.
- 8) It produces an arc with a high excitation potential.
- 9) It may be porosified simply by heating.
- 10) It sublimes rather than melts in an arc.
- 11) It is chemically inert at room temperature and not wetted at arc temperatures.

PRODUCTION

THE impetus for high-purity graphite production came during the war with the construction of the first atomic piles. From almost the beginning of the crash fission program, it was clear that the purity of the best commercial grades of both uranium and graphite was not good enough to let the chain reactions proceed efficiently. However small, traces of neutron absorbing isotopes would inhibit or prevent the desired reaction. Two ppm of boron, for example, was found to have an adverse effect on efficiency. Fortunately, the manufacturers of spectroscopic electrodes were able to upgrade their existing processes for the initial piles. Graphite was leached with various combinations of acids at elevated temperatures for long periods to extract metallic impurities.

But as refinements in atomic energy technology progressed, what was considered suitable as spectroscopic graphite turned out to be a nuclear handicap. Better graphite was needed in a hurry. The outcome of an intensive investigation was a number of halogen gas processes which, through the code designation "F", remained secret until patents (1) were granted in the middle '50s. In one process, a metallic carbide such as SiC, was added to the carbon stock as a nucleating agent. According to the patent, it promoted the formation of graphite when reacted with chlorine at around 1100°C. Later, when the temperature was raised to around 2000°, the entire mass graphitized and, at the same time, chlorides of impurity elements volatilized. A better process, one still in commercial use, employed fluorine, not as the element, for it is much too corrosive and toxic, but as a fluorinated hydrocarbon (Freon). This dissociates into elemental fluorine above 1000°.

The halogen purifying process, combined with controlled use of selected raw materials by Union Carbide's Carbon Products Division, results in a more uniform product, one consistently free of all impurities. This is AGKSP and SPK grade of "National" spectroscopic graphite.

The first step in the production of graphite is to blend such common materials as petroleum coke, pitch and lamp black. Formulated proprietarily, the raw materials—their concentration, particle size distribution, shape and structure—determine to a large extent the physical properties of the end product. To obtain the 250 different grades of graphite manufactured at the Fostoria, Ohio plant, Union Carbide varies both the ingredients and their treatment. In this way, an optimum combination of properties is attained for a specific product. Electrical brushes require a product with good conductivity and low-friction characteristics; dry cell anodes require high permeability to the ammonium chloride slurry electrolyte; motion picture projector arc carbons must burn smoothly and flicker-free.

After blending, the "batter" is extruded through a nozzle and on to a long trough where, emerging at a rate of several feet per second, the "spaghetti" is chopped off into workable lengths. The "green stock" is then given a preliminary low-temperature bake to remove the volatiles and set the binding agents. A second baking operation at upward of 1000° removes even more of the impurities, especially the low-boiling metals. At this stage, the material is still amorphous carbon. Graphitization at around 3000° is accomplished by electrical resistance heating of the stock, a process first developed in 1896 by E. G. Acheson. (The "AG" in spectroscopic grades is an abbreviation for Acheson grade.) Cut to 12" lengths, the rods are now centerless-ground to become "National" spectroscopic grade AGKS, with a total impurity content of around 50-300 ppm.

The addition of the "P" to signify the purified grade of AGKS spectroscopic graphite represents a relentless striving and achievement. When our 1957 article was written, the total concentration of impurities in AGKSP averaged 20-30 ppm. Today it is around 2 ppm. The ash content, then around 10 ppm, now is kept below 1 ppm. (The apparent contradiction between ash and impurities results from ashing losses. In the oxidizing atmosphere necessary to convert graphite to carbon monoxide, some metals are lost as well.) "Spot" impurities—the *highest* concentration found in at least nine determinations—never exceed 2 ppm per element or 6 ppm total. Impurities have a tendency to nest in the graphite; spot impurity contents, an indication of the maximum that might be found by the practicing spectrochemist, are thus well above the average values. With continuing improvements in manufacturing operations, there seems to be no doubt that when this article is next revised, spectrographically pure graphite will be a reality.

After all machining operations are completed, "National" preforms are purified in a graphite capsule. But the purity battle is not won until the batch is inspected and packaged. On the basis of rigorous statistical control at 95% confidence levels, at least 6% of every batch of electrodes is sampled spectroscopically. A preset pattern of where in the capsule to take the sample is dutifully followed and the capsule carefully resealed in the event further purification is indicated.

Older spectroscopic evaluations of graphite were empirical, arbitrary and subjective. An "X" was reported to mean not detected or a series of numbers starting with 0 showed the relative intensity of the particular line examined. Not only did estimates vary between elements and operators but the practice encouraged manufacturers to lower their numbers and thus imply that their product was better than their competitors'. As an actual example, "O" reported by Manufacturer A represented about 1 ppm for Si and 0.2 ppm for B. To Manufacturer B "O" signified 5 and 0.1 ppm, respectively.

To bust the numbers game, in 1961 Union Carbide introduced its present analytical system of reporting real ppm, a practice now followed by several foreign manufacturers as well. Like all spectrochemical methods, the first requirement to achieve this was a set of standards which ordinarily means obtaining a base material purer than the materials to be analyzed. Obviously, this was impossible. Another alternative, that taken by Dr. J. Weinard (2), was to test a vast number of samples, relying on a statistical approach for ever-increasing accuracy. In all, about 9000 determinations were made to establish acceptable working curves for the elements of concern. Electrodes were ground to a powder, loaded into carrier-distillation electrodes, arced at 5 amp and exposed on 103-0 and I-N plates in a 3.4-meter Ebert spectrograph. A preburn of 2 seconds was followed by the exposure of 15 seconds. While the method was not unusual, Dr. Weinard must be credited with a monumental task in amassing the voluminous data needed to solidify his figures. The occasional wild "flyers" caused by spot impurities in the preforms themselves had to be first isolated and then discarded by plodding through reams of statistics.

The result of all of this work is a quantitative procedure in which the spectroscopic analysis is performed with the cathode layer method on a large Littrow spectrograph in a laboratory near the production area. Each rod to be examined is broken in three, the untouched ends arced in pairs. Depending on the diameter of the electrode, current is varied from 10-24 amp so that uniform spectra are obtained. SA#3 and 33 emulsions are employed for the ultraviolet, IV-N for the alkali metals.

Table II shows the lines monitored and their sensitivity.

TABLE II

	Line, A	ppm		Line, A	ppm
Al	3082.1	0.05	Mn	2596.1	0.5
	3092.7			2593.7	
B	2496.8	0.01	K	7664.9	0.1
	2497.7			7699.0	
Ca	4226.7	0.01	Si	2881.6	0.1
Cu	3247.5	0.001	Ag	3280.7	0.001
	3274.0			5890.0	
Fe	2483.3	0.1	Na	5895.0	0.05
	2488.1			5895.0	
Pb	2833.1	0.5	Sn	2840.0	1
	2833.1			2840.0	
Mg	2795.5	0.001	Ti	3239.0	1
	2802.7			3242.0	
			V	2908.8	10*

*Insufficiently sensitive by this technique, vanadium is determined by the spray-in-spark technique on an acid-dissolved ash.

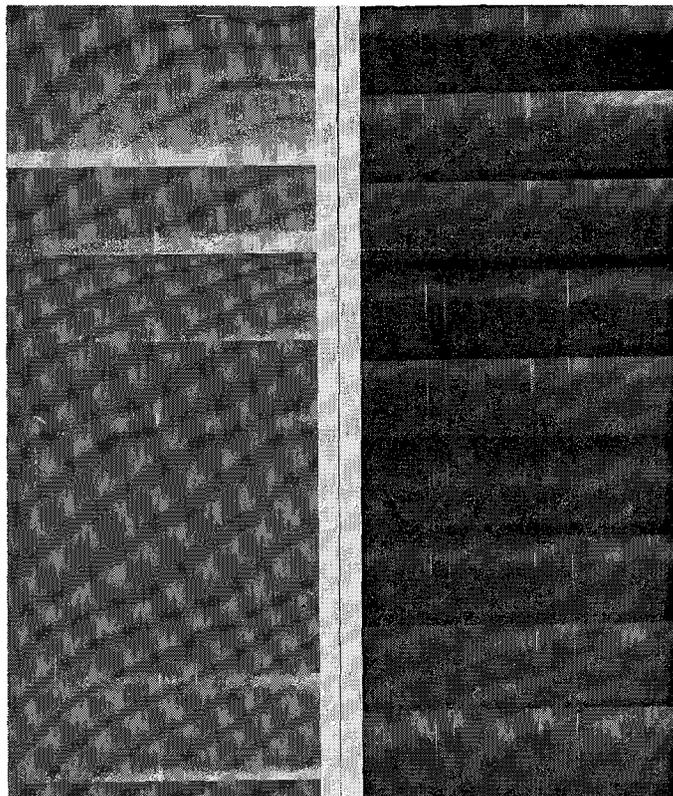


Fig. 1—Nine successive spectra of two graphite rods. On the left is shown an acceptable rod, one in which the total "spot" impurities do not exceed 6 ppm and no individual one exceeds 2 ppm. On the right are nine burnings of a rod from a rejected batch with spot Mg values ranging up to a reported 1.7 ppm, Si up to 4.2 ppm. The extreme variability of impurities makes it undesirable to report average concentrations since the spectrochemist is much more interested in knowing what maximum amount is apt to appear as a blank. Nesting of impurities is depicted in both rods: several elements rise and fall in unison.

In Fig. 1 a spectroscopic comparison is shown between an accepted and a rejected batch of graphite. In the latter, there were two areas of contamination: one spot Si test showed 4.2 ppm and the total spot metal content was 7.5 ppm. In the accepted X-28, all spot impurities were below 0.5 ppm and the total was only 0.9 ppm. The rejected batch can usually be repurified to meet the specifications.

Fig. 1 helps show why analyses are reported as "spot" rather than average. Impurities tend to congregate in pockets in an electrode so that if one element is high one or two others are likely to follow. Despite a high spot determination, the ash content will indicate whether the total metal content is below 2 ppm. While a bulk chemical analysis would represent the average of a large number of determinations, the spectroscopic figure actually furnished indicates the maximum value found in a particular batch. This figure tells us what the worst likelihood of contamination from our electrodes is apt to be. Suppose we are determining silicon at the 1 ppm level and run a sample in triplicate; the fact that the average silicon content of the electrode is only 0.5 ppm is of much less interest than that we might pick a single electrode in which the arc will hit a nest impurity at the 2 ppm level. By carefully choosing and specifying electrodes sufficiently free of trace elements of specific interest, the spectrochemist can work with further assurance of accuracy.

At this stage, "National" spectroscopic electrodes have been subjected to their first spectrographic test but, having passed it, they are still not released by Inspection. In the wrapping room next door to the spec lab, cellophane and plastic boxes are subject to routine checks as well. Here boxes are washed in distilled water and dried in a dust-free atmosphere. The room is kept at a slight positive pressure, walls and floor are scrubbed down periodically, and the women packers wear special lint-free clothing. The company finds it necessary to pry into the private lives of these women by approving the cosmetics and soap they use. Hair sprays, a source of silicon and calcium, were recently banned. Final purity checks are on the packaged electrodes as they would be received by the ultimate customer. Again a routine is followed where a fixed percentage of the finished product is fed back to the spectrographic laboratory for approval.

From the packing room, the tail-end of a production line whose length is measured in days rather than in feet, one emerges with an extra degree of respect for the product and the analysis slip tucked into each box of "National" spectroscopic electrodes. The concentrations reported are not only real, and better than determinations performed in most laboratories, but can also be an excellent reference for trace-element analyses. The given spot determinations represent a limiting concentration for all elements above which results can be safely reported on the basis of two or even one determination. Below this concentration, the spectrochemist is cautioned to make several runs. He can expect an occasional "flyer" which can assuredly be discarded with the knowledge that the source of this erroneously high concentration is, in all probability, the electrode.

Chemical control is but one-third of the story at Union Carbide. Physical uniformity of the product is equally important to the spectrochemist, a fact the company is well aware and in control of. Density, for example, influences thermal conductivity. The temperature to which a sample is raised is a function not only of the arc current but of the rate of heat conduction along the electrode. Density is thus maintained to 1.57-1.63 in AGKSP and 1.88-1.92 in the SPK grade. Understandably reluctant to divulge their exact methods for such close control plant supervisors do point out that the bulk dens-

ity of any pressed product is a function of its particle size and shape distribution. Consider a powder consisting of spheroids of exactly the same diameter. These cannot be closely packed so the bulk density will range much below that of the individual particles. If, as with SPK, the particle size distribution is carefully controlled, smaller particles can be squeezed into the voids left by the larger ones. The result is extruded graphite approaching the theoretical density of graphite, 2.25.

The metallograph is one of the more important tools for keeping tabs on the physical structure of graphite. Particle size and shape, pore size and shape are measured with it. Other regular tests include: x-ray diffraction studies to furnish information on the degree of graphitization; weight loss comparisons on arcing under fixed conditions; surface area determinations by means of helium adsorption; flexural and tensile strength measurements; gas and liquid permeability tests; oxidation resistance effects at different temperatures; thermal and electrical conductivity properties.

Holding dimensional tolerances is the third part of the quality control program. Graphite is an abrasive lubricant, a contradiction in terminology to the layman but an everyday reality to the machinist. To drill, undercut, face-off and chamfer preforms automatically, it is necessary to fit lathes, milling machines and drill presses with carbide tools. Even so, tool wear must be compensated constantly in order to keep the preforms within the strict specifications laid down by ASTM (3).

WHY QUALITY CONTROL?

A good question at this point is whether it is really necessary to apply stringent quality control to graphite electrodes. What effects do small amounts of impurities have on trace element analysis? Do physical properties of the graphite stock influence precision? Are the dimensional tolerances on preforms too loose, too tight, or comfortably snug?

In an effort to seek answers to such questions, Dr. Weinard recently conducted a series of preliminary experiments. To determine how unpredictable impurities would influence results, he compared samples run in identically shaped preforms of the high-purity AGKSP and the regular grade AGKS. To correlate physical properties with precision, he again ran identically shaped preforms this time machined from three grades of graphite differing only in density. To check on dimensional tolerances, he frustrated his machine shop by asking for preforms, deliberately out of spec in one dimension.

Arc tests were run with the Spex G-3 standard containing 10 ppm of 49 elements in a high-purity graphite base. The procedure was typically semiquantitative. National L-3912 (Spex 4000) preforms were filled and tamped with an unweighed amount of the standard. A dc arc of 5 amps was the source, 103-0 the plate emulsion and a Jarrell-Ash 3.4-meter Ebert spectrograph was used with a Spex 9010 Arc/Spark Stand.

Table III presents the data indicating what happens to precision when dimensions are not rigorously controlled. Modification 1 refers to 10 preforms made to conform dimensionally to L-3912 with but one exception. Instead of the $1/16'' \pm 0.005''$ wide undercut specified, 10 preforms were prepared with the undercut varying randomly from $1/16''$ to as much as $1/8''$. In Modification 2, the results of changing the depth of the undercut are shown. Here, again in 10 preforms the depth was deliberately cut randomly smaller by as much as $0.01''$ than the $0.121''$ nominal (ASTM specifications permit $\pm 0.005''$). In the third modification, the wall thickness of the crater was decreased randomly up to $0.01''$ where specifications call for $0.031'' \pm 0.003''$.

TABLE III

Effects of Random Dimensional Variations on Precision

Element	Standard deviation of Transmittance, %			
	L-3912	Mod. 1	Mod. 2	Mod. 3
Si	34	33	55	35
B	15	14	12	45
Mn	14	83	69	29

Although the transmittance values were measured and compared for but three elements, it is apparent that there is a decided trend toward worsening of precision if dimensional tolerances are relaxed. In a semiquantitative procedure, the spectrochemist does not expect close duplication of transmittance values. If he did, he would tie in the Stallwood Jet, run samples to completion, weigh them and take whatever other precautions are demanded to tighten the precision. Nevertheless, he is interested in attaining the maximum precision with the minimum amount of care. He expects the manufacturer to hold close dimensional tolerances so his precision does not go astray through no fault of his own.

In Table IV, the results of an experiment on purity of electrode stock, again silicon, boron and manganese at the 10 ppm level were chosen as representative elements. These are present in AGKS material at levels of around 10 ppm as are iron, vanadium, sodium, calcium and magnesium. While large variations in concentrations of impurities are to be expected among batches of AGKS, impurities in any one rod are reasonably constant. They are not subject to the "nesting" behavior of tramp elements in purified stock so a spectrochemical analysis is quite representative of the material.

TABLE IV

Effect of Graphite Electrode Purity on Precision

Element		Standard deviation of Transmittance, %	
		AGKSP	AGKS
Si	2881A	34	57
B	2498A	15	44
Mn	2576A	14	58

The first column of Tables III and IV are, of course, identical. They represent average % variation in transmittance of the three chosen lines. When AGKS preforms are substituted, the variation jumps markedly. Since the base material has a reasonably constant impurity level, the reason for this is apparently the different amount of graphite consumed during successive arcs. It is well known that, despite control over the current of a dc arc, wandering—sometimes over the graphite, sometimes over the material—causes decided differences in graphite consumption. This, in turn, adversely affects the precision. It is thus never advisable to attempt to substitute relatively impure electrodes for trace-element determinations by correcting for blank levels introduced by known impurities in the electrode stock.

The last experiment performed by Dr. Weinard was an attempt to pin down the need for maintaining constant density in the graphite stock. The density of AGKSP is controlled to about 1.6, SPK to 1.9. For these tests a third, experimental grade, with a density of 1.71 was chosen.

TABLE V

Effect of Electrode Density on Spectral Intensity

	Average Relative Transmittance, %		
	AGKSP	Exp. Stock	SPK
Mn 2576A	22	30	41

Table V depicts the results of the experiment in which a point-to-plane spark technique was employed. An L-3957 type tapered electrode was sparked ten times against NBS steel Standard 1163. It is clear that the intensity drops about 40% as the density of the graphite increases. Whether this is true for all elements has not been investigated but an intelligent guess would be to the contrary. And if all elements do not behave in the same fashion, then the intensity ratio of a particular line pair would be a function of the density of the graphite. Unless the density is maintained reasonably constant, it can adversely affect the precision of a spark procedure.

In spark analysis, the principal difference between sparking with a medium-density AGKSP and a high-density SPK is in the cross-sectional area of the spark scar. With the lower density graphite the area is quite a bit larger. This, in turn, tends to sample a greater amount of surface and to iron out difference arising from inhomogeneities in standard or sample. Counteracting this is the fact that the intensity, as viewed through the slit, is held more constant when sparking is kept on axis. Realistically, and this has been shown with aluminum wrought alloys, the AGKSP is the better choice unless special precautions are taken to prepare homogeneous standards.

As far as I am aware, nothing has been published to indicate superiority of either a high-density or a low-density graphite in arc analysis. Yet the sales record indicates a gradual acceptance of the SPK over the equivalent AGKSP cratered electrode. There are several possible explanations. By virtue of its greater density, SPK has a flexural strength more than twice that of AGKSP. Less care is necessary in loading electrodes; they are less likely to break in handling. One insidious source of error in arc analysis is a cracked electrode which, though apparently sound, burns hotter than perfect ones. Because the micro structure of SPK is much more uniform than that of AGKSP, it is reasonable to expect that preforms of SPK can be produced and will burn to closer tolerances. If anyone has any comparative data on reproducibility, he will be doing a service to other spectrochemists by publishing the information.

At this point it would be well to see how some of its other properties favor graphite for spectroscopic electrodes. The spectrograph is a trace-element analytical tool and part of its high sensitivity can be directly attributed to graphite. In an arc graphite produces a high energy discharge path capable of exciting the *raies ultimes* of all elements. Further, graphite provides a reducing atmosphere, preventing the formation of non-conductive refractory oxides which are often difficult to excite. As it burns away, a graphite electrode continues to support the sample because graphite does not melt. By contrast, a copper electrode in an arc droops in a few seconds; the sample droops and the precision plummets with it. That graphite may be porosified so easily is the basis for many solution techniques in which the treated electrode is dipped into the liquid. That it is not wetted is advantageous in the analysis of metals which remain intact in a graphite crater where they would alloy with a metallic electrode. Finally, simplicity of machining makes it the principal choice for spark analysis. Between samples graphite electrodes can be resurfaced in what amounts to an electrical pencil sharpener.

GRAPHITE POWDERS

THE suffix designation 1 and 2 for the briquetting and mixing grades of graphite are not always understood. Why is one better for one purpose than the other? The answer is largely particle shape. SP-2, the grade recommended for purposes other than briquetting, is a synthetic product in which the particles are roughly spherical. Conversion of amorphous

carbon to graphite does not materially affect its particle size or shape. SP-1, on the other hand, is actually a blend of natural graphite consisting of flat platelets or needles depending on whether it is of the Madagascar or Ceylon type. Both of these shapes compress along their long slippage planes, the particles cohering against a large contact area. The point contact of spherical particles, characteristic of SP-2, results in less cohesion. Pressed pellets of the latter are thus subject to disintegration in sparking or handling.

What is poor for pelletizing is, however, good for mixing. The spherical particles flow more easily, can be transferred and mixed thoroughly with other materials. Incidentally, the SP-2X grade—screened to -100, +200 mesh—is coarser than the normal SP-2 and is recommended for most spectrochemical work. It is far easier to weigh out, to transfer and to load.

A rule of thumb in mixing with a sample is to keep the ratio of any two ingredients below 1:10 and to keep constant the particle size cut of all ingredients. If dilutions in excess of ten-fold are needed, they should be prepared in successive stages with a Mixer/Mill.

ELECTRODE TYPES AND TECHNIQUES

WHEN a dc arc is struck between two electrodes, at the anode (lower in most work) a bright circle of illumination appears. This anode spot increases with the arc current until the spot envelops the entire cross-sectional area of the electrode. Above this current the ordinary dc arc becomes a so-called high-intensity arc with entirely different characteristics. One of the most important, spectrographically speaking, is that the temperature of the arc begins to rise with the current. By contrast, when the current is raised in an ordinary arc only its cross-sectional area increases, not the temperature.

One method of determining the cross-over point between the two types of dc arc is to plot the voltage across the arc vs. current as shown in Fig. 2 where a comparison of 1/8" rods of carbon and graphite is shown. Note that a minimum appears for both carbon and graphite although it is less distinct for the latter. The minimum is the cross-over value. Table VI indicates cross-over points for the standard electrode diameters.

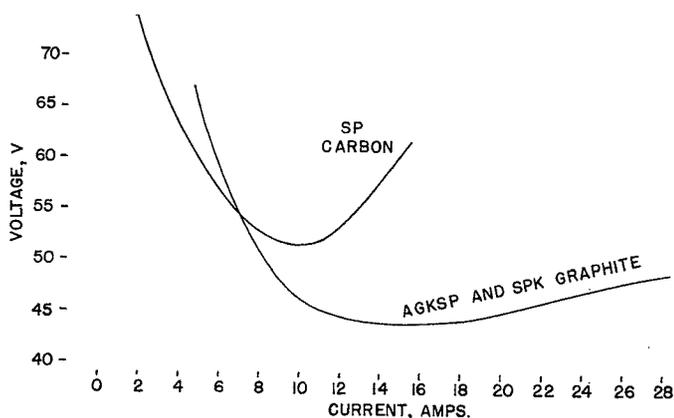


Fig. 2—A plot of voltage drop vs. arc current shows a dip, sharp for carbon, broad for graphite. Here the anode spot diameter has increased to a point where it just covers the entire electrode surface. The arc is changing from normal to high-intensity. At around 13 amp for a 1/8" dia. graphite preform, where the conversion begins, arc wandering ceases and the temperature of the arc begins to rise.

TABLE VI

Approximate Cross-over Currents from Ordinary to High-intensity dc arc for Graphite and Carbon Electrodes

	Graphite	Carbon
1/8"	13	10
3/16"	26	20
1/4"	52	40

These values are important for several reasons. First of all, they are attainable in most laboratories only with 1/8" diameter electrodes. Although very few comparisons have been reported in the literature of spectrochemical differences attributable to the two distinct types of arc, it seems likely that higher sensitivity should be achievable with the high intensity arc particularly for elements of high ionization potential and/or high refractoriness. Further, arc wandering which, in reality, is the motion of the anode spot over the electrode surface disappears entirely with a high-intensity arc. Both are good reasons for using 1/8" diameter preforms in trace-element investigations.

Faced with a vast array of preforms catalogued by the manufacturer, a newcomer is justifiably confused. Why are there so many different cratered electrodes, or uppers with points and rounded ends in three diameters? The truth is that there is little reason. Like ladies' hats, the electrode is sometimes a reflection of the taste of the individual rather than a scientifically optimum shape for a particular purpose. Before the advent of manufactured preforms, spectrochemists "rolled their own" often with home-made shapers. More important than exact dimensions was uniformity from one electrode to the next. When these same spectrochemists were offered manufactured preforms, it was only natural that each should request his own specifications. The result is a hodgepodge of preforms, many so similar that everyone agrees, "Sure, let's eliminate the ones that look almost like mine!"

To do exactly that, some years ago, the American Society for Testing Materials embarked on a program of standardization which would reduce the inventory burden to the manufacturer and thus the cost to the ultimate consumer. Through extensive work of its Committee E-2, 28 shapes of preforms were finally accepted. With few exceptions, all new tentative and fully accepted methods published by ASTM must employ only these 28 types (indicated by ASTM number on our preform chart P. 8-9).

GENERALLY speaking, cratered preforms are meant for the arc analysis of powders and other solids. Almost all are constricted below the crater to increase the temperature of the sample while it is arced by throttling the heat flow along the electrode. The size of the crater varies from one about 1/32" in diameter by the same depth to another 3/16" x 1/2". The smaller ones are designed for the analysis of micro samples where it is desirable to burn the sample with as little carbon as possible to keep the background down. The largest ones are often used for the determination of trace elements in a matrix when both are of relatively high volatility, e.g. germanium and selenium.

Between the two extremes dozens of preforms are listed; no fixed rules really apply to their proper choice. It's nice to run a sample under such conditions that all of the lines of interest appear at measurable densities. This, of course, depends on the speed of the spectrograph, the emulsion and a host of other parameters under the control of the analyst. In practice, with a variety of materials to analyze, one finds it

impossible to set up all methods for the convenience of microphotometer readings. When enough sample is burned for the arsenic to appear, the copper and silver lines are typically too dark. Rather than vary the sample and electrode size, an alternative is to insert a neutral density stepped-filter or sector in the path of the light and so be enabled to read the step where the light transmission falls within the bounds of the microphotometer. Thus fewer electrode shapes are needed.

Lessening the need for electrodes of different crater capacity in this fashion, the experienced spectrochemist relies on very few cratered types of preforms for the bulk of his work. In general, he finds it good practice to burn the smallest sample in the narrowest electrode; the former to save time, the latter to reduce the amount of arc wander which has been shown to result in a significant loss of precision and accuracy.

A few of the listed cratered preforms sport a center-post. Arc wandering is sometimes licked by this simple expedient of constraining the conducting path to the optical center line. The price paid for center-post preforms is in cash and in time; such electrodes cost about 2¢ more than standard undercut equivalents and they take much more time to load. Since most arc procedures do not call for weighing the sample into the cup, a packing and tamping operation is specified, internal standardization correcting for differences in weight as well as other factors. Center-post electrodes are just too difficult to load reproducibly, especially when the task is the responsibility of more than one technician.

Now only rarely specified for powder analysis, center-post electrodes have found application in the analysis of liquid residues. The electrode is first sealed by dipping it in colloidion or a weak solution of Apiezon (actually any wax free of undesired tramp elements will do). Next the electrode is filled, often several times with a heat evaporation step interspersed. Determinations down to ppm levels and below are routine with such techniques, the sensitivity depending on the amount of sample evaporated and arced.

Returning to the analysis of powders, probably the most popular cratered preform is ASTM S-14 (Spex 4005). It is a sensible compromise for a great many materials to be exposed on a wide range of spectrographs. With a diameter of 3/16", it is comparatively easily loaded yet the arc wander is appreciably lower than with 1/4" diameter preforms. S-14 also ties in well with the Stallwood Jet, that popular device which simultaneously enhances sensitivity, stabilizes the arc and damps out matrix effects. Mounted in the Jet assembly with the top of the electrode just above the mouth of the Jet, the electrode is advanced upward as the arc burns away the graphite. The cooling argon-oxygen mixture promotes slow consumption of the sample in successive layers. Volatile as well as refractory elements thus tend to be excited uniformly.

Not all popular electrodes are undercut like the S-14. When a very volatile material is to be analyzed for equally volatile impurities—sulfur, for example—the heat transferred to the sample should be kept down permitting the sample to be excited in the arc column rather than escape to one side. A deep-crater is specified and sometimes a second such preform, inverted, is used for the counter.

Volatile impurities present an even more difficult analytical problem since their limit of sensitivity can be severely affected by evaporating too rapidly. Here the boiler cap has turned out to be advantageous, improving the detectability for mercury and arsenic particularly. Fig. 3 is a comparison of the spectra obtained with and without a boiler cap of an ore and an ore concentrate containing a trace of mercury which line is significantly enhanced by this technique.

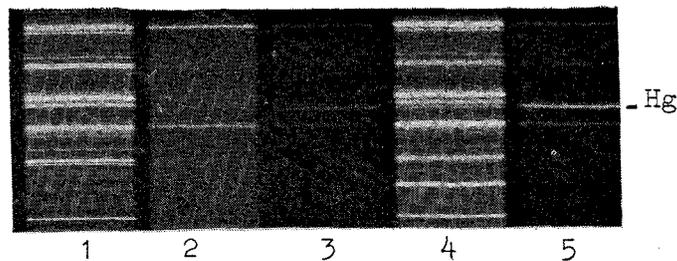


Fig. 3—Boiler caps are indispensable for the determination of traces of volatile elements in a relatively non-volatile matrix. The four upper exposures compare two samples, one an ore, the other an ore concentrate. Burnings 2 and 4 were conducted without a boiler cap; 3 and 5 with the cap placed over the cratered preform. Note the remarkable improvement in sensitivity of Hg in the latter. (Courtesy T. P. Sheehy, American Smelting & Refining Co., Research Labs., S. Plainfield, N. J.)

The carrier-distillation method was devised for a similar reason: the need to detect relatively volatile impurities in a highly refractory matrix of uranium oxides. This material exhibits a complex spectrogram that would mask and interfere with the spectra of the elements sought. By adding CuOHF for example, the base spectrum is suppressed and sensitivity for impurities is heightened. The electrode proposed and in widespread use today is perched on a narrow pedestal to insulate the sample thermally and so raise its temperature. At the same time a carrier of relatively low boiling point sweeps the more volatile impurities into the arc column.

A technique gaining in popularity is one in which the sample is pressed into a 1/4" or 1/8" diameter pellet which is then placed in a cratered electrode. Metal chips and turnings can be so analyzed, the sample weight remaining relatively constant of the cross-section of the individual chips. A hand press such as the Spex 3525 is all that is required to prepare the pellet which can then be either sparked or arced in any of several compatible preforms.

With regard to spark analysis of solid samples, usually held on a Petrey stand, the choice among preforms appears to have narrowed down to two types: the 1/4" diameter, blunt-pointed type and the rounded type. In theory either would be better than a flat-topped rod because a spark tends to fly from sharp edges as well as a sharp point. Edge sparking to flat-topped rods results in dimensional spread of the sparked area and consequent loss in precision. For a "cold" spark of comparatively low inductance the 120° included angle pointed electrode is popular. On the other hand when the spark is arc-like, the rounded end stands up better during the burn and is preferred.

IN a dc arc, the point or rounded end on a narrow upper electrode is rapidly eroded away and, for this reason, it would appear economical simply to break off a piece of graphite rod stock for the purpose and, as a matter of fact, this is the practice in many laboratories. With some samples, however, the arc has a tendency to strike irreproducibly to a rough-ended electrode and for these a rounded or pointed end, undoubtedly, does promote precision. No one has published results of an investigation into what upper electrodes work best for a given problem and in at least one ASTM suggested method (SM 6-11) a flat-ended, necked upper is specified although no reason is given for the choice in this dc arc powder method for the analysis of tin-cadmium acid dissolved residues.

UNSETTLED for spark and arc analysis of solids, the question of whether to use a high-density, non-porous grade of graphite or its opposite for solution analysis usually gets a clear-cut answer depending on the method chosen. In the rotating disc technique—the oldest and still perhaps most popular—the amount of material delivered to the spark is a function of the porosity of the graphite stock. Since the rotating electrode method, like most liquid spectroscopic methods is sensitivity-limited, AGKSP is the choice. Where precision is the more important consideration and with viscous solutions, SPK grade preforms are preferable.

One solution technique where there is no choice is the porous cup method. Here the SPK grade is unsuitable because the solution simply does not seep through its tiny pores. When the porous cup was first suggested (7) it was looked upon as a neat advance in the art. With no gadget to set up and the comparative ease in running a sample, many hoped it would replace the rotating electrode. Two hurdles intervened. One was the structural variability of the AGKSP grade as it was then produced. The other was the fact that the floor thickness was not maintained to strict enough tolerances. A 0.003" variation in the depth of a cratered cup is equivalent to but a few percent in the capacity of the cup. The same variation in the depth of drilling, however, is equivalent to a 12% difference in the 0.025" nominal floor thickness. With the introduction of a more uniform AGKSP grade a couple of years ago and tighter dimensional tolerances, there seems to be a gradual return to the porous cup.

The vacuum cup electrode is a newcomer to the liquid scene (8). Here the graphite serves merely as an aspirator. The spectrochemist demands of the electrode only that it stand up during the burn, not contaminate his sample and deliver the liquid uniformly from sample to sample. Because of the superior machinability and strength of SPK, Union Carbide manufactures this preform in the one grade only. Of two types offered, the one with a longer throat is the more popular. Hotter burns are possible with it, its greater length reducing the sample temperature and therefore its tendency to boil. In addition to sparks, both dc and ac arcs of low wattage may be directed to the vacuum cup electrode.

The graphite spark technique, counterpart to the copper spark devised during the war to analyze micro samples of solutions of new isotopes and elements, requires a non-porous surface obtained by treating the end of a flat electrode with a wax. A drop or two of sample is dried on the end and later sparked.

ONCE a controversy raged over carbon vs. graphite as a choice for electrode material. European spectrochemists appeared to be at loggerheads with their contemporaries in the United States, who, for their part, simply ignored carbon. True, from time to time, an American paper appeared in which carbon preforms were touted but, generally speaking, the authors failed to provide a convincing argument for their cause. Carbon electrodes have two serious disadvantages: they are hard to machine and even harder to ship without breakage. On the credit side, carbon's poorer conductivity means that samples can be heated hotter with less current. Sometimes this can result in a mild increase in sensitivity, particularly with refractory materials.

Two independent groups of researchers (4, 5) have shown that carbon as a counter electrode does result in better precision than graphite in dc arc excitation. Here a readily-machined 3/16" dia. rod was all that was needed.

Mellichamp (6) has shown that a decided improvement in reproducibility can be achieved by using a counter cathode of graphite cored and filled with a material of lower ionization potential than graphite. The mixture chosen is 1:2 of either BaO or Li_2CO_3 in graphite.

The latest word in this controversy is an article by Mellichamp and Buder (10) in which the authors indicate that, despite the distinct differences in the burning characteristics of carbon and graphite, it is preferable to stick with the latter, adjusting preform geometry and current to achieve essentially similar results.

Now pyrolytic graphite has become a possible contender to pressed graphite for spectrochemical applications. Prepared by vapor deposition, the pyrolytic material may be coated on a graphite preform or be fabricated in the form of a shell which, in turn, is placed inside a graphite preform. Mooney (11) has shown that the thermal conductivity of pyrolytic graphite is so low that the entire rim of a crater glows during an arc. Of course, this increases the temperature of the sample and may result in improved sensitivity. Working against this is the purity of the present pyrolytic material with an ash content of around 6 ppm compared to 1 ppm for the best pressed graphite. The non-porous surface may be exploited advantageously for solution techniques. Zotov (12) devised a means for spraying the sample on a disc of pyrolytic graphite as it is rotated. Significant improvement in reproducibility appears possible by this technique.

The inconclusiveness of our last few paragraphs shows the many holes in our present understanding of electrode effects. Any information, published or not, in areas not covered here would be widely appreciated, we feel, and well worthy of space in a future issue. We shall gladly compile and report communications we receive along these lines.

ACKNOWLEDGMENTS

This article was prepared with the extensive help of a number of Union Carbide personnel in production, services and the laboratory. Chief among those to whom I owe a deep debt of gratitude are Floyd Hunsaker, Applications Manager in its Marketing Department, who arranged my tour of Carbide's Fostoria manufacturing and laboratory facilities and Dr. Jacob Weinard, Division Manager of its Development Laboratory, who provided many of the data presented.

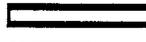
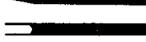
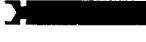
—AJM

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SPECTROSCOPIC PREFORMED ELECTRODES

HIGH PURITY GRAPHITE

Spex	Dia."	Description		National		ASTM	Price per 100
				AGKSP	SPK		
4000	1/4	necked crater, 5/32" dp.		L-3912*	L-3712	S-12	\$22.00
4001	3/16	necked crater, 3/16", dp.		L-3903	L-3703	S-13	22.00
4002	1/4	crater, 3/16" dp.		L-3900	L-3700	S-8	20.00
4003	1/4	angular platform, center post		L-3948	L-3748	P-2	28.00
4004	3/16	necked crater, 3/32" dp.		L-3906*	L-3706		19.00
4005	3/16	necked crater, 3/16" dp.		L-3909	L-3709	S-14	19.00
4007	1/4	flat necked upper		L-3960	L-3760	C-8	20.00
4008	1/4	undercut, center post upper		L-3963	L-3763	C-7	22.00
4009	3/16	double-ended, 1/16" r., 2" l.		L-3955	L-3755		24.00
4010	1/4	pointed upper, 120°		L-3966	L-3766	C-2	20.00
4011	1/2	solution disc, 1/8" thick		L-4075	L-4275	D-1	14.00
4012*	1/2	platrode, extruded		L-4078		D-3	18.00
4014	1/4	porous cup, .025" floor, 1-1/2" l.		L-3927			24.00
4015	1/4	porous cup, chamfered floor, 7/8" l.		L-3933		PC-1	23.00
4016	1/4	crater, 1/16" dp.		L-3982	L-3782	S-5	21.00
4017	1/8	pedestal, 1-1/2" l.		L-3919	L-3719	S-1	16.00
4018	1/4	anode cap, 9/32" dp., thin wall		L-3918	L-3718	S-3	16.00
4019	1/8	pointed upper		L-4036	L-4236	C-1	16.00
4020	1/8	crater, 1/4" dp.		L-3979	L-3779		16.00
4021	1/4	necked crater, 1/16" dp.		L-4012	L-4212	S-4	22.00
4022	1/4	boiler cap		L-3915	L-3715		26.00
4023	3/16	boiler cap		L-3916	L-3716		26.00
4024	1/4	flat rod		L-3921	L-3721	C-3	18.00
4026	1/4	mandrel for rotating electrode, 2" l.		L-3970	L-3770		23.00
4027	1/2	solution disc, .200" thick		L-4072	L-4272	D-2	16.00
4028*	1/2	platrode, molded		L-4081			18.00

GRAPHITE POWDERS

- 4061 National SP-2X—Consists of 90-95% -100 mesh.
- 4062 National SP-1—Consists of 65-75% -200 mesh.
- 4063 National SP-1C—Consists of 90-95% -200 mesh.
- 4064 National SP-2—Consists of 90-95% -200 mesh.

Two general types of spectroscopic graphite powders are available differing principally in particle shape. These are designated by the final number 1 or 2. Number 1 is used for briquetting and Number 2 for use as a conductor and buffer.

Prices for the above are as follows:

1 oz.	\$ 6.00	1/2 lb.	\$35.00
1/4 lb.	\$20.00	1 lb.	\$60.00

* Spex 4028 is high-density and less porous than 4012.

* Available with small venting hole through crater at \$4.00 additional per 100.

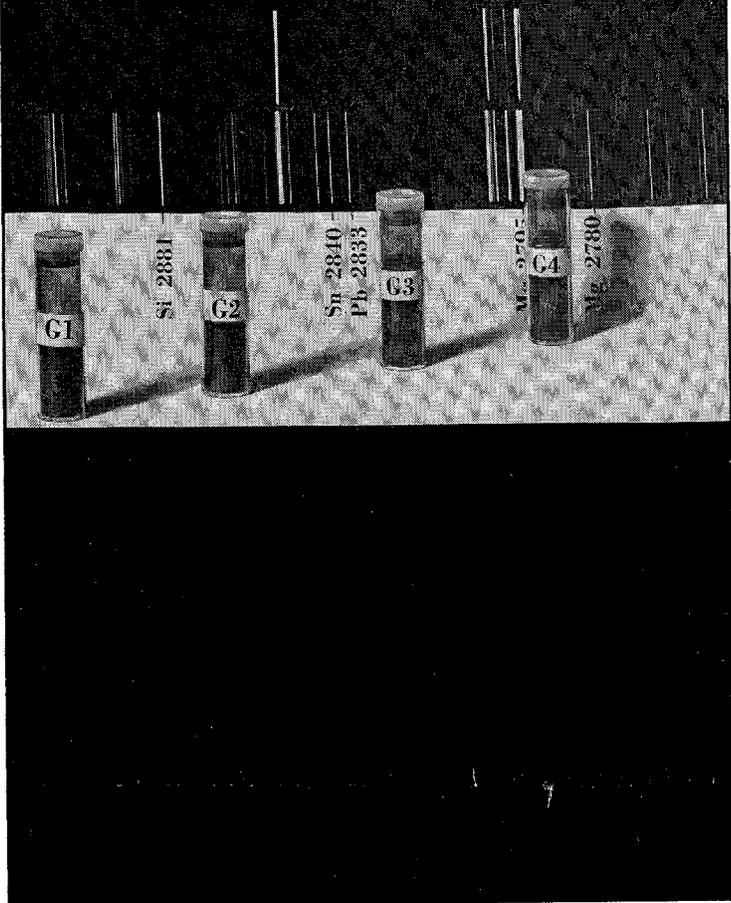
Spex	Dia."	Description		National		ASTM	Price per 100
				AGKSP	SPK		
4029	3/16	necked crater, 3/16" dp.		L-4000	L-4200		19.00
4030	3/16	necked crater, 3/32" dp.		L-4006	L-4206		19.00
4032	1/4	mandrel for Combination Analyzer		SP-1003			22.00
4033	1/8	necked crater, 1/8" dp.		L-3905	L-3705		19.00
4034	1/8	crater, .059" dp.		L-3975	L-3775		16.00
4035	1/8	crater, 3/16" dp.		L-3977	L-3777		16.00
4037	1/4	porous cup, .025" floor		L-3928			24.00
4038	1/4	anode cap, 9/32" dp.		L-4024	L-4224	S-2	16.00
4039	3/16	rounded upper, 1/16" r.		L-3951	L-3751		17.00
4040	3/16	rounded upper, 1/16" r., 2" l.		L-3954	L-3754		18.00
4041	1/4	rounded upper, 1/16", r.		L-3957	L-3757	C-5	20.00
4042	1/4	necked crater, 3/16" dp.		L-4018	L-4218		22.00
4043	1/8	pedestal, 1" l.		L-4042	L-4242		12.00
4044	1/4	anode cap, 1/32" dp.		L-4030	L-4230		16.00
4046	1/4	center post crater, 1/4" dp.		L-4054	L-4254		21.00
4049	1/4	curved platform, center post		L-3945	L-3745		24.00
4070	1/4	anode cap, 1/16" dp.		L-4031	L-4231		16.00
4071	1/8	flat rod		L-3922	L-3722	C-6	14.00
4072	3/16	flat rod		L-3923	L-3723	C-9	14.50
4073	1/8	rounded upper, 1/32" r.		SP-1009			17.00
4074	1/4	vacuum cup, 3/8" post, 2" l.			L-3790		35.00
4074A	3/4	O.D. Teflon Cup for 4074 or 4075			L-3791	ea.	1.20
4075	1/4	vacuum cup, 5/8" post, 2" l.			L-3789		35.00
4078	1/4	tapered mandrel, 1-1/8" l.		L-3969	L-3769	D-4	18.00
4079	1/4	.054" micro-cup, .062" dp.			L-4257		22.00
4080	1/4	.096" micro-cup, .075" dp.			L-4259		22.00

GRAPHITE RODS 12" LONG

1/8"	(.120") diameter		
	L-4303	National Regular	\$18.00/100
	L-3803	AGKSP or L-3823 SPK	\$49.00/50
3/16"	(.180") diameter		
	L-4306	National Regular	\$17.00/100
	L-3806	AGKSP or L-3826 SPK	\$30.00/25
1/4"	(.242") diameter		
	L-4309	National Regular	\$20.00/100
	L-3809	AGKSP or L-3829 SPK	\$21.30/15
5/16"	(.305") diameter		
	L-4312	National Regular	\$23.00/100
	L-3812	AGKSP or L-3832 SPK	\$14.40/8

Graphite rods are available in three types. The least expensive are the regular purity National Carbon rods having a maximum ash content of 0.06%. The highest purity rods are AGKSP and SPK with an immeasurably small ash. These high-purity rods are packed individually in cellophane and an analysis slip accompanies each box. Graphite rods are also available in diameters of 3/8" and 1/2". National Carbon also manufactures high-purity carbon rods and powder. Send for catalog A-4010 for further details.

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To illustrate the kind of accuracy you can expect with little, more and most patience, we ran two unknowns three ways. Preparation for the first was simply to scoop up the sample and about the same volume of SP-2X powder, then shake them together in our 5000 Mixer/Mill for about a minute. In the second procedure, the sample was weighed and diluted to successive ratios of 10, 100 and 1000 with graphite powder. In both procedures, samples and G Standards alike were tamped into National L-3706 preforms, arced to completion at 10 amp and compared visually on SA#1 plates.

In the best method, that charted as "Dens. Meas.," sample preparation was identical with that in No. 2 but the G Standards were spiked with lithium as an external standard. The Stallwood Jet was enlisted to sober up the arc and dust off some of the background. Densitometry established the analytical curves against which the unknowns were interpolated.

Now here are the results.

ANALYSIS OF NBS BOROSILICATE GLASS (a) AND B.A.S. MANGANESE ORE (b) WITH SPEX G STANDARDS

	Method	Si, %		Mg, %		Fe, %		Al, %		Ti, %		Mn, %	
		a	b	a	b	a	b	a	b	a	b	a	b
1	Unweighed	M	M	.02	M	.2	M	M	M	.2	—	—	M
2	Weighed	30	7	.03	.2	.1	.8	1	1	.05	—	—	15
3	Dens. Meas.	33	2.7	.012	.4	.05	1.8	1.0	.73	.01	—	—	Not determined
	Standardized Values	37.7	3.87	.016	.422	.053	1.49	1.03	.64	.016	—	—	51.3

M=Major



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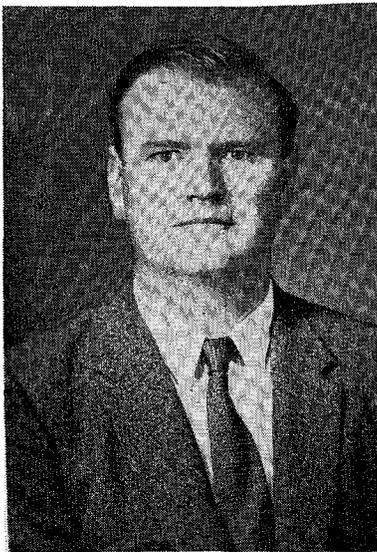
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Unweighed refers to method requiring 40 minutes elapsed time for both samples.

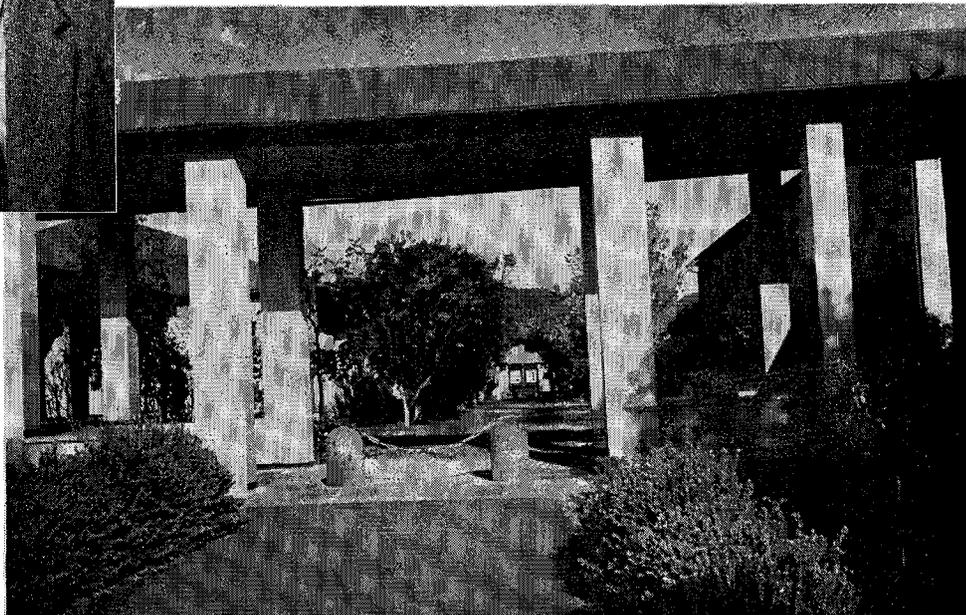
Weighed refers to method requiring 80 minutes elapsed time for both samples.

Dens. Meas. refers to method requiring 150 minutes elapsed time for both samples.

Standardized Values are those furnished by the National Bureau of Standards and the British Bureau of Analysed Samples, respectively.



PROFESSOR PITTWELL IS RECIPIENT OF SAS JOURNAL AWARD (1962, Vol. 16)



At the Third National Meeting of the SAS in Cleveland, October, 1964, Lawrence R. Pittwell was announced winner of the Spex Industries sponsored award for the most outstanding paper published in Volume 16 of *Applied Spectroscopy*. The author of the paper entitled "Equations for Working Curves in Emission Spectroscopy" is at present in Addis Ababa, Ethiopia at the Haile Sellassie I University.

When we contacted him there last October for the purpose of obtaining a photograph and some biographical information he kindly complied in a letter enchanting in its revelation of a warm and vibrant personality as much as in its description of activities far afield of those with which most of us stateside residents are occupied. There being nothing we could find to edit out, Prof. Pittwell's letter is herein reprinted along with the photos he submitted. If perhaps someone not overly tethered to responsibilities here will find in it the inspiration to seek out a like experience, many of which must certainly be awaiting takers, we hope he will also have occasion to cross our path so we can sometime again share with you a tale of spectroscopy-plus.

Dear Mrs. Mitteldorf:

Thank you for your letter of October 19th, and for your congratulations. The delay in reply was due to the time required to get the enclosed photos. The building is the Laboratory Block of the Science Faculty of Haile Selassie I University.

We teach Ethiopians and also students from other African countries who are on scholarships donated by His Imperial Majesty, and recently also by the U. S. Government. We also have a few U. S. and other foreign students—children of UN staff, commercial companies, etc. These on the whole are no better than our local students. Equipment-wise we are not too

well off. Thus analytical spectroscopy is dealt with almost entirely theoretically with the qualitative demonstration using a 1 ft. prism visual observation flame machine. We did, however, make one recent discovery (*Canadian Spectroscopy* 9.11. 1963) using a 4" direct vision gadget. This doesn't mean that spectroscopy is abandoned. At the present time a part time student in West Australia is working on a project of mine by remote control, whilst trace analyses, for a geochemical problem I am investigating, are being done for me by courtesy of British Dry Houses Ltd. in England. I prepare the electrodes and they expose and read the plates, and send back the results. In absorption spectroscopy we have several colorimeters and a very early Beckman DU which runs off flashlight batteries and is always with the maintenance department at the Swedish Hospital. We lack UV and IR which would be a great help to our organic people investigating the local drugs, some of which used to be in the U. S. Pharmacopeia but have since been dropped for lack of methods for standardization. In general, we try to tailor our research to our resources with lots of ingenuity to replace equipment. The other big snag is lack of literature. This summer I managed three days in the Chemical Society Library in London, England. As one elderly fellow remarked, I was literally running, but he was quite tolerant when he heard I had only three days to survey everything for the next two years' work.

I trust you can make something of this.

With thanks.

Yours sincerely,

L. R. PITTWELL
Dept. of Chemistry
Associate Professor

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