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The article in this issue discusses the future. Always a risky topic, our predictions may be as far off as the last horse on whose nose we lost \$2.00. We point out that the growth of other sciences depends in large measure on the growth of spectrochemical methods. If nothing else, we hope we shall have stimulated discussions concerning and perhaps research in those areas where advancements are sorely needed.

GAZING INTO THE CRYSTAL PRISM*

By A. J. MITTELDORF

Introduction

Around the turn of the century, someone muttered his famous last words to the effect that science had just about reached a dead end. Sure, he continued, there were still a few gaps to be filled in; the handbooks would undoubtedly contain several extra pages of data each year. But no further major advances could be expected. The steam engine was the ultimate in power and transportation; the telephone, the ultimate in communication; TNT, the last word in explosives.

One may be tempted to view emission spectrochemical analysis just as wrongly today. Especially is this true when we visualize a production laboratory with its thousands of routine determinations being performed each day and compare this with the humble beginnings of the science when men like Bunsen and Kirchoff first observed a relationship between elements and spectral lines. Spectroscopy might seem to be over the horizon with no place further to go.

The purpose of this article is to take the opposite stand. We aim to show that, not only are there broad areas where spectrochemical research can be carried out, but more important, this research *must* be carried out in order to hasten and even permit parallel advances in other sciences.

There are at least four areas where such break-throughs are needed. These will be enumerated below and then described in further detail:

1. Improve sensitivity by at least several orders of magnitude.
2. Extend analytical range to *all* of the elements.
3. Develop a universal quantitative method of analysis.
4. Improve accuracy of results.

Improve Sensitivity

The first problem, that of improving sensitivity, is of urgent importance in several fields. Take electronics, for example, where so many current research programs center around semi-conductors. Consisting of crystals of germanium, silicon or other elements, semi-conductors are almost immeasurably pure. A few parts per million of an unwanted element will convert a germanium transistor from a powerful amplifier to a tiny disc of ceramic nothingness. Yet the presence of this impurity must often be guessed at rather than detected and measured for want of a suitable analytical tool. This particular analysis problem is also exemplified by solid state physicists who add a few parts per million of activating elements to the crystal and then want to make sure that they have actually added the desired amount and, in addition, have it uniformly distributed throughout the material.

For the time being, the physicists have to resort to indirect—and admittedly not completely satisfactory—means for studying the effects of impurities in transistor materials. They measure the resistivity of the semi-conductor and thus obtain an overall figure of merit. What they need, however, is a sound method of keeping tabs on every element which might affect the performance—beneficially or detrimentally—of the transistor.

Metallurgists, too, are seeking the help of spectrographers in their studies. When they discovered that a few parts per million of boron would improve the hardenability of steel, they had an early verification of their suspicions that trace elements have far-reaching effects on the properties of common alloys. Recently, General Electric scientists discovered an even more fascinating effect of purity. They showed that a pure and perfect crystal of iron has a strength ten times greater than the strongest steel alloys used commercially.

In these two fields then, and in many others, the spectrographer is faced with a tremendous challenge. Improve your sensitivity

*Invited paper delivered at the Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Feb., 1956.

and you will be responsible for basic technological progress, he is told.

Well, what is being done to improve sensitivity? One contribution here has been the development of the new plane grating spectrographs. Until now, the concave grating has been the heart of most modern spectrographs. Doing the work of two optical elements, it offered an inexpensive and efficient optical layout. Practically, however, it has certain disadvantages. The concave grating, itself, cannot be fabricated as perfectly as the simpler plane gratings. As a result, the user has to accept inferior specifications regarding such imperfections as ghost and satellite intensities. He finds, too, that his gratings often have regions of poor intensity or "holes".

Of equal importance, the concave grating physically imposes a limitation on the highest order in which the spectrograph can be used. Research spectrographs using the Wadsworth mount, for example, can be used to no higher than the third order and those using the Eagle mount to the fourth order.

In contrast, the new plane grating spectrographs can be used in the tenth and even higher orders. With the higher dispersions that go along with the higher orders has come better sensitivities. Theoretically, the signal-to-noise ratio of a particular spectrograph depends on its dispersion. Thus, the higher the order in which it is used, the higher the dispersion and the better the signal-to-noise ratio or sensitivity. In addition, plane gratings are much easier to rule than the conventional concave gratings and more stringent specifications have been placed on their performance.

In addition to improvements in the spectrograph itself, techniques are being devised and developed to enhance the sensitivity of spectrographic methods. One such technique is the hollow-cathode source. This consists of an enclosed chamber in which the sample is placed. The chamber is operated at low pressure and low temperature so that the lines that are emitted are exceedingly sharp and with very low background. Further, the sample remains in the vessel so that it is excited over and over again instead of being lost as happens in an open chamber. All of these factors make it apparent that sources such as the hollow cathode will become increasingly important as the spectrographer is taxed for greater and still greater sensitivity.

Extend Analytical Scope to All Elements

In the latest issue of "Applied Spectroscopy", there is an article by E. F. Runge and F. R. Bryan (10: 68, 1956) on the determination of nitrogen in steel. According to the authors, Cr-Mn-Mo steels containing 0.5% of nitrogen are "proving to be valuable replacements for conventional alloys of high nickel content." Dr. V. A. Fassel gave a more general paper entitled "Spectrographic Determination of Gaseous Elements in Metals", at the Pittsburgh Conference last March. A few months ago, I learned of the necessity of purging gases from stainless steel tubing used for transporting liquid lithium. Quality control tests vital to the performance of titanium alloys are the determination of oxygen and hydrogen.

It is apparent from the above examples that there is a growing interest in the determination of gases. Yet the analysis techniques are still far from perfect. They are time-consuming and involve a sizable initial outlay in equipment.

Another illustration of the interest in and magnitude of the problem is in the animal feed industry. Through the ever-increasing use of fertilizers and improved farming techniques, the yield per acre of crops has steadily increased. Often, however, the increase is coupled with a corresponding decrease of the nutrient value of the crop. For this reason, a crop such as corn is graded on the basis of its protein content. To the analyst,

this has traditionally meant a Kjeldahl determination of nitrogen. But such a determination takes about one-half hour. How much more profitable it would be to the processor if he could put an instrument on the conveyor belt which would continuously and almost instantaneously record the protein content!

By comparison with the spectrochemical analyses now routine in the metals industries, this problem seems enticingly simple. Atmospheric nitrogen, however, interferes with any direct measurement of the nitrogen in the sample and thus imposes one obstacle. A second is the necessity of removing the organic matter so that the material may be sparked without a flame.

There are some of the challenges. What has the future in store? Well, for one thing, it is obvious that new techniques such as the use of enclosed chambers where atmospheric gases are excluded will be necessary for such determinations. More basically, however, we can assume that the far ultra-violet will have to be opened up if much progress is to be made. This region is also known as the Schumann region, after the man who made extensive studies in the far ultra-violet back in the 1890's. Although known for such a long time, the latest ASTM "Index to the Literature on Spectrochemical Analysis" lists not a single paper utilizing the far ultra-violet.

But do not conclude that the far ultra-violet offers little promise to the spectrographer. Quite the contrary. In this region are prominent lines of arsenic, carbon, the halogens, hydrogen, nitrogen, oxygen, phosphorus, selenium, sulfur. In the ordinary ultra-violet, these elements have, thus far, either eluded detection altogether or are so insensitive as to call for methods other than spectrographic.

The principal deterrent in the far ultra-violet is instrumentation. While it takes but a few minutes for a determination in the 2000-4000A region, present instrumentation would require at least 1 man-hour to determine an element in the vacuum ultra-violet. Presently, however, major strides are being made to overcome the obstacles in the vacuum region. One instrument currently available (McPherson Precision Instruments) is completely self-contained: vacuum pumps, controls and measuring instruments are in the same housing as the spectrometer itself. The instrument is designed to operate with electronic detectors because of the limitations of photographic emulsions in this region. Further, provisions are made for admitting samples without breaking the vacuum and wavelengths are scanned mechanically at any of several rates of speed.

Incidentally, a future article in the SPEAKER will discuss in fuller detail the potentialities of the vacuum ultra-violet.

A Universal Quantitative Method

Just about every spectrographer finds himself daily with a sample which is a complete unknown on which he is requested to provide quantitative determinations of all elements found and "less than" figures on those elements not found. Since present methods do not permit a quantitative assay, the spectrographer usually begs off and reports semi-quantitative figures, results accurate to, at best, plus or minus 30% of the amount of each element detected.

Even so, his problems are knotty. The major difficulty is the matrix effect: the intensity and therefore apparent concentration of each element depends very strongly on the base material.

The introduction of the Spex semi-quantitative standards about a year ago, simplified the problem by providing standards which relieved the spectrographer of the necessity of laboriously preparing these standards himself. But we want to go one step

further: semi-quantitative analysis must be elevated to quantitative analysis.

To achieve the required accuracy, it seems to me that trace-element techniques are going to have to be improved. This is because, in my opinion, the best way to overcome the matrix effect is to work with the same matrix. In other words, a sample to be analyzed must be greatly diluted with a common material so that standards and sample are, essentially, alike. This means that elements present in relatively high concentrations in the original sample are changed to trace elements. The problem then boils down to determining perhaps 1 ppm of an element with such accuracy that, when the figure obtained is multiplied by the dilution factor, a sound quantitative determination is the result. All this adds up to the requirement that the accuracy of trace-element determinations must be greatly improved in order for us to achieve a universal quantitative method of spectrochemical analysis.

Greater Accuracy

In the section above, when we spoke of quantitative accuracy we meant plus or minus 2% of the concentration present. For many applications, this is still not good enough. Take medicine, for example, where we feel that spectrochemical analysis has certainly lagged. The human body has mechanisms for controlling the body weight to 0.5%; day to day variations in the blood count, blood pressure, temperature, the concentration of water, hormones, minerals are all kept equally small. Are we not, therefore, using a carpenter's rule to make toolmaker's measurements when we try to use a spectrograph in the study of disease? To put it another way, the change of the concentration of an element in blood by 1% may have immense significance. Today's spectrographic methods, however, would not detect such a small change.

Another example of the need for better accuracy is the happy prospect of saving money. The steel industry uses sizable amounts of such alloying ingredients as nickel, niobium, tungsten, vanadium and cobalt—all expensive and some strategically scarce. Although specifications permit a concentration range of these elements, the mill naturally strives to keep them at the minimum values. But, if the accuracy of the measuring tool is 2% of the amount present, the mill must add at least that much more to ensure that the minimum value has been attained. Improved accuracy thus potentially means large savings in money to the mills.

The Day After Tomorrow

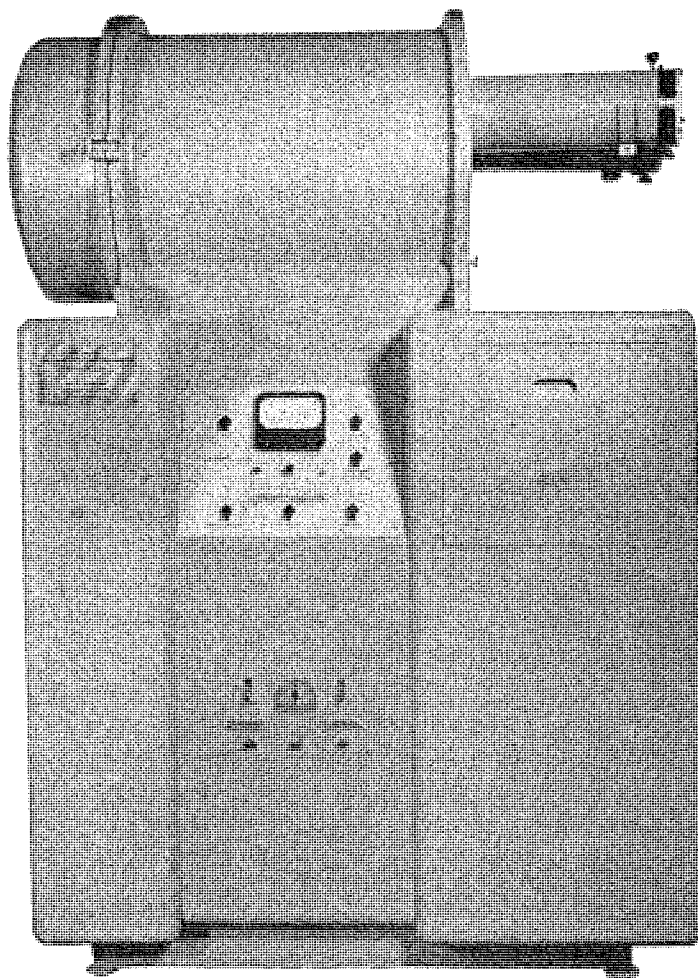
Shall we look further ahead into the Buck Rogers—pardon, Captain Video—era? What will spectrographic methods be like then?

In the field of metallurgy, we can safely predict the Specrobot. This is a machine which takes its own sample from the melting pot, analyzes it in seconds and then actuates the appropriate hoppers so that automatic corrections are made to the heat. When it finally rings a bell to notify the sleeping attendant that it is ready for the next heat, the Specrobot will have adjusted the composition of the present heat to exactly the minimum values for each alloying ingredient. In addition, it will have made sure that all tramp elements—metallic and non-metallic alike—are well below specification limits.

In medicine, spectrographers will have discovered important relationships between many trace elements and health. Just as today a technician routinely checks blood for iron, the future technician will examine blood for zinc, cobalt, copper, magnesium and other elements. The diagnostician will be able to draw as significant conclusions from these spectrographic measurements as he now does from blood pressure measurements.

The spectrograph will help advance the developments in pure materials. Steels with strengths many times their present values; copper with much higher conductivity; materials with undreamed of electronic and electrical properties; still brighter phosphors; these and many more will be developed with the help of the spectrographer.

And the spectrograph itself, what will it be like? It will have a range from 10A in the long x-ray region to 100,000A in the deep infrared. It will record accurate results directly in percent concentration regardless of the size, shape or nature of the sample. In seconds, every element will be determined in concentrations from a few ppb to 100%. And on it no operator—however experienced—will be able to make a double exposure.



McPherson Model 220, One Meter Scanning Ultra-Violet Monochromator

HOW ARE YOU "FIXED" FOR ELECTRODES AND PHOTOGRAPHIC SUPPLIES?

WE ARE WELL STOCKED WITH THOSE MOST USED. IN ADDITION, IF YOU HAVE SPECIAL REQUIREMENTS WE SHALL BE HAPPY TO KEEP ONE STEP AHEAD OF YOU AND HAVE YOUR PARTICULAR SUPPLIES STOCKED FOR IMMEDIATE DELIVERY.

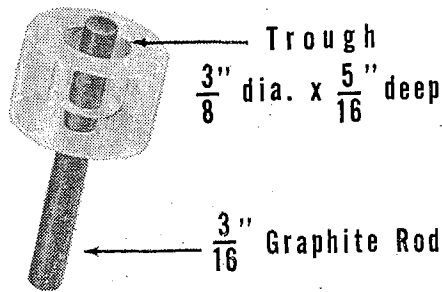
tricks of the trade

IMPROVING SENSITIVITY OF VOLATILE ELEMENTS

Mr. William E. Publicover of the U. S. Metals Refining Laboratories in Carteret, N. J., uses an ingenious system for vastly improving the sensitivity of volatile elements in high-purity silver and copper. He starts with a conventional cupped electrode (crater about $\frac{1}{4}$ " deep x $\frac{1}{4}$ " dia.) in a $\frac{5}{16}$ " graphite rod. Around the electrode he pastes a band of old-fashioned mending tape, the kind so widely used before pressure-sensitive tapes were known. The tape sleeve may be slipped up and down effectively to lengthen or shorten the crater in the electrode. The metal in granular form is loaded inside, just filling the cup and paper extension. It is then arced in the normal fashion using dc. The paper rapidly burns away, but at the same time, the metal melts. Surface tension keeps the metal upright for the duration of the burning during which time the electrode separation is maintained. Since comparatively large amounts of the base metal are used (1 gram of silver, for example), the actual amount of the trace elements consumed is proportionately large. Burning, of course, is to exhaustion of the elements determined. Publicover reports that, with this technique, he regularly determines a few tenths of a ppm of bismuth and lead in silver. In copper, he is able to determine 1 ppm of zinc and about 2 ppm of phosphorus. Copper samples are first briquetted for convenience. Care must be exercised in selecting the grade of paper mending tape, since some varieties contain trace quantities of zinc and other elements.

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STILL ANOTHER METHOD FOR SOLUTION ANALYSIS



Messrs. William Henry of Battelle Memorial Institute in Columbus, Ohio and George Dugan at the American Viscose Labs. in Marcus Hook, Pa., use a neat little gadget for solution analysis. Pictured here, it consists of a Plexi-glas cup into which

a $\frac{3}{16}$ " diameter heat porosified graphite rod is forced. A drop of Duco cement on the rod prevents leakage. The rod is pushed about 1 mm above the top of the cup using a washer as a fixed stop. In use, the solution to be analyzed is poured into the cup. A spark is directed to the top of the electrode which, being porous, feeds the solution into the spark by capillary action. The cup may be washed and used over and over again.

If you would like to try out this technique, order:

3450 Solution analysis cups, methacrylate
Set of six \$9.00

THE HOUR-GLASS MIXER

Although the Wig-L-Bug is a far better overall tool than the Hour-Glass Mixer (#3100), the latter still is extremely useful when it is desired to mix materials without reducing the particle size and also when as many as 10 ml of materials are to be mixed. It has been reported to us that a vibrating instrument such as an electric razor or a Vibro-tool scriber held against the vials of the Hour-Glass mixer greatly speeds the mixing action.

★ ★ ★

WIG-L-BUG HINTS

So many of these instruments have recently been delivered that those of you who have them will be interested in some of the techniques worked out by others.

Item: The mixing of very small samples is simplified by the addition of a drop of alcohol.

Item: The Tech-Pen (#3910 at \$4.00) may be used to label the plastic and metal vials.

Item: Certain metal sponges such as platinum may be pulverized in the plastic vials.

Item: Electron microscopists obtain particles in the sub-micron range by grinding the sample with a drop of water in the tool-steel vial for upwards of 5 minutes. The model #3140 Wig-L-Bug is used as it is fan-cooled and has a 1-hour timer. After standing awhile, the coarser particles settle out and the finer ones are removed from the surface of the water.

Item: Varnishes such as those used to coat tin cans and electric wires may be ground into KBr briquets using the stainless steel vial and ball. Grinding time is at least 5 minutes.

Item: To grind materials which have a tendency to pack or mat such as asbestos, two or more grinding balls are used with the sample.

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ANALYSIS OF PURE MATERIALS USING SPEX MIX

Many queries have come our way on the use of SPEX MIX for analyzing "pure" materials. The method suggested is the additive one.

First mix 0.100 g of SPEX MIX with ^{1.24} 1.24 g of the material to be analyzed. Since SPEX MIX contains 1.34% of 43 elements, the mixture will add 0.100% of these elements. Dilute 1:9 with the unknown to obtain 0.0100% and again to get 0.00100% of the 43 elements, etc. It is obvious that these standards will immediately allow you to obtain "less than" values on all elements not detected and the order of magnitude on those elements detected. More refined semi-quantitative work is obtained through the preparation of intermediate standards and working curves.

chemically pure - - spectrographic grade - - SPECTROGRAPHICALLY PURE CHEMICALS

Metallurgists, solid state physicists, physical chemists and others are using purer and purer materials in their research programs. Time was when "trace" meant less than 0.01% of an impurity. Today it is likely to mean less than 1 ppm. Closely linked with the pressing need of these scientists for such pure materials is the analyst's task of guarding their purity. The spectrographer, particularly, is finding it increasingly necessary to improve both his techniques and his reagents in order to determine progressively smaller concentrations of impurities.

With this in mind, we announce our first two SPECTROGRAPHICALLY PURE materials. These are GERMANIUM OXIDE and SILICON METAL. Both of these substances are components of transistors where impurity levels are kept orders of magnitude below the present levels of spectrographic detectability.

SPECTROGRAPHICALLY PURE GERMANIUM OXIDE promises to find many uses as a spectrographic buffer. It has few spectral lines, is non-toxic, relatively inexpensive, mixes well with other powders, burns smoothly, is non-hygroscopic and—above all—is free of all detectable impurities. By comparison, lithium carbonate—one of the most widely used buffers today—contains 10-100 ppm of impurities. The determination of these impurities is certainly hampered by their presence in the buffer.

The second material now available is SPECTROGRAPHICALLY PURE SILICON METAL. While it offers no immediate uses as a buffer directly, it may be converted into silicon dioxide which is a useful buffer. The SILICON METAL itself will serve as an invaluable primary standard for judging the purity of other grades of silicon or silicon compounds. It will serve, too, for the preparation of other standards.

- 6001 Germanium Oxide, Spectrographically Pure, Powder.
Per 5 grams \$8.00
- 6002 Silicon Metal, Spectrographically Pure, Needles.
Per 5 grams \$8.00

HODGE SEMI-QUANTITATIVE SCALE

The Spex semi-quantitative standards are used for the spectrochemical analysis of samples which are complete unknowns. They are particularly applicable to materials such as slags, ores and rocks, all organic ashes, wet chemical precipitates, sludges, etc. *Spex Mix*, the base from which the standards are made, is used for the determination of impurities in "pure" materials.

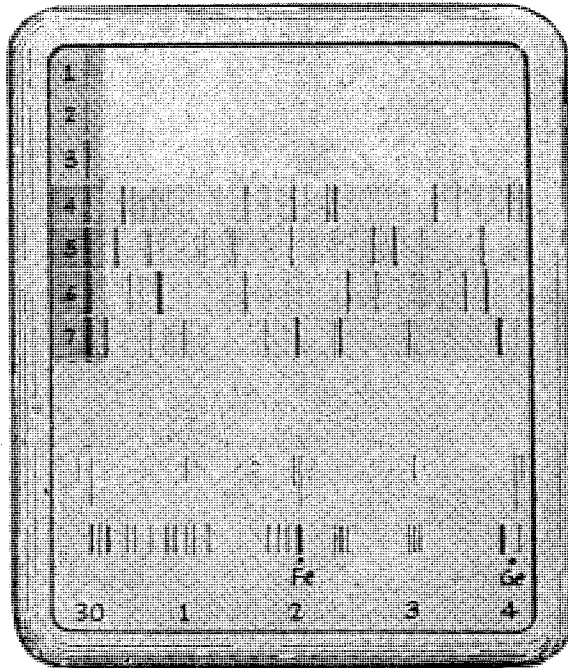
The technique recommended depends on burning an entire set of three or four standards on the same plate with the prepared unknown. Dr. E. S. Hodge, of Mellon Institute, described a technique at the last Pittsburgh Conference on Applied Spectroscopy and Analytical Chemistry which saves a good deal of time. Instead of burning the standards on each plate, Hodge suggested that an arbitrary scale be made up which had previously been compared with the standards. The lines in the unknown can then be compared with the lines of different densities on the scale.

As shown below, the scale consists of seven lines of increasing density on a transparent film strip. This is mounted inside the viewing screen of the comparator-microphotometer. In use, the spectrographer first matches a chosen line against one of the lines of the Scale and assigns it this number. Then, referring to a previously made chart, he obtains percent concentration directly from the assigned number.

The accuracy of the method, of course, depends on how well day-to-day conditions are maintained in the laboratory. The same emulsion (SA #2) is recommended; also the same optics, electrodes, etc. When these precautions are taken, the method is capable of accuracies sufficient for analyzing most such "semi-quantitative" samples. Dr. Hodge proved its effectiveness in the analysis of over 25 National Bureau of Standards and U. S. Geological Survey standards.

In order further to simplify the laboratory operations, we

are supplying the Semi-Quantitative Scale together with a kit. In addition to a complete set of instructions, the kit contains 100 data sheets (enough for analyzing 100 samples) and a set of conversion charts for converting the density matching figures to percent concentration. The G (graphite base) Standards are recommended for setting up the method which, incidentally, involves no more than two hours.



- 1100 Hodge Semi-Quantitative Scale. Included with the scale are 100 data sheets, instructions and a set of conversion charts mounted in celluloid folders to protect them in use \$21.00
- 1101 Additional data sheets for above
Per 100 \$2.80
- 1002 G Standards, set of 4; G-1 contains 0.1% of 43 elements, G-2 contains 0.01%, G-3 contains 0.001% and G-4 contains 0.0001% of the 43 elements. Graphite base.
Per set \$44.00
- 1000 Spex Mix, base from which the standards are made. Contains 43 elements, each one at exactly 1.34% conc.
Per 2 grams \$36.00

SPEX presents the
Crescent
WIG-L-BUG
 (Patented)



*end mixing-grinding
 drudgery!*

EMISSION SPECTROGRAPHIC ANALYSIS

"Saves us 70 minutes per plate in the preparation of our diesel crankcase oil ash samples."

X-RAY DIFFRACTION

"The best scheme we have found for pulverizing asbestos fibres."

"We have improved our powder patterns in two quite significant ways: reduction in preferred orientation and much better uniformity from film to film because of controlled particle size."

X-RAY SPECTROSCOPY

"Ideal for diluting samples to bring intensity levels down to optimum values."

INFRA-RED SPECTROSCOPY

"Perfect system for grinding our samples with KBr; improves resolution tremendously."

"We obtained far superior band structure after mulling samples for two minutes with mineral oil in the Wig-L-Bug than 20 minutes by hand."

Such are the enthusiastic comments on the Wig-L-Bug a short time after we introduced accessories tailored for the spectroscopy and diffraction laboratories.

SEND US A SAMPLE FOR MIXING OR GRINDING WITH THE WIG-L-BUG. AS REQUESTED, WE SHALL GRIND IT IN STAINLESS OR TOOL STEEL OR MIX IT IN PLASTIC VIALS. THE SAMPLE WILL BE RETURNED TOGETHER WITH FULL INFORMATION ON THE CONDITIONS USED FOR MIXING OR GRINDING.

SPEX MAKES SPECTROSCOPY EASIER