

# Speaker

## SOLID STATE MASS SPECTROSCOPY

PROGRESS in analytical chemistry has been interrupted repeatedly by sensitivity lags—periods when technology had bogged down painfully for the lack of analytical techniques of sufficient sensitivity. Various breeds of spectroscopy have, through the years, saved the day. One famous example in the '30s was the exasperating habit of zinc-base die cast automobile door handles to snap off in the hand of an astonished motorist. Perfectly sound when produced, the faulty casting would develop intergranular corrosion after months of exposure to moist air. It took diligent sleuthing to conclude that the handles subject to failure came from particular lots of metal. Yet the most exhaustive wet chemical methods then employed could detect no significant differences between good and poor metal. Not until emission spectroscopy pinned down the culprits as traces of tin, cadmium and lead was the mystery solved.

Titanium dioxide as a pigment represents a well-known case of x-ray diffraction to the rescue. After all other analytical methods failed to distinguish between batches of  $TiO_2$  with good and poor whiteness and hiding power qualities, x-ray diffraction studies eventually revealed that the crystal structure was the determining factor. One form of  $TiO_2$  (anastase) is poor while the other (rutile) is so good that it has become the most extensively used pigment in paints, paper, cloth and plastics.

If it had no other virtues, California smog served as an excellent testing ground for infrared analysis. Thick as it appeared, the actual weight of air pollutants was so small as to defy analysis by most methods. Only through the use of cells folded to stretch to an effective length of many meters, could infrared analysis furnish a detailed story. The analyst can now pinpoint the source of pollution and estimate how much originates from the exhaust and engine vents of autos, how much from oil refineries and other sources. So well established is this method that automatic analyzers have been installed in several cities.

But insufficient sensitivity is still the problem in many fields. Semi-conductor technology is a good illustration. Here the emission spectrographer simply cannot differentiate between various grades of germanium or silicon now sorted—and priced—on the basis of electrical characteristics. While the wet chemist bows to the emission spectrographer at around the 0.01% concentration level of elemental impurities, the latter now finds himself squirming when faced with impurity levels in parts per billion.

To detect such concentrations (incidentally a few ppb still involves around  $10^{13}$  atoms/ml), there appear to be only two techniques known. These are neutron activation and solid state mass spectroscopy. The former, making use of samples made radioactive by high-intensity irradiation has the disadvantage of requiring an expensive reactor or accelerator plus

the attendant shielding and safety measures. There are, nevertheless, several government and private laboratories providing irradiation services. When the half-life of an impurity product is sufficiently long, such services are quite valuable. To determine traces of sodium with an isotope having a half-life of 15 hours is practical using a distant reactor; to determine aluminum ( $Al^{28}$  half-life = 2.3 minutes) is impractical.

Because of these limitations, the best approach to ppb elemental determinations appears to be the mass spectrograph adapted to handling solids. This is an instrument designed to vaporize all of the elements, ionize them and beam them individually to a detector. With this technique, theoretically every element may be detected—as contrasted with neutron activation—and at trace levels where they influence the performance of semiconductor devices.

THE mass spectrograph had its origins in England with J. J. Thomson's work with positive rays dating back to 1912. By then, it had been known that, if a perforated metal disc was placed in a discharge tube and a gas admitted under low pressure, luminous rays would be produced when a voltage was applied. The rays corresponded to the holes in the disc and were associated with the positive charge. Thomson directed the positive rays through first an electric field, then a magnetic field at right angles to one another and finally to a photographic plate. He showed that the parabolic streaks obtained on the plate corresponded to the mass-to-charge ratio of the atomic and molecular species present in the gas. In his historic experiments and those of his assistant, F. W. Aston, the groundwork was laid for the use of mass spectroscopy to separate elements and their isotopes. By 1920, Aston had examined 19 elements and discovered that nine of them consisted of two or more isotopes.

Working independently in the United States at the University of Chicago in 1918, A. J. Dempster designed a mass spectrometer to determine the relative proportions of the elements present as well as their masses. In his instrument, the detector for which was an electrometer in place of a photographic plate, the magnetic field was so arranged as to be "direction focusing." That is, by adjusting the strength of the magnetic field, particles with any desired mass number could be fed one by one to the detector. By arranging his source so that all particles would emerge from the source with the same energy, Dempster could thus quantitatively analyze a sample.

Early mass spectrometers had two limitations when applied to trace analysis of solid samples. Utilizing a heated crucible (Knudsen cell) to volatilize the sample, elements would vaporize selectively with different ionization efficiencies precluding accurate analysis. Furthermore, the highest temperature the cell could attain ( $2500^\circ C$ ) was limited by its own composition and even at that temperature elements whose vapor pressure

was below  $10^{-6}$  torr were not detected. Present practice for trace analysis is to use a radio frequency spark of high intensity. Here instantaneous discharges with a power output of up to 15 KW produce gaseous ions of all constituents at an equal rate without regard to their vapor pressure. Up to 100 KV at a frequency of about 1 megacycle are applied to the sample. The length and frequency of each pulse are adjustable between 25 and 200 microseconds and 1-10,000 pulses per second, respectively. The ion beam, carrying a maximum current of  $10^{-9}$  amperes, is directed to a photographic plate.

The second limitation of early mass spectrometers was resolution. To provide a high signal-to-noise ratio, present practice is to use a Mattauch-type spectrometer. In this system, a double focusing principle is employed which, in optics, is analogous to achromatism. Just as an achromatic lens focuses at the same plane for all wavelengths, with a Mattauch instrument a sharp image of the primary slit is obtained on a flat photographic plate at any mass number. The ions pass first through an electrical field and then a magnetic field, the geometry and parameters of which are so specified as to perform the desired focusing. Mass resolution up to 2500 is characteristic of most modern instruments.

Although the theory behind the Mattauch design is beyond the scope of this paper, his double focusing principle compensates for a problem common to all known spark sources. Instead of ions emerging perfectly linearly and with constant velocity, there is always some degree of angular divergence and variation in velocity. To the mass spectrometer, unless controlled, these would appear as deviations in mass-to-charge ratio with consequent line broadening.

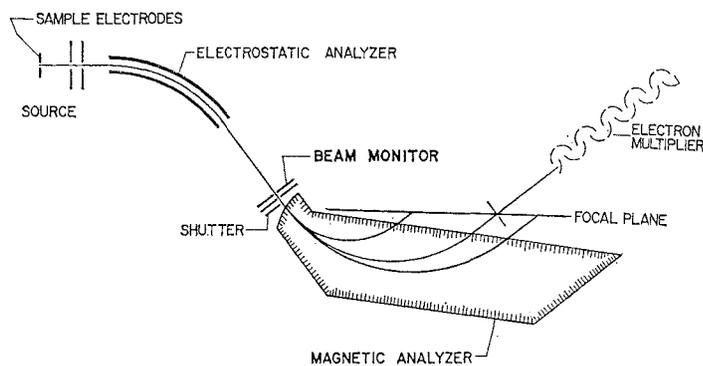


Fig. 1. Schematic diagram of a Mattauch Analyzer. This instrument is designed for photographing Li to U in one exposure. Alternatively, the mass spectrum may be recorded with an electron multiplier (courtesy Nuclide Analysis Associates, State College, Pa.)

THE all-out effort to produce an atomic bomb during World War II gave impetus to research on many mass spectrometric devices. The calutron was developed as a means for separating on a production basis  $U^{235}$  from its sister isotopes. The helium leak detector was invented. Dempster designed and built a double focusing instrument for the analysis of solids and specifically to determine impurities in uranium metal. Making use of a vacuum spark similar to that in today's commercial instruments, Dempster showed that with but 10 mg of uranium metal and exposures of around 3 minutes, the detection concentrations of Li, Be, B, C, O, F, Ne and Mg ranged from 0.02 ppm for Be to 40 ppm for O, presaging the use of the methods to detect even tinier impurities. He also pointed out that the very elements difficult to determine by optical emission spectroscopy—S, P, Na, O, N and C—seemed to be

particularly amenable to mass spectrometric analysis. Still another advantage of the method observed by Dempster, in contrast with optical emission, was the very simple spectrum obtained. The mass spectrum of each element consists of a principal line repeated at fractional mass values (but at reduced intensities) due to ions with multiple charges.

Identification of an element is thus made with assurance by measuring the position of but two or three of its lines in an uncluttered spectrum. This, of course, is in contrast with a many-lined optical emission spectrum, especially of transition elements such as uranium.

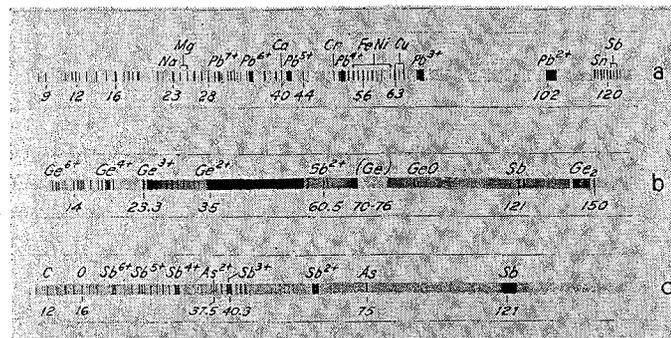


Fig. 2. Typical mass spectra. The top is of "high-purity" Pb exposed for 2 minutes. The middle is of Ge with 6 ppm of added Sb. The bottom is of Sb with 100 ppm As (courtesy A. J. Ahearn, Bell Telephone Laboratories, Murray Hill, N. J.)

Though optimistic about the eventual potentialities of solid state mass spectroscopy, Dempster felt that progress might be slow like that in emission spectroscopy where for 50 years following Bunsen's work, very little practical exploitation of the principle was made. But the need for determining ever-smaller traces of impurities hastened the utilization of the solid state mass spectrograph and today a half-dozen organizations manufacture units.

In addition to the pioneering work of Dempster further impetus came from N. B. Hannay and A. J. Ahearn of the Bell Telephone Laboratories in Murray Hill, N. J. With the invention of the transistor, also at Bell Labs., it became apparent that some means had to be found for determining impurities in semi-conductor materials in the ppb concentration range. Learning of Dempster's work, Hannay set out to build a similar instrument which was completed in 1953. Restricted initially to the analysis of solids 0.030-0.040" dia., the instrument was used to show that detection limits for most elements were easily in the atomic concentration range  $10^{-7}$  to  $10^{-4}$ , the limit being set by 1) faint background lines due to traces of organic constituents in the source and the chamber; 2) background due to ion scattering and change of ion mass or charge during transit. With the original instrument Hannay and Ahearn were encouraged to find traces of Sb in Ge at levels too low to be seen by emission spectroscopy. They also came to the tentative conclusion, since verified, that the intensity of lines of any element at the same atomic concentration is roughly equal. Greatly facilitating semi-quantitative analysis, this is in sharp contrast with emission spectroscopy where each element acts quite unpredictably.

This property of almost constant intensity with concentration irrespective of the element is probably the most attractive feature of solid state mass spectroscopy. Based on the analysis of many samples of known composition, the assumption appears to be valid within at least a factor of two. What it means in practical terms is that the technician need not go to great lengths to calibrate his instrument and procedure using samples closely approximating those he wishes to analyze. He

merely obtains information for one set of standards interpolating the data to his unknowns. At the ppb levels of greatest interest to the method, he is readily forgiven if his results are inaccurate by only a factor of two. On the other hand, an emission spectrographer would normally be forced to prepare a number of standards (often a tricky job indeed when the elements to be calibrated are in trace levels) in order to report concentration values accurate to a factor of even ten.

**M**ASS spectrometers must have a resolution of at least 1500 in order to separate lines of interest. The resolution is defined as the mass divided by the difference in mass between two distinguishable neighboring lines. A typical problem is the determination of sulfur in the presence of oxygen, an impurity associated with all high-vacuum instruments. The  $O_2$  line has a mass of 31.9898 while that of sulfur is 31.9721. A resolution of 1800 is thus necessary to free the sulfur line from oxygen interference.

Oxygen is but one of the impurities found in vacuum systems. Carbon and hydrogen from the air and organic materials are two other common ones. These plus the fact that outgassing associated with the ion beam causes a pressure rise to about  $10^{-5}$  torr during sparking in the spark chamber emphasize the need for a good vacuum system. The best vacuum, in the order of  $10^{-8}$  torr, is required for the highest degree of sensitivity. This, however, increases the analytical time as well as the complexity and cost of the pumping system. In general, a practical compromise is to work in the  $10^{-7}$  torr region using separate diffusion pumps in the source and analyzing regions of the spectrometer backed by a single roughing pump.

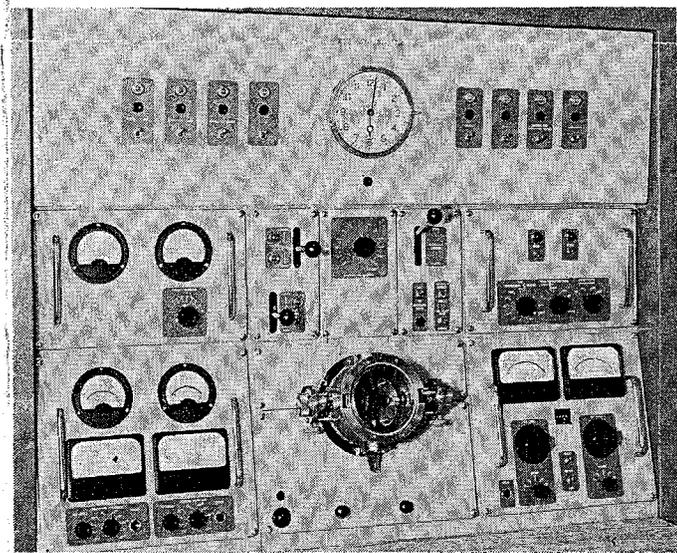


Fig. 3. The control panel and sample chamber of a commercial instrument (Associated Electrical Industries, represented in the U. S. by Picker X-Ray Corporation, White Plains, N. Y.)

To attain ultra-high vacuums and thereby greater sensitivity, some instruments are designed to be baked out in order to remove adsorbed gases. Separate vacuum locks are provided for both the source and photographic plate compartments to facilitate pump down. Also, instruments have been built with a magazine source, permitting the operator to run several samples in succession without breaking the vacuum at all. The camera is generally rackable permitting up to 15 exposures to be made. The Ilford Q-2 emulsion, also used for the region 50-2500A, is the photographic plate often chosen.

**T**HE mass spectrum of a material, as shown in Fig. 2, closely resembles an optical emission spectrum. Sharp lines are superimposed on a background of varying blackness. The strongest line or group of lines is due to the singly ionized isotopes of the major constituent. The same group of lines appears at  $1/2$ ,  $1/3$ ,  $1/4$  and  $1/5$  of their respective masses due to the multiply ionized species. Intensities of the latter fall off progressively.

Identification of lines is simplified not only by the relative sparsity of lines but also by the intensity ratio of isotope lines corresponding to their abundance ratio. This is often used as a means of quantitative calibration because natural abundance ratios are well established.

At the high mass end of the spectrum polymer species are observed. These groups are more complex as combination of isotopes of different masses occur.

At low concentrations of impurity elements, only the lines produced by the singly ionized isotopes are recorded as contrasted with higher concentrations where the multiply ionized lines appear. Positive identification is established if two or more isotopes of the impurity element are detected at the intensity ratio corresponding to the abundance ratio. Only for monoisotopic elements is it necessary to double check by finding the line of a second ionized species.

Near the detection limit of an element generally only one line will be detected and here interferences should be studied closely before reporting. The presence of complex ions such as  $SiO^+$  as well as elemental ions must be considered.

As contrasted with optical emission spectroscopy, where the sensitivity for elements varies by several orders of magnitude, in mass spectroscopy the thresholds are about the same for all elements. With the exception of O, N, C which, as mentioned previously are troublesome below 10 ppm because of residual traces in all vacuum systems, all elements may be detected down to about 10 ppb at an exposure of around  $1 \times 10^{-6}$  Coulomb. This corresponds roughly to around 30 minutes. An increase of exposure time above this, in general, increases both the noise and signal although some elements, especially those with single isotopes, have somewhat higher sensitivities. To attain appreciably higher sensitivities, higher vacuum helps considerably.

**T**HE intensity constancy of mass lines of the same concentration permits a generalized formula for semi-quantitative analysis. Typically, a series of exposures with increasing and known exposure levels (e.g.,  $3 \times 10^{-13}$ ,  $1 \times 10^{-12}$ ,  $3 \times 10^{-12}$ , up to approximately  $3 \times 10^{-6}$  Coulomb) is recorded. The density of the line of an isotope of the impurity element is visually matched against the density of an isotope line of the major constituent. The concentration of this impurity can then be calculated from the following formula:

$$C(\text{ppm, atomic}) = \frac{E_2}{E_1} \times \frac{I_2}{I_0} \cdot \frac{S_2}{S_1} \cdot \frac{A_1}{A_2} \cdot \frac{M_1}{M_2} \cdot 10^6$$

where

$E_2/E_1$  is the exposure ratio where the same density is observed for the impurity and the matrix isotope.

$x$  is the concentration of the major constituent in per cent.

$I_2/I_1$  is the ratio of the abundance of the matrix and the impurity isotope.

$S_2/S_1$  is the ratio of the relative sensitivity of the emulsion to the isotope of the matrix and impurity element. This is usually unknown and taken to be unity.

$A_1/A_2$  is the ratio of the areas of the mass spectral line. The quantity is close to unity and usually disregarded.

$M_2$  and  $M_1$  are the ratios of the intensities of the singly charged ions to those of the multiply charged ions on which the estimate is based. Usually singly charged isotopes are used and this factor becomes unity.

Example: In a silicon sample the boron line at mass 11 at an exposure of  $10^{-6}$  Coulomb matches the silicon line at mass 30 in density at an exposure of  $10^{-13}$  Coulomb:

$$\text{conc. (boron), ppm atomic} = \frac{10^{-13}}{10^{-6}} \cdot \frac{100}{100} \cdot \frac{3}{80} \cdot 10^6 = .0037$$

**Y**ES, there are disadvantages to the method! Foremost are the cost and complexity of the apparatus. To perform, the solids mass spectrometer must have a fast pumping high-vacuum (better still ultra high vacuum, i.e., capable of attaining  $10^{-8}$  torr) system. It must have an electrostatic compartment with a voltage stabilized to better than 0.01% and with a field uniformity of better than 0.1%. The magnetic section must have current stability even better than the voltage stability of the electrostatic section and the magnetic field must be uniform and variable from 2000-15000 Gauss.

Another disadvantage is the relatively poor speed of analysis, certainly by contrast with optical emission spectroscopy. A typical sample requires about a day to analyze for trace constituents. This allots time to the clean-up of the source compartment between runs. Contamination from sample to sample must be guarded against at all times, particularly since a sample is sparked for several hours during which time a good deal of material may be spattered and sputtered inside the instrument. Thus, although magazine loading devices have been built for running several samples without breaking the vacuum, the possibility of contamination discourages their use in trace-element analysis. What does help improve the picture on speed is the use of vacuum locks at both the source and camera ends, enabling the operator to change samples and plates without having to repump the entire instrument.

Speed of analysis may be materially improved if the mass spectrometer can be adapted to photoelectric detection with integrating circuits similar to those used in direct reading optical spectrometers. The problem here is to detect the extremely small currents corresponding to ppb intensities.

Still another shortcoming is the limitation on sample shape and form imposed in many designs. Ahearn devised a method of releasing ions from a solid insulator by sparking between it and a semi-conductor chosen for its high purity. He has also devised procedures for detecting impurities on surfaces by sparking to the latter while it is advanced manually. Ahearn claims to be able to detect surface contaminants equivalent to 0.01 of a monoatomic layer in this fashion, a feat that fills the optical emission spectrographer with envy. In one problem, he showed that the surface of a supposedly pure sample of silicon had actually become contaminated with boron when it was heated in a boro-silicate glass vessel.

Although this article was written primarily with the idea of trace element analysis, the Bendix Time-of-Flight Mass Spectrometer deserves mention. This instrument separates masses in time rather than displacement, the more conventional approach. With it 10,000 complete mass spectra may be obtained every second, lending the system to the use of

oscillographic readout with its attendant speed over photographic recording. At present its principal disadvantage is low resolution precluding its application to ultra-trace analysis of solids. If the resolution can be improved to match the Mattauch instruments, the decided advantage of instantaneous readout will unquestionably suggest many applications.

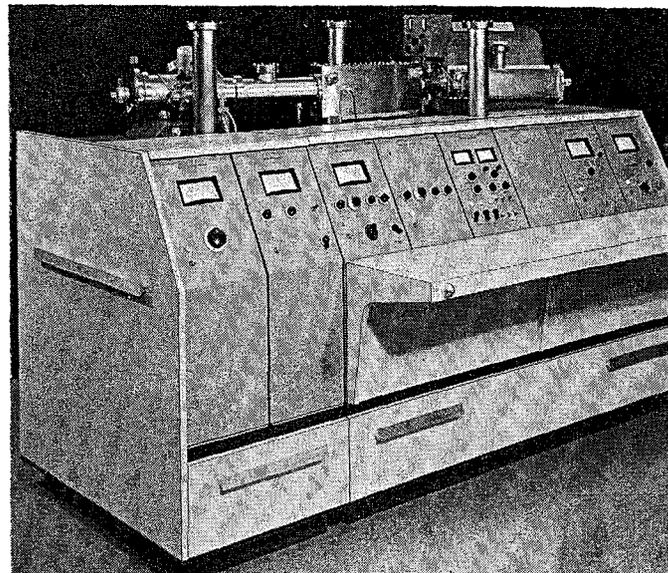


Fig. 4. The CEC 21-110 Mass Spectrometer (courtesy Consolidated Electroynamics, Pasadena, Cal.)

**A**CTIVELY competing manufacturers, a group of inspired workers and a growing need. Such a combination is certain to swell the science-art of solids mass spectrometry. We owe a debt of gratitude to Dr. Wilhad Reuter of the Thomas J. Watson Research Center, IBM Corporation for his help in assembling many of the data for this paper and to Dr. A. J. Ahearn of the Bell Telephone Laboratories for taking the time to review this manuscript in detail before its publication.

—A. J. Mitteldorf

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## CONTRIBUTIONS SOLICITED

Not money but information. Since its introduction less than two years ago, we have sold literally hundreds of Stallwood Jets. Presumably, the word has spread that there are decided advantages in its use. Yet only scanty information has returned to us. How many spectrographers are actually making good use of the accessory? In what way or ways has it aided your procedures? Is it of value in ways other than those of which we are aware?

To be sure, several applications have come to our attention. One company has been able to improve the detectability of zinc in nickel-plating solutions to the point where they can determine when the zinc interferes with the bath. Another has found it exceedingly valuable in localizing the spattering from silver samples while boosting sensitivity for impurities. Others are known to be using the Jet for freeing the *raies ultimes* of many rare earths, tungsten, iron, molybdenum and uranium to obtain an overall gain in sensitivity of as much as 10-fold.

We would be happy to publish additional information. If you would jot down a short note telling us of your experiences—pleasant or otherwise—with the Stallwood Jet, we shall be happy to publish it in the next issue of the SPEAKER.

## CONTROLLED ATMOSPHERE CHAMBER

As an increasing number of elements are hunted at ever decreasing concentration levels it becomes evident that that complex mixture of gases at 960 cm pressure known as air is not the best atmosphere in which to excite samples. Surely, it is easiest for the spectrographer to run his analyses in the open atmosphere. No special containers and vacuum equipment are required; there is relatively little fogging and cross-contamination between samples; samples are readily loaded into electrodes. Yet the odds are that a different mixture of gases at a lower pressure than atmospheric would probably be better for many analyses and that a mixture and pressure could probably be found which, though not optimum for a particular analysis would, nonetheless, be far better overall than air.

The search for such a mixture might have been delayed for many years were it not for the work of Dr. V. A. Fassel's group at Iowa State University, who, faced with the job of determining oxygen in titanium at a time when advances in the metallurgy of the metal were being thwarted by accidental pickup of oxygen, found it necessary to run their samples in the absence of this gas. They devised methods which, though nicely applicable to the measurement of oxygen in many metals, show considerable promise also to the determination of metals at much lower concentrations than can normally be detected.

It was W. A. Gordon, a former graduate student of Dr. Fassel's now employed by the National Aeronautics and Space Administration, in Cleveland, who suggested that the same methods be tried on metal determinations. He felt, and some of his predictions have already been borne out, that an improvement in sensitivity could be attained for many elements when run at low pressures of gases with a comparatively high ionization potential.

With Mr. Gordon's technical assistance, we designed a chamber overcoming many of the objections he had pointed out. Below are enumerated the problems as well as our solutions to them:

1) Degassing electrodes. Graphite rods adsorb air which, when arced, is excited contributing heavily to the background particularly if any element present in air is sought. The solution worked out by the Ames group was to preburn the electrode without a sample in a low-pressure argon atmosphere; then, after increasing the argon pressure above atmospheric, to remove the upper electrode and drop a pellet through the hole into the sample electrode. Although the positive pressure of argon prevented further adsorption of atmospheric gases, this sequence of operations was laborious. Our solution is depicted below. Up to 11 electrodes are loaded in their individual stations in a turntable and arced in low pressure argon one after the other. Before sealing the chamber, the samples, in the form of solid chunks are placed in holes in a disc as shown. Immediately below this disc is another to prevent the chunks from falling through. In one position, there is a mating hole. When the top disc is turned, a chunk will fall through this hole and into the waiting electrode below. Tiny funnels are placed in the bottom hole in order to make sure that the chunk will drop accurately into the electrode crater. The disc is turned by means of an external gear segment and a pinion turned from outside the chamber. In our design the same shaft positioning the electrodes is used to drop the samples. Two pinions are so placed on the shaft that by pushing the latter upwards or downwards one or the other will engage its ring gear. In practice, therefore, it is a simple matter for the operator either to turn the electrode into position or drop a sample by pushing the shaft up or down through its high vacuum seal.

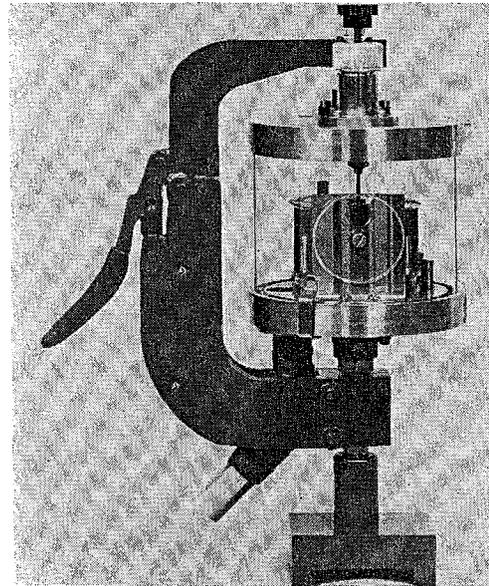
2) Fogging of the window. All samples when arced vaporize to an extent that clouds the window and blocks light from the spectrograph. In some of the earlier designs to counteract this, the fogged quartz window had to be replaced between burns. Just as with loading electrodes, this required blowing in a gas to keep out the air and then reevacuating. In our design, a quartz disc rimmed with iron protects that section of the quartz chamber acting as a window to the spectrograph slit. The disc is baffled except for a small section through which the light passes. As it clouds over, the disc is turned to a clear area from outside the vacuum with a small magnet.

Our Chamber, incidentally, does not make use of the traditional design in which a quartz window is placed in a side arm. Light passes directly through the quartz cylinder. For ordinary spectrochemical work, there is no perceptible effect, spectral lines appearing as they do normally.

3. Cross-contamination. Vapors not only cloud windows; they also contaminate samples waiting their turn. To prevent this we have provided an arrangement whereby each electrode is maintained in a compartment with a cover to catch the fallout. Only when the electrode is to be arced is it advanced to an uncovered compartment. The covers (which also serve to support the sample pellets) as well as the walls are easily disassembled for cleaning.

4) Assembly and disassembly. The entire unit is mounted on a bar which, in turn, fits an optical rider for the individual spectrograph. A toggle clamp seals the top and bottom sections through a quartz cylinder and neoprene washers. Simply releasing the toggle lever lifts the top metal plate out of the way so the quartz cylinder can be removed and the electrodes replaced. When necessary, baffles and the magnetically turned quartz disc are removed for cleaning.

Another feature of the instrument permits the use of electrodes of different diameters. Buttons with the appropriate i.d. are placed in holes in the turret. With this arrangement, 1/8", 3/16", 1/4" and 5/16" dia. electrodes can be used in all or any of the stations.



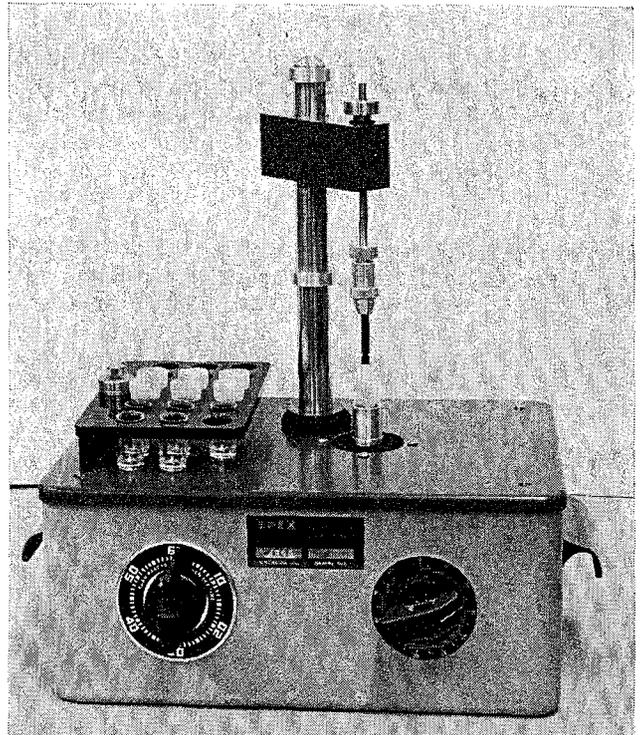
- 9700 **Controlled Atmosphere Chamber**, mounted on rider for optical bar (specify manufacturer), complete with set of 11 collets to accommodate 1/8" dia. 3/16" dia., 1/4" dia. or 5/16" dia. (specify) electrodes .....\$1,450.00
- 9701 **Collet**, specify diameter as 1/8", 3/16", 1/4", or 5/16" dia. ....Each \$ 9.00

# ELECTRODE LOADER

We think we now have it, a device for quickly and reproducibly loading graphite electrodes through a vibratory tamping action. This loader is somewhat belated, perhaps, in the wake of No. 1 (which was too highly priced for most of our pockets) and No. 2 (which impatiently broke loose before finishing school).

The #4510 boasts a variable collet which automatically adjusts for electrodes of  $\frac{1}{8}$ ",  $\frac{3}{16}$ " and  $\frac{1}{4}$ " diameters. In test performances we have been packing 20-40mg of Graphite or Lithium Carbonate reproducibly in 15 seconds per sample. Sticky substances such as Zinc Oxide, however, do not behave as obediently because they adhere to the outside of the electrodes.

So before hastening to your requisition pad we suggest you have us make trial runs with your own materials. Only then can you be sure that the Loader will do your job better than by hand. Send us your materials together with a few of your pet electrodes and we'll return them promptly—loaded to the brim, we hope!



# 2

## NEW SPEX INSTRUMENTS

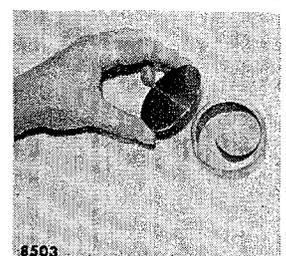
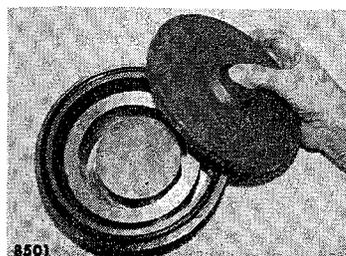
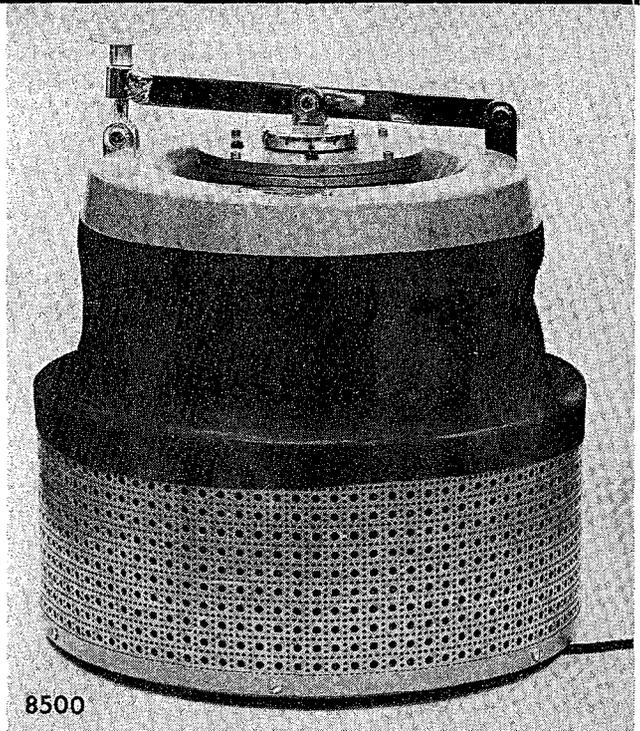
### SHATTERBOX<sup>®</sup> HIGH SPEED GRINDER

In this field, when something new is designed you can always count on the first prospect to ask for a bigger one. So it was with our No. 8000 Mixer/Mill about 1000 units ago when we were out scouting for customers. The first man we contacted was delighted by the speed with which blast furnace slag could be pulverized, and he liked the idea of having the material stay put in a closed container, but he simply needed more material than could be ground in a single load.

Well, we now have the answer in the SHATTERBOX, a grinder operating as swiftly, efficiently, and reproducibly as the Mixer/Mill but capable of loads up to 100 ml compared to 10-25 ml. The SHATTERBOX swings its container like a hula hoop at about 900 rpm. Inside the closed hardened steel dish (#8501) a heavy ring and puck (also of hardened steel) batter the sample, reducing the typical one to usable fineness in 3 minutes or less. Alternatively the #8500 dish will hold seven #8503 vials each with a capacity of 15 ml.

The SHATTERBOX appears to be equally suitable for grinding the same wide ranges of brittle materials now ground in our Mixer/Mills. These include rocks, ores, slags, many metals, ceramics, oxides and finished products.

#8500 can grind 100 ml of sample or hold seven #8503 vials for multiple sample grinding.



# ACCURACY REPORT ON SEMI-QUANTITATIVE ANALYSES

Of the questions asked us ever since our semi-quantitative standards were formulated seven years ago, one most often posed relates to the accuracy potential of the method. Our stock answer is that this depends on the time and effort devoted to the analysis which, in turn, relates to its importance. Often, for quality control, it is necessary to ascertain only that all impurities are below, say 10 ppm. In another typical problem, the spectrographer is merely called on to find out how two samples compare. Still another problem involves a survey to serve as a guide to geologists or chemical engineers where accuracy requirements again are not too severe.

But, increasingly, the spectrographer is called upon to furnish a complete elemental analysis of a sample with as high an accuracy as he can achieve commensurate with the time savings expected over non-instrumental methods. In order to find out for ourselves and other users how best to go about handling such samples, we ran five standards by a technique modified for the purpose.

The problem is many-faceted. A sample may run the gamut both in the number and concentration of anions and cations. Volatile, low ionization point elements may exist as impurities in a refractory base and vice versa. The need may be for a picture of the major elements and/or those at trace levels.

All considered, we decided to use the following:

1) Spex L Standards (No. 1004) mixed 1:1 with National SP-2, -100 mesh graphite powder. Internal standardization was, of course, necessary and the  $\text{Li}_2\text{CO}_3$ -based L Standards met this criterion. For refractory materials the addition of graphite prevented the formation of non-conducting oxide beads. The particular graphite chosen was easy to handle and weigh out and particles did not tend to fly out of the cup during arcing.

2) DC arc excitation with the Enclosed Stallwood Jet (Spex No. 9027, water-cooled). The combination has been

shown by numerous spectrographers to result in a reduction in background in many areas of the spectrum. At the same time, by stabilizing the excitation, the Stallwood Jet thus offers real improvement in precision and accuracy. Eight amperes were used in the source and a flow rate of 9 cfh of a 30:70 mixture of oxygen:argon through the Stallwood Jet.

3) National SPK preformed electrodes. We have not seen data to substantiate this but are convinced that the superior physical uniformity of this grade of graphite should result in improved reproducibility. The sample electrode was an under-cut 3/16" preform L-3706 (Spex No. 4004); the upper a pointed 1/8" preform L-4236 (Spex No. 4019).

4) SA No. 2 plate (the work was performed before the SA No. 3 emulsion was announced). Our reasoning here was to have a long, relatively shallow-sloped characteristic curve, uniform for all wavelengths. In the final figures, we limited our data to lines with transmittances in the range 10-70% because, as a simplifying compromise, we used but one internal standard line, Li 2741.2A. A three-step filter (Spex No. 1090) assured obtaining at least one step of each line in the specified transmittance bracket.

5) Dilutions of samples with the one: one  $\text{Li}_2\text{CO}_3$ : graphite mixture of 1:9, 1:99 and 1:999. The rule followed was to choose the greatest dilution which would give spectral lines of the elements sought in the 10-70% transmittance range.

We have not treated the data statistically but, quite obviously, it would be regarded, on the whole as good, semi-quantitative information. If quantitative accuracy is required, probably the fluxing technique of Tingle and Matocha (see Vol. VI, No. 4 of the Spex Speaker) offers the best choice. The time and effort, however, well exceed that of the present method. Furthermore, since spark excitation is normally used on the pellets, obtained by pressing the flux together with graphite, sensitivity suffers.

ELEMENT	USGS G-1		USGS W-1		BAS MANGANESE ORE		NBS LEAD BARIUM GLASS		NBS BOROSILICATE GLASS	
	A	B	A	B	A	B	A	B	A	B
SI	33.9	31	24.6	28	3.87	2.7	30.5	23	37.7	33
CA	.97	.87	7.8	-----	.557	-----	.15	.16	-----	-----
MG	.24	.25	3.98	3.8	.422	.4	.018	.017	.0157	.012
FE	1.37	1.4	7.76	8.5	1.49	1.8	.034	-----	.0532	.05
MN	.021	<.05	.14	.18	51.3	-----	.068	.064	-----	-----
AL	7.54	6.7	7.94	8.7	.641	.73	.095	.076	1.03	1.0
TI	.144	.16	1.647	.85	.012	.03	.06	.10	.016	.01
CR	-----	-----	-----	-----	.893	.84	-----	-----	-----	-----

In Column A appear the % concentrations as standardized

In Column B appear the % concentrations as determined

The first two standards are ground rocks prepared by the U. S. Geological Survey; the others are by the British Bureau of Analysed Samples, Ltd. and the National Bureau of Standards.

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INDUSTRIES INC.



### UNIMAT LATHE—AUTOMATIC FEED ATTACHMENT

The almost universal acceptance of preformed graphite electrodes for spectrochemical analysis has benched many an electrode shaper. Yet there is often the need in the laboratory for a specially shaped electrode and the best device for its preparation is a small lathe with its inherent flexibility.

The Unimat, basically a lathe but capable of innumerable adaptations—to a drill press, milling machine, a hand drill—is particularly well suited for many such laboratory operations. With the addition of a new accessory, an automatic feed attachment, it becomes even more attractive. With a flip of a lever, the tool carriage travels uniformly at a rate of .0008" per spindle revolution.

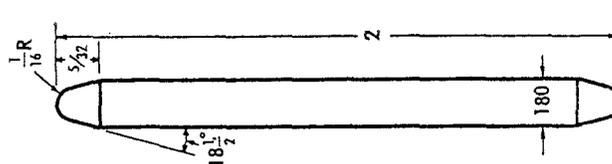
Daily uses will be found in many laboratories for the Unimat to face off small discs as well as to shape graphite, copper, silver and other metallic rods. When used as a drill press, the spectrographer can speedily obtain chips for solution work.

Send for the leaflet in which all of the accessories are described.

**7200 Unimat**, dimensions of lathe bed: 14-1/2" long x 4" wide x 5" high. Complete with 3-jaw reversible chuck which will hold pieces up to 2-1/4" d. rotating headstock, tailstock, cross-slide, 3500 rpm, 1/15 hp motor, 115 vac, 1/4" drill chuck, face plate, lathe dog, grindstone arbor, tool post, 2 dead centers, upright steel post, eleven speed belt drive. In wooden chest. Shipping weight 38 pounds. Each \$136.00

- 7201 Set of 6 tool bits .....Set \$ 10.00
- 7202 Lathe Chuck, 4-jaw, independent .....Each \$ 23.00
- 7203 Collet Holder, including 1/4" collet .....Each \$ 14.00
- 7204 Collet, from 1/64" to 5/16" dia. in 64ths (specify) .....Each \$ 4.00
- 7205 Live Center, for high-speed turning .....Each \$ 4.50
- 7206 Automatic Feed Attachment, complete with instructions, can be mounted on Unimat Lathes already in use .....\$ 26.00

### NEW COUNTER ELECTRODE



National Carbon Co. has added a double-pointed counter electrode to their catalog items. Available in SPK and AGKSP, this preform is identical with L-3954 and L-3754 except that both ends are pointed. This feature allows double use for each electrode and thus affords considerable savings particularly for users of large quantities of electrodes.

- L-3755 SPK grade Double-pointed Counter Electrodes, 3/16" dia. ....100 \$ 24.00
- L-3955 AGKSP grade Double-pointed Counter Electrodes, 3/16" dia. ....100 \$ 24.00