

# The

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# Speaker

## WORK AHEAD IN EMISSION SPECTROSCOPY

A sampling of 30 recent articles on emission spectroscopy revealed only four dealing with theoretical aspects of the subject. One discussed a minor new accessory, another the use of inert gases for spark analysis, and still another a fusion technique and its advantages in homogenizing samples. But almost half, bearing nearly identical generic titles, "The Determination of—in—", told of the specific problems faced by the authors and went on to describe the conditions applied for their solutions. Data included such prosaic things as temperature and type of the developing bath, slopes of hordes of analytical curves, methods of calibrating the photographic emulsion, and transmittance of individual filters used to attenuate various lines.

While it is heartening that, within the limitations of his instrumentation, the particular spectrographer was able to solve his problem, it is extremely unlikely that the reader could match those conditions even in the coincidental event that his equipment was identical with the author's. In these circumstances, it seems odd that so many articles discussing individual elements and matrices still appear. True, they all have their peculiarities. They are volatile or refractory; have too many lines or too few; are present as ordinarily unseen traces or in such high concentrations that precautions against matrix effects must be taken; are determined as liquids, solids, or gases. By now, however, shouldn't we all be aware of most of these problems? Are we not expected to extrapolate our experience and knowledge to other areas?

The broader question is on the positive side: shouldn't there be more papers on subjects bordering on the unknown aspects of the science-art of spectroscopy? Certainly all of the fundamental questions have not been answered. Despite the fact that spectrochemistry serves so well, deep gaps remain in both its theoretical and practical phases.

### Sensitivity

Take sensitivity, for example. As more is learned about pure materials, it becomes evident that often they have remarkable properties. Ductile tungsten was recently reported. Iron with a tensile strength far greater than known steels was prepared by a research team. In production for several years are high conductivity copper and aluminum and vacuum-cast (gas-free) ferrous alloys. The most fascinating examples are, of course, in the electronics field where germanium and silicon had to be prepared in purities well beyond the reach of the spectrograph before they turned up with semi-conductor properties. But the development of some other potentially useful semi-conductors such as the so-called three-five intermetallic compounds lags largely for the lack of suitable analytical methods. Analysis is even more significant than purification itself. If a method of purification can be shown to reduce one impurity by even a few per cent, the method can be successively reapplied

until the desired purity is attained. The rub, however, is the lack of reliable analytical methods capable of distinguishing between small differences in composition at the trace level. So small are the concentrations of impurities sought that, presently, only such laborious techniques as neutron activation and solids mass spectroscopy offer any promise of detection. Would it be wise then to reinvestigate emission spectroscopy fundamentally, from all possible angles in the hope of eking out a few more orders of magnitude of sensitivity? Are there approaches which, alone, would extend sensitivity just a little but together would have cumulative, perhaps synergistic effects?

Immediately old, unanswered questions come to mind. Should the sample be made the anode or cathode in a dc arc? It is 25 years since Strock's famous pamphlet (1) on the cathode layer phenomenon appeared. In it he concluded that, made negative, the sample shows the higher sensitivity. So many illustrations were furnished depicting the trailing off of lines from cathode to anode that the effect appears indisputable. Strock generalized that the enhancement of lines at the cathode gradually waned as the concentration of the emitting element was increased. In modern terminology the cathode layer effect should therefore be applicable to *micro* rather than *trace* analysis. Yet the one place where American spectrographers are known regularly to utilize the cathode layer method is in the analysis of high-purity graphite and carbon electrodes. With a virtually unlimited sample (the electrode itself in which successive layers are burned away) the cathode layer effect is exceedingly pronounced. Here then is one apparent exception to Strock's hypothesis that a micro sample is required for cathode enhancement. Is this really an exception, however, or is the rule itself open to question?

At least for carbon matrices, it seems there are pronounced increases in the line-to-background ratios at the cathode, not worthlessly stronger lines and background. But how much? What is the theoretical explanation of the tapered lines and can it be correlated with densitometric measurements? The effect is obviously either electrical or thermal. Can it therefore be optimized in another fashion altogether? That is, supposing the effect to be electrical, can a source be devised such that conditions existing at the cathode of a dc arc are not only simulated but enhanced?

One question concerning the cathode layer effect we partially answered in our own laboratory. The other day we had to analyze a one-of-a-kind micro sample for which it was necessary to run many preliminary samples to optimize conditions for the actual unknown. In the course of these preliminary experiments we tried reversing our normally positive polarity and found that the sensitivity threshold for antimony and arsenic improved by a factor of about five. The strange thing is that the sample was being excited in an atmosphere of argon not air. Is the cathode layer effect applicable in other atmo-

spheres? If so, is it perhaps more marked than in air? What happens when the pressure is changed?

In short, the cathode layer method of analysis needs to be thoroughly reinvestigated in the light of our present knowledge of spectrochemistry. Impurities in the carbon electrodes of 1935 were many times higher than today's and they, undoubtedly, interfered with the measurements. Spectrographs of that day employed Littrow mounted prisms notably subject to fog at the plate due to reflectance from the front surface of both prisms and collimating lenses. Most significant of all, however, is the fact that, at that time, there was not the need for and consequently the interest in trace and micro analysis that there is today. Then a trace element was one below 0.01%; today, without a generally accepted definition, an element would have to be below at least 0.001% or 0.0001% to be entitled to the distinction of that designation.

Whether or not cathode or anode excitation is used, a relationship between arc current and sensitivity has, to my knowledge, never been established. When one reads an article in which the spectrographer states that 5 amperes or 30 amperes were used in a specified trace element determination, he does not mean to imply that this is the optimum current. For when the arc current is increased, the temperature of the arc does not increase correspondingly. Instead, the cross-sectional area of the arc enlarges to a point where the "anode spot" finally engulfs the face of the electrode. Above this value a so-called high-intensity dc arc is produced in which the arc temperature does begin to increase. This kind of arc is not ordinarily attained when 1/4" diameter electrodes are employed because the current capacity of most sources is not large enough. With 1/8" diameter electrodes, however, the high-intensity dc arc is well within the reach of most commercial sources. Would someone care to investigate the effect of current vs. sensitivity, starting with very low currents and breaking through to the high-intensity region? At the same time it would be well to reverse the polarity and compare results. Such experiments should prove extremely useful for establishing once and for all a set of ground rules in an area where, surprisingly, in view of the tremendous amount of work done with dc arcs every day, very few appear to exist.

Extending work with the dc arc still further, the role of the atmosphere needs additional study. Burned in argon, a few micrograms of sample will remain unconsumed in the electrode for several minutes as compared with but a few seconds in an oxygen-rich atmosphere. Is this because of the absence of oxygen or the presence of argon? In addition to having different ionization potentials, the inert gases differ in heat conductivity. Through experiments with gas mixtures, one ought to be able to establish whether both are factors and find conditions for optimum gas mixtures and pressures if not for all elements, for groups of similar elements. A good deal of work has been done in this area already, notably by Vallee and his associates (2, 3), who found considerable enhancement of volatile elements in an argon atmosphere using calcium carbonate as a matrix and, more recently, by Morrison and his associates (4, 5) who confirmed the enhancement using argon on matrices of silicon carbide and nickel. In view of the seriousness of the problem, however, much more work of a fundamental nature begs to be done. I can visualize a nomograph which would tell the spectrographer with a specific determination to make what gas or gas mixture to use and at what pressure to achieve maximum sensitivity. Welcome, too, would be a series of persistent lines as registered in gases other than air. For example, the arsenic line at 2780A is more intense than 2349A or 2288A in argon while the reverse is, of course, true in air. Also, spark lines of zinc and cadmium become the Raies Ultimes in argon rather than those listed in the handbooks.

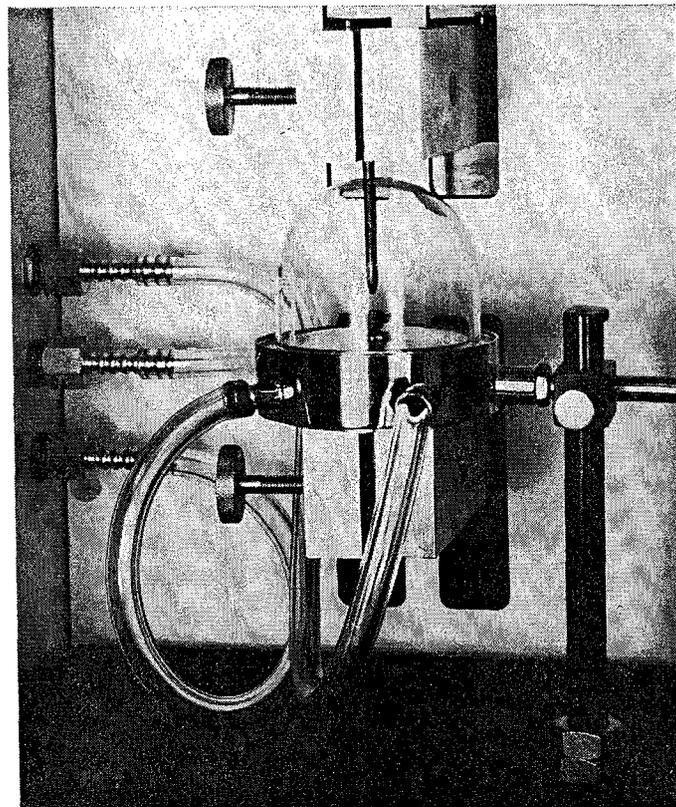


Fig. 1—Enclosed Stallwood Jet No. 9027, for running a stabilized arc in different gases.

Two other variables deserving further study with regard to sensitivity are electrodes and source units. As for electrodes, granted that graphite, used almost exclusively in the United States, has a combination of attractive properties not the least of which is its cost for almost spectrographically pure grades. Considering the need, however, some of the properties could be sacrificed if a material offering higher sensitivity could be found. Silver, copper, aluminum are a few possibilities especially if arced in inert atmospheres. Again let me emphasize that such studies would not necessarily be directed towards the use of metallic electrodes for regularly conducted analyses. Rather, by plotting data on their ionization potential and the temperature of their arc, it is hoped that some generalized conclusions can be reached. If, for instance, a high ionization gas enhances sensitivity, does an arc between two electrodes with a high ionization potential improve sensitivity even more?

Let's now consider the source from the viewpoint of sensitivity. In recent years, several new sources have been introduced commercially and, naturally enough, claims have been made inferring that they are more sensitive than previous ones including the dc arc. But there has been a notable absence of literature in which such comparisons have been conducted. I, for one, would welcome the opportunity of seeing a thorough paper on the determination of traces of—in—using the sustained arc, the high voltage ac arc, the ignited low voltage ac arc, the interrupted dc arc, and the continuous arc. Although it would be unfair, if not impossible, to make the comparison on the basis of current (power consumption would be more realistic), it should be possible for someone who has a deluxe source unit to arrive at generalizations concerning line-to-background ratio for a particular line. Such work cannot and need not be too accurate because it is difficult to establish the exact limit of sensitivity of a line above its background within a factor of two or three. If there is indeed an improvement of one order of magnitude with a particular source over the dc arc, many spectrographers are eager to have the news.

A method in which there is a good deal of hope is that devised by Bardocz (6) in which the spectrograph sees time-resolved spectra. The principle here is that at a particular millisecond or microsecond portion of a spark discharge, the signal-to-noise ratio of a line is greatest. It would be a good plan for an independent laboratory to check the results of Bardocz, to match these against results obtained using a dc arc.

While on the subject of spark sources for high sensitivity, the copper and graphite spark techniques come to mind. During the war, the copper spark was extensively employed for the examination of micro samples of plutonium. After dissolving the sample in acid, a drop was placed on the end of two copper rods, which, after drying, were sparked. Fifteen years later an explanation of the high absolute sensitivity is not yet forthcoming although Morris (7) and later Owens (8) showed that similar and even better results were possible using graphite instead of copper electrodes. Why is ordinary spark analysis relatively insensitive while these special techniques permit the observation of as little as  $10^{-10}$ g of an element? Can the detection limits be further extended with other atmospheres or in a vacuum?

The original copper spark method of Fred, Nachtrieb and Tomkins (9) demonstrated that sensitivity was related to dispersion of a spectrograph. Having obtained figures for sensitivity thresholds using the first order of their spectrograph, the authors went on to show that they could detect about half those amounts in the second order where the dispersion doubled. The reason is that the intensity of a spectral line, being an image of the slit, is independent of dispersion while the background fades inversely with the dispersion. The obvious temptation is to use the 10th or higher orders of modern spectrographs for tremendous boosts in sensitivity. Unfortunately, however, there is a limitation here: the "natural" width of a spectral line. Depending on how they are excited, all spectral lines have a minimum width caused by a number of factors, the greatest being the Doppler effect. Those excited atoms racing towards and away from the slit emit lines of shorter and longer wavelengths respectively than the true wavelength. An excellent discussion of this is to be found in a recent article by Jarrell (10) who terms the optimum point beyond which additional dispersion decreases rather than improves sensitivity "critical dispersion". This point varies inversely with the atomic number and Fig. 2 shows that uranium lines are successively enhanced up to the sixth order of a large spectrograph. What is needed here is a nomograph, once more, relating atomic number and source conditions with dispersion in such a fashion that a spectrographer can tell how to set his spectrograph to achieve the critical dispersion for the particular element sought.

As just indicated, the source is a parameter affecting the width of a spectral line. By decreasing power and pressure, line widths drop. This is one of the principal reasons for interest in the hollow cathode discharge, a source about which many discussions have centered but which, nonetheless, remains a shelf curiosity not an analytical tool. Is it possible to design a hollow cathode for routine use for the analysis of solids? Spectrographers accustomed to filling an electrode and pressing the "start" button on the source would welcome a means of utilizing a hollow cathode so simplified that it can be used almost as conveniently as a dc arc.

But perhaps the hollow cathode is not the most practical approach towards obtaining fine lines. Can a way be found to eliminate the Doppler effect in the dc arc? Is it possible with magnetic or electrical fields to constrain the ions so they cannot move to and from the source and slit? Can a relatively simple chamber be built in which the pressure is lowered thus reducing pressure broadening of lines, too?

What is the optimum slit width setting for a spectrograph in order to obtain maximum sensitivity? Theoretically, an answer will be found in Van Cittert's criterion (11) (Sawyer p. 111) for coherent illumination of the slit. Practically, however, there are problems, such as optical aberrations, which are ignored by Van Cittert. First of all, we desire an exposure above the inertia point of an emulsion, in fact just above the toe of the characteristic curve, in order that a small increment in exposure will yield the maximum contrast on the plate. One way to accomplish this is to pre-fog the plate to bring it into the straight-line portion of the curve. Another is to have an exposure sufficiently long to obtain an equivalent background behind the lines of interest. Assuming the latter, the next step is to choose a slit setting with the highest signal-to-noise ratio. Common sense would dictate that this be as narrow as possible but is this necessarily so? A study should be conducted to determine the optimum slit width necessary for a particular spectrograph to obtain the highest sensitivity. This should, if possible, be correlated with theory. Experiments should be conducted with both trace and micro samples, for with the latter a wide slit is often used to utilize the full speed—rather than best signal-to-noise ratio—of the instrument.

### Determination of Non-Metals

Now 80 years old, the Kjeldahl technique for determining nitrogen remains prevalent. Variations abound in the instruments, in the method of preparing samples and, where originally the method required hours of time for organic materials, today a comparable analysis can be done in under ten minutes. But still it is Kjeldahl with its digestion of the sample, evolution and measurement of the ammonia. Ironically, nitrogen is the most annoying element to the spectrographer: it reacts with his graphite electrodes to obliterate extensive regions of the spectrum. Can the resulting cyanogen bands be put to use in the determination of nitrogen, known to change the properties of most metals?

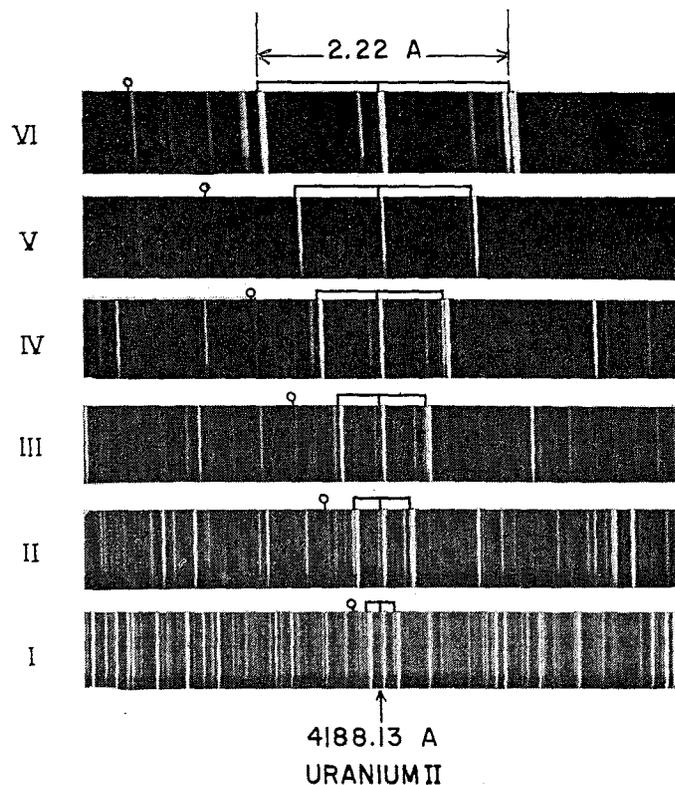


Fig. 2—Spectra illustrating progressive improvement in sensitivity with increasing orders from I to VI.

Can nitrogen be determined directly in organic materials? Here is a real practical problem. Animal feeds are sold on the basis of their protein content which in turn is gauged by the nitrogen content. Feed processors have long sought a device to measure nitrogen continuously as the material moves along a conveyor belt. Ultimately, they want it to go one step further and blend batches to produce an end product with a fixed protein value.

Organic materials have always been troublesome to the spectrographer because, when arced, they go up in flames. The low temperature of the flame is insufficient to excite spectral lines. Is it possible to use inert atmospheres to snuff out the flames? The use of inert atmospheres on highly inflammable materials such as gasoline would permit direct arcing to improve sensitivity by a few orders of magnitude. Present spark methods are limited by the heat dissipation. In the rotating electrode technique the power must be kept below the point where the sample bursts into flame.

Fluorine is the one halide determined regularly by spectrographic methods. CaF emits band series detectable down to around 50 ppm. Practically, however, analagous bands have not proved satisfactory for the other halogens. The reason appears to relate to the instability of most molecular fragments formed in the arc. Thus, while CaCl emits bandheads at 5934 and 6211A, the sensitivity for chlorine is not nearly so great as it is for fluorine. Bromine and iodine, having greater atomic dimensions and, consequently, smaller binding forces, are progressively less sensitive when determined through molecular bands. Surely more work is called for, however. The use of cations other than alkaline earths should be investigated. The sensitivity of their bandheads should be correlated with their structure. Since dissociation occurs at relatively low temperatures, the use of cooler sources is indicated.

Several older articles appear in the literature claiming the successful determination of the halogens directly, that is from their line spectra instead of molecular bandheads. Thus, in 1940, Pfeilsticker (12) developed a source in which extremely high currents (1000 amperes) were flashed at a frequency of 10 cps by discharging a capacitor. Traces of all of the halogens plus S, Se, N and O were readily detected by this technique. In 1955, (13) he showed that sensitivity could be enhanced considerably by reducing the inductance in the circuit. In fact, he reported that 0.02% S could be determined in steel by this technique. In 1951 Mansfield (14) showed that Br, Cl and S could be determined by sparking ashed engine deposits. Yet the methods do not seem to be in widespread use. Why?

Then there is the omnipresent oxygen, now known to affect detrimentally many metals and alloys. For several years the technology of titanium and zirconium was hampered by undesirable traces of oxygen. An elaborate vacuum fusion method was devised for the analysis which, while accurate, leaves much to be desired. In 1952, noticing the strong TiO bands in the spectrum of titanium burned in air, I (15) attempted to make use of these for determining oxygen. Though it showed promise, the method proved insufficiently sensitive, 0.001% being the goal, 0.1% the detection limit. The work, however, was performed on a relatively small spectrograph whose grating was poor by today's standards. It should be repeated.

A more successful approach is that of Fassel (16) who used an arc to release oxygen from titanium contained in a chamber. Oxygen, as well as nitrogen and hydrogen, can be determined from the sample's line spectrum excited after the gases are released in an argon atmosphere. While this method has the advantage of being applicable to most metals—once the gas is released, the base metal loses its importance—it is not suitable

for large-scale analysis. Summing up, a method of spectrographic determination is needed for the gases and non-metals—a practical method, one comparable in simplicity and speed with existing methods for metallic elements.

## Sources

How important are the parameters in a spark source? Commercial units have almost as many controls as the cockpit of a jet plane but are they all necessary? To my knowledge, no one has taken the trouble to report on the systematic change of any parameter—capacitance, inductance, resistance, spark gap, primary voltage, to name a few—to learn their roles. It would seem that some useful correlations could be obtained in this fashion. Reducing the capacitance will lower the power of a spark and the intensity of lines with it. But is there a loss of signal-to-noise ratio? Of spark lines as well as arc lines? Increasing the inductance enhances arc lines. All arc lines equally or is there a relationship with ionization potential? What about stability? Is there a relationship between any one parameter and reproducibility of intensity of lines?

How about a source which would overcome metallurgical history effects? A few years back, spectrographers at Alcoa Research Laboratories, were reported to be working on a small induction furnace to provide a molten pool of aluminum for the spark. By converting all samples to the same form, the effects of aging, chill casting, etc. would, it was hoped, all be eliminated. For some reason the work seems to have been dropped but, in principle, the idea is an excellent one. If it didn't work for aluminum, would it accomplish anything for other metals? If not, are there other sources which would accomplish this?

## Accuracy

The effect of focus of a spectrograph on accuracy has never been fully evaluated and until Arrak (17) developed a method for determining true focus there was no means for doing so. The older way of focusing a spectrograph is visually in which several spectra are taken, the slit moved in and out in increments of 1/2 or 1 mm between exposures. By this method, a practiced eye is needed to find the position of best focus within 1 or even 2 mm. Arrak's method, on the other hand, is much more objective and permits the position of best focus to be found to much closer limits. Noticing that lines doubled as his spectrograph was defocused, he discovered that the distance between the twins increased linearly with the position of the slit. Simple extrapolation thus fixes the position where the twins merge into a single image of the slit—the position of best focus. For his instrument, Arrak claimed that the method was so critical that the position of best focus was not the same for all wavelength regions. To correct this, he had to change the focal curve of the camera.

Arrak's work was mainly theoretical. But how about the practical aspects? What happens to the intensity of lines as they are defocused? Does the intensity of the background behind a line change at the same rate as the line itself? If so, there should be no effect on accuracy and precision. But if, as is much more likely, there are wide differences, this could account for unexplained phenomena such as "curve shifts", poor sensitivity in summertime, etc.

Summertime brings with it high humidity in addition to high temperatures. Both affect photographic emulsions adversely, but again no one seems to know for certain their magnitude in spectroscopy. It would seem possible for an enterprising spectrographer, whose laboratory is air conditioned, to take a series of identical spectra, one immediately after his

air conditioner was turned off and others at intervals until the room warms up uncomfortably. If the dehumidifier could be switched off independently, the resulting data would be even more revealing. One complication here would be distortions of the spectrograph: as it warmed, it would defocus. The spectrograph, however, is a much more massive heat sink than a photographic plate. If the room temperature were allowed to rise rapidly, the temperature of the spectrograph would remain fairly constant.

### Instrumentation

Regarding the spectrograph proper, there have been many significant advances in the past decade. Modern gratings far surpass older ones in speed, resolution, freedom from ghosts and satellites. The plane-grating mounts have a winning combination of properties: dispersion and resolution are high, astigmatism is all but gone. In the past year, three new high-speed spectrographs have been announced, setting the stage for greater sensitivity. Direct reading instruments using the "near" vacuum ultraviolet (1600-2000Å) are in production and, according to reports from users, will probably permit spectroscopy to handle the entire analysis of steels, including the determination of carbon, sulfur, and phosphorus which have remained steadfastly in the province of the wet chemist.

One hole persists in the electromagnetic spectrum—the region spanning the soft X-rays and 1650Å. Here, no practical instrument exists. Waiting to be discovered are: a window transparent below about 1200Å; a source providing a continuum below 1650Å; materials with reasonable reflectivity so that gratings do not have to be used at grazing incidence.

In photographic emulsions we all anxiously await a high-speed, high-contrast, high-resolution, broad-coverage plate with a uniform H&D curve for all wavelengths.

We await a filter adjustable to any wavelength region by turning one knob for the upper wavelength cut-off, another for the lower.

We await radically new sources: ones capable of eliminating matrix effects; capable of easily exciting non-metals; of extending sensitivity especially in liquids; of high stability.

In electrodes, we await the announcement of absolutely pure graphite—and carbon—available from stock.

In theory, we await an absolute formula relating intensity with concentration. Can the simultaneous goings-on in an arc or spark be predicted? Is Slavin's total burn method correct in principle? Slavin proposed that when a sample is burned to completion a fixed weight of an element should emit the identical integrated intensity regardless of the matrix it is in. The theory has been found to have merit in some matrices. Can it be applied with predictable correction factors to others?

In methodology we await a really universal quantitative method of analysis, one completely free of the whims of the matrix. Here the scheme employing a lithium borate flux developed by Tingle and Matocha (18) may be the answer. Results reported were accurate within remarkably close limits for a convincingly large number of unrelated samples. Substantiation of this work has come from C. R. Hodgkins of Esso Research & Engineering, Linden, N. J., who, privately, has indicated that he is using Alcoa's method regularly for the analysis of petroleum ashes, deposits, slags and residues.

### Conclusion

My neck is stuck way out. By publishing this little essay, it would seem I tacitly assume that I have not only read every-

thing on the subject but have the power of total recall. Won't you please tell me where I may have erred in commission or omission? If this article has prodded a few spectrographers into either reporting work unpublicized outside of their own laboratory or encouraged experimental work in the areas proposed, it will have served its purpose—to promote the science-art of emission spectrochemical analysis.

—A. J. MITTELDORF.

### References

- (1) Strock, L. W., "Spectrum Analysis With The Carbon Arc Cathode Layer", Adam Hilger, London (1936)
- (2) Vallee, B. L. and Adelstein, S. J., *J.O.S.A.*, **42**, 295 (1952)
- (3) Adelstein, S. J. and Vallee, B. L., *Spec. Acta.*, **6**, 134 (1954)
- (4) Morrison, G. H., Rupp, R. L. and Klecak, G. L., *Anal. Chem.*, **32**, 933 (1960)
- (5) Rupp, R. L., Klecak, G. L. and Morrison, G. H., *Anal. Chem.*, **32**, 931 (1960)
- (6) Bardocz, A., *Z. Natur.*, **10a**, 1031 (1955)
- (7) Morris, J. M. and Pink, F. X., *ASTM Spec. Tech. Pub.*, No. 221, 39 (1957)
- (8) Owens, E. B., *App. Spec.*, **13**, 105,
- (9) Fred, M., Nachtrieb, N. H. and Tomkins, F. S., *J.O.S.A.*, **37**, 279 (1947)
- (10) Jarrell, R. F., "Encyclopedia of Spectroscopy", 245, Reinhold, New York (1960)
- (11) Sawyer, R. A., "Experimental Spectroscopy", Prentice-Hall, New York (1951)
- (12) Pfeilsticker, K., *Spec. Acta.*, **1**, 424 (1940)
- (13) Pfeilsticker, K., *Mik. Acta.*, **1**, 358 (1955)
- (14) Mansfield, W. O., Fuhrmeister, J. C. and Fry, D. L., *J.O.S.A.*, **41**, 412 (1951)
- (15) Mitteldorf, A. J., Private Report to Watertown Arsenal (1952)
- (16) Fassel, V. A. and Tabeing, R. W., *Spec. Acta.*, **8**, 201 (1956)
- (17) Arrak, Arno, *Spec. Acta.*, **12**, 1003 (1959)
- (18) Tingle, W. H. and Matocha, C. K., *Anal. Chem.*, **30**, 494 (1958)

## — CAN THE HAY-FEVER SEASON BE FAR BEHIND?

When we designed our No. 5000 Mixer/Mill, the field of medicine was farthest from our mind. The goal was a high-speed, reliable mixer and grinder for small laboratory samples. But, while we were playing with prototypes, a couple of physicians specializing in allergy independently approached us suggesting that the instrument's rapid, wavy motion might be fine for emulsifying allergens before injection. So prepared, the material is absorbed slowly by the body to arouse the antibodies out of hibernation by the time the pollen starts to blow. In theory, a single massive dose should do the work of the usual 20-30 graded doses.

Nor is allergy the only area for this repository treatment. Last winter some 200,000 members of the Armed Services were immunized with a single injection of an emulsified anti-flu vaccine with remarkable results compared with the untreated control group.

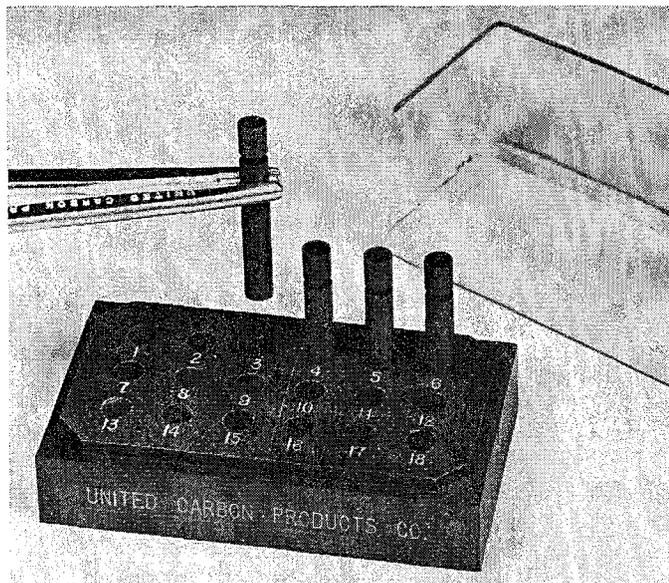
The active ingredient, a saline extract of pollen, is sucked into a hypodermic syringe together with a purified oil, an emulsifying agent, and some air, in a predetermined ratio. The syringe is then oscillated at 3300 rpm in the Mixer/Mill for about ten minutes. The emulsion is checked for particle size before injection.

To date, the work is on a clinical investigation basis and the emulsions are not commercially available. Hollister-Stier Laboratories are distributing our No. 5010 Mixer/Mill to physicians and medical researchers. But if you are interested in saving a whale of a lot of sample preparation time in your laboratory, contact us about the No. 5000.

## GRAPHITE ELECTRODE STANDS

In addition to our plastic electrode stands, we now offer the United Carbon Products Stands made from the highest spectroscopic purity graphite. These are particularly useful for igniting and drying samples directly in the electrodes. The electrodes are loaded, placed in the stand where each position is numbered and the assembly placed in a furnace. Temperatures as high as 450°C have a negligible effect on the graphite.

Stands are available for crater-type 1/8", 3/16" or 1/4" electrodes and also for platrode type electrodes.



- M-589 Graphite Electrode Stand**, for 1/8" dia. electrodes ..... \$19.25
- M-588 Graphite Electrode Stand**, for 3/16" dia. electrodes ..... \$19.25
- M-587 Graphite Electrode Stand**, for 1/4" dia. electrodes ..... \$19.25
- Graphite Electrode Stand**, for platrodes or discs (Soon Available)

## THE ENCYCLOPEDIA OF SPECTROSCOPY

Following closely the eminently successful formula he used in the Encyclopedia of Chemistry, Prof. G. L. Clark of the University of Illinois has edited the new Encyclopedia of Spectroscopy. One hundred twenty well-versed research leaders in the fields of absorption, emission, x-ray, Raman, nuclear magnetic, gamma, mass and microwave spectroscopy have contributed over 160 articles in nearly 800 pages, broadly encompassing the current state of the art. The book will help everyone interested in the field of spectroscopy to extend his understanding in many diversified areas of instrumental analysis.

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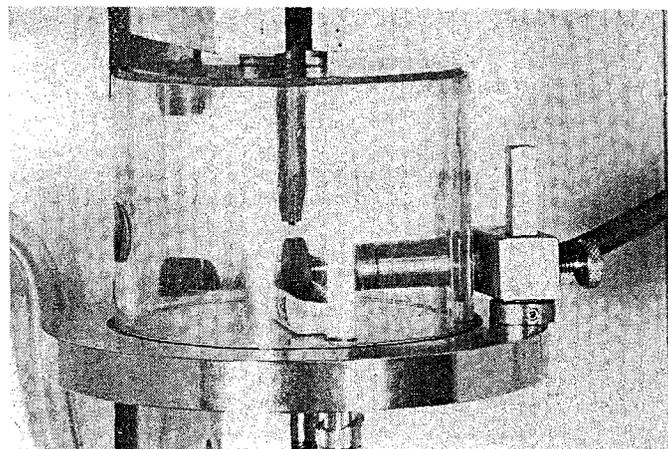
## SYMPOSIUM ON SPECTROSCOPY

The 17 invited papers presented at the Third Pacific Area National Meeting of ASTM in San Francisco, October, 1959, have been compiled into a 245-page report. It is available from ASTM as its Special Technical Publication No. 269 at \$7.00 to non-members, \$5.60 to members.

## ENCLOSED COMBINATION ANALYZER

The success of our Enclosed Stallwood Jet prompted us to look into the possibility of enclosing the Combination Analyzer—the accessory for analyzing solutions either by the rotrode or platrode techniques. It turned out to be quite a simple task. By modifying the base and perching a Pyrex dome on top, the accessory can be flushed with any gas. The analysis of substances which would ignite in air is performed in an oxygen-free atmosphere. Where cyanogen bands interfere with an analysis, nitrogen-free gases are used.

- 3400-2 Enclosed Combination Analyzer**, accessory for the analysis of solutions by rotrode or platrode techniques. Complete with 10 rpm, 115 v. 60 cy. motor; stainless steel and tantalum shafts; Pyrex dome for the use of atmospheres other than air ..... \$ 198.00
- 3404 Pyrex Dome**, spare. Several are recommended in order to expedite the analysis of numerous samples .....each \$ 12.00
- 3400-K2 Assembly Kit** for converting existing Combination analyzers to enclosed units, all necessary parts including one Pyrex dome and complete instructions ..... \$ 33.00
- 3401 Porcelain boat**, spare. One supplied with 3400. Per doz. \$ 10.00
- 3402 Table adapter**, stainless steel for 1/4" or 1" dia. disc .....each \$ 12.00
- 3403 Aluminum Boat**, spare, one furnished with 3400 .....each \$ 5.50
- 4032 Graphite mandrel**, used to protect tantalum or stainless steel from extremely corrosive substances .....Per 100 \$ 22.00
- 4011 Graphite rotating disc**, highest purity, for solution analysis, 1/2" dia. x 1/8" thick. Per 100 \$ 14.00
- 4012 Graphite platrode electrode**, highest purity, for rotating platform technique, 1/2" dia. Per 100 \$ 18.00
- 4027 Graphite disc electrode**, highest purity, for solution analysis (like 4011 but thicker to permit electrode to run cooler). 1/2" dia. x 0.200" thick .....Per 100 \$ 16.00



# tricks of the trade

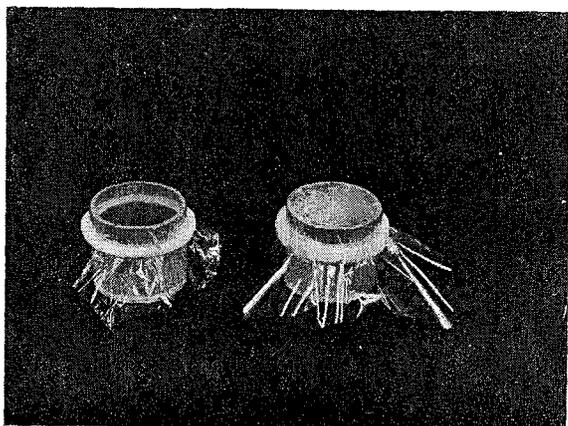
## SENSITIZING PHOTOGRAPHIC EMULSIONS

The highest sensitivity emulsions for use in the region below 2000A are those referred to as Schumann plates which have most of the absorbing gelatin removed. Examples of these plates are the Ilford Q Series (we stock the Q-1 and Q-2) and the Eastman SWR (Short Wave Radiation). An expedient method of sensitizing an occasional plate right in the laboratory is to coat it with a fluorescent material which responds to short wavelength radiation by fluorescing at a wavelength to which the plate is sensitized. Most materials suggested for the purpose are oils which must be washed away with an organic solvent before developing the plate. In their place, M. Artaud of the French Atomic Energy Commission suggests sodium salicylate commonly used to coat phototubes for the same purpose. A 2% solution of sodium salicylate in methyl alcohol is swabbed on the surface of the emulsion with a piece of absorbent cotton and allowed to dry in the darkroom. After exposure, the plate is developed normally.

## EXPENDABLE CELLS FOR X-RAY ANALYSIS

Infinity, that's the ideal number for any customer-to-problem ratio. And, at least for those purposes for which the No. 3515 X-ray cells were designed, we seem to have approached this. Hundreds of X-ray spectrographers have now received the cells they ordered and, judging from the generous compliment-to-complaint ratio, the X-ray analysis of liquids has been made a wee bit more elegant.

Somehow the impression has gotten around that the cells are handy for powdered samples, too. Here they are needlessly large except in one novel technique expounded by Mr. M. L. Salmon, an ingenious gentleman who runs the Fluo-X-Spec Analytical Laboratories out in Denver. Mr. Salmon has refined a semi-quantitative method of analysis in which a weighed but very small powdered sample is sandwiched between two 1/4 mil films of Mylar. Using our cell, first one film of Mylar is positioned with a Teflon snap ring. After the sample is spread out on the film, a second Mylar film is stretched over the top with another Teflon snap ring.



## No. 8000 MIXER/MILL MODIFICATIONS

So many of our No. 8000 Mixer/Mills have been modified for special applications that it would seem sensible to put this information on record for others. The simplest change permits the instrument to be used for mixing or grinding several small samples simultaneously. What we supply is an adapter drilled out to hold the appropriate containers:

- 8010 **Vial Adapter**, for holding seven No. 3111 (1/2" x 1" plastic); or seven No. 3116 (1/2" x 2" plastic) or seven No. 3114 (1/2" x 1" stainless); or seven No. 3117 (1/2" x 1" hardened tool steel)...\$ 14.00
- 8011 **Vial Adapter**, for holding four No. 3127 (3/4" x 2" hardened steel or four No. 6133 (3/4" x 2" plastic) .....\$ 14.00

The above are for a relatively light load on the instrument. For handling larger and heavier vials, special machined rather than the standard cast jaws are required. The one pictured below is in use in two instruments of a large steel company. Here the problem is to grind individual samples on a 3-shift basis using our No. 8004 tungsten carbide vial. It was found that the cast aluminum clamp normally supplied with the Mixer/Mill wore excessively in this production—rather than laboratory—operation.

An oil company had the problem of mixing three 30 ml samples simultaneously prior to x-ray spectrometric analysis. At around the same time, a large American electrical manufacturer asked us to build an instrument to grind three samples at once. For both of these organizations we made identical clamp assemblies:

- 8012 **Special Clamp** for No. 8000 Mixer/Mill. For holding three 60 ml No. 6135 (1-1/4" x 3" plastic) or three 25 ml No. 8005 hardened tool steel vials .....\$ 88.00
- 8005 **Vial**, hardened tool steel, 25 ml capacity, slip-fit end caps at both ends .....\$ 38.00

Still another clamp was made for several customers who wanted to handle four 30 ml plastic vials at one time:

- 8013 **Special Clamp**, for No. 8000 Mixer/Mill. For holding four 30 ml No. 6134 (1" x 3" plastic) vials .....\$ 88.00

To modify your instrument, the old clamp is readily removed with a wheel-puller. The price of a new Mixer/Mill with either the No. 8012 or No. 8013 special clamps is \$340.00.

## CLEANING 10-MICRON SLITS

We've already suggested the cellophane on packs of cigarettes for cleaning slits 25 microns or wider. The 1/4 mil Mylar we supply for X-ray liquid cells under No. 3517 can be used for cleaning 10-micron slits. If you can't borrow a piece from your X-ray man, send to us for a complimentary piece. But please, please enclose a self-addressed envelope.

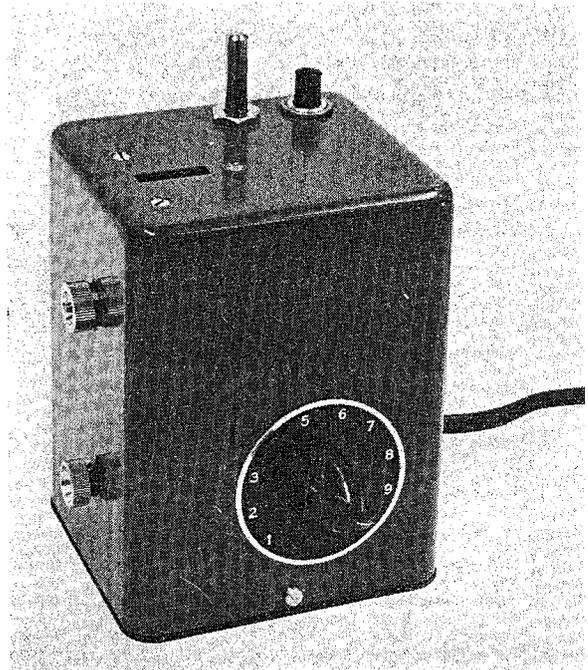
## No. 3702 SERIAL MARKER

Trouble with most laboratory and industrial photographic plates is their close resemblance. One spectrogram or one electron micrograph is often very much like the next or last one. A mix-up usually means a time-wasting do-over.

Our Serial Markers are designed to prevent just this. Plates or films are serialized by projecting a 5-digit number in the corner or any unused portion of the emulsion. The plate is held above the window of the instrument and a button is pressed for about 3 seconds—the actual time depending on the speed of the plate. To compensate for differences in emulsion speed, a rheostat is adjusted to the light intensity required. A few minutes of experimentation gives the operator the optimum exposure which is not at all critical and can be varied by as much as 50% to still produce clear, legible numbers. In practice, therefore, you can merely count out the exposure time.

To advance the number a second button is pressed. This is raised above the level of the first button, to facilitate operation of the Serial Marker even in total darkness. To assure placement of the numbers neatly in the same relative location on each plate, a right-angle fence may be cemented anywhere on the top surface. By unlocking and moving a lever on the outside of the case, the size of the number may be varied from about 3 x 15 mm to 4 x 20 mm.

Although the instrument finds particular application for numbering spectrographic and electron microscopic plates, many are used in industrial laboratories for ordinary photographs.



**3702 Serial Marker**, for numbering photographs consecutively. Operates on 115 volts ac; attenuator for adjusting light intensity; size of 5-digit number may be varied from 3 x 15 mm to 4 x 20 mm; fence for aligning plates or films; spare 7.5 watt lamp .....\$ 75.00

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