

THE SPEX SPEAKER

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We're pleased to announce our first move to larger quarters. As we write this, "Wet Paint" signs surround us, and a plumber has just disconnected us from civilization while the phone man is trying his best to reconnect us. When you're in the vicinity, please accept our cordial invitation to visit. Not much to see but we could discuss our favorite topic awhile.

As part of this expansion program, we are proud to tell you that we now represent Paul M. McPherson Precision Instruments, a principal manufacturer of specialized, optical equipment. One of their chief regions of interest is the vacuum ultraviolet, 50 to 2000Å. McPherson's vacuum monochromator is the foremost instrument for studies in this rapidly growing field. Another area of McPherson's interest is that of precision linear and angular measurement. In spectroscopy, such measurements are required to chart the lines of newly discovered isotopes, molecular bands and fine structures as revealed by modern spectrographs. We invite inquiries concerning such instrumentation.

OPTICAL vs. X-RAY SPECTROCHEMICAL ANALYSIS

By A. J. MITTELDORF

I'll wager that more burettes will be bought this year than were bought fifteen years ago. Since 1941, the optical spectrograph, the ultraviolet and infrared absorption instruments, the polarograph, x-ray units, chromatograph and mass spectrometer have all made the grade. They have become commercial instruments. Each, in turn, has been heralded as a replacement for the wet analytical chemist. Yet he has not only remained but his numbers have increased. And, during this time, his qualifications, tasks and abilities have grown at an even faster rate than his numbers.

The conclusion? When the salesman's glowing praises finally cool off, a new instrument slowly settles down into its proper place in the analytical lab. It may be assigned just one job: determining the plating thickness continuously on tinned steel strip, for example. Here its principal function will be to save management money. At the opposite extreme, an instrument may be so flexible and versatile that it is capable of pouring out a wealth of information. Such a tool finds its way into the research and development laboratory as well as the production laboratory. But a tool rarely completely replaces another or a wet chemist. It merely supplements existing tools or improves and augments certain analyses.

The newest instrument on which the glitter has not as yet faded is the vapor phase chromatograph. So inexpensive that almost any lab can afford one, it has been extolled as a tool which will antique the mass spectrograph at 50 times its cost. Using history as our prophet, however, we predict that the mass spectrograph will not only remain but its applications will spread.

The gold plating has long worn off the optical emission spectrograph and signs of tarnish are beginning to appear on an x-ray spectrograph here and there. The two have paid their way in literally thousands of laboratories. The question is having both, which is to be used for a particular analysis; or, having neither, which is to be purchased.

Scope of the Two Instruments

Both the x-ray and optical spectrograph are used for the determination of bare elements. Many of the elements for which they are useful are the same as is the concentration range of these elements. The two are essentially non-destructive. In other words, in many instances, the instruments are competitive. But not completely so. Some elements are particularly amenable to determination by one; some to the other. This is true for concentration ranges as well.

For a variety of reasons, many elements lie outside the jurisdiction of both instruments. Here we find their major limitations. The optical spectrograph reigns over about 70 elements. It can be used to determine all of the elements except the halogens, the inert gases and the non-metals such as carbon, sulfur, selenium, nitrogen and oxygen. The loyal subjects of the x-ray spectrograph are those of atomic number greater than 12, magnesium. Because they emit soft, easily absorbed x-rays, the lighter elements are not readily detected by x-rays. Just a few years ago, chromium was considered the lightest element which could be determined. Recently, the introduction of a helium or vacuum path and thinner, less absorbing windows has added about 11 elements to the scope of x-ray spectroscopy.

The second essential difference between x-ray and optical spectroscopy is the optimum concentration range of elements to be determined. The former shines in the major concentration range, 1-100%; the latter in the range below 5%. The optimum concentration depends on the element itself. Lead, a sensitive element by the x-ray method, is determined in leaded steels nicely in concentrations of 0.1-0.5%. Likewise a sensitive element for the optical method, lead is determined in zinc in the range 0.0005%-0.005%. In the one example, lead is added to steel to improve its machinability. In the other, it is a bad actor. Zinc containing 0.003% lead is considerably more expensive than the metal containing 0.006% lead.

One of the major contributions of optical spectro-chemical analysis has been in qualitative and semi-quantitative analysis of complete unknowns. By forewarning the wet analyst of interferences, by letting him know what to expect, by providing information on samples too tiny to be handled in any other way, optical spectroscopy proves its worth every day. Now x-ray spectroscopy fills some gaps. The latter may miss the trace constituents but permits the determination with a fair degree of accuracy of many major elements missed by optical means.

In summary, then, a laboratory having both tools at its disposal is quite fortunate. Nearly all of the elements over exceedingly wide concentration ranges can be handled. The only elements which fall outside the scope of both instruments are:

hydrogen, helium, carbon, nitrogen, oxygen and neon.

True, this list includes some of the most common elements. But covering all but six elements, the two instruments together make a uniquely powerful combination.

Precision and Accuracy

Using the best *photoelectric* techniques, the precision and accuracy of which optical spectroscopy is capable is about the same as that for x-ray spectroscopy. Standard deviations of around 1% of the amount present are reported. It may be argued, however that this comparison is not fair. The photoelectric optical spectrograph is twice the cost of the x-ray instrument. Another comparison would be of the *photographic* optical and the *photoelectric* x-ray spectrograph since these two instruments cost roughly the same. Photographic measurements permit a precision of around 3% of the amount present, giving x-rays the edge in this characteristic.

As many of us have unhappily discovered at one time or other, however, precision sometimes bears little resemblance to accuracy. Differences between the standards and samples in surface condition, in particle size or shape, metallurgical history, chemical compounds all affect accuracy. In x-ray analysis, particle size and shape are particularly important. The exciting as well as the fluorescent beams are absorbed differently by particles whose physical characteristics are not controlled. Campbell and Carl¹ report data which show the necessity of grinding niobium oxides for 30 minutes with acetone in order to stabilize the intensity of tantalum x-radiation in the sample. Standards are prepared by mixing -325 mesh niobium and tantalum oxides 10 minutes by hand, then brushing through a -200 mesh screen five times and finally grinding for 30 minutes in a mortar. With the recent introduction of the Wig-L-Bug, however, sample preparation time for analyzing powders by x-ray spectroscopy promises to be shortened materially.

Another way to overcome or compensate for particle size and shape differences is by the addition of an internal standard to the powder and/or the briquetting of the powder in a metallurgical specimen press. Samples are best handled as liquids,

however. If they can be conveniently dissolved, their analysis is greatly simplified and precision is greatly improved.

Thus far, we have spoken of the best precision obtainable. In many analyses, especially of the trace element variety, precision values of the order of 50% of the amount present frequently must be accepted. In other words, for both x-ray and optical spectroscopy, as the intensity of a line approaches its background, precision suffers accordingly. In general, optical methods are more sensitive than x-ray so that trace-element work is better performed with the optical spectrograph.

Interferences

No comparison between the two methods of analysis would be complete without a section on interferences, that is a line of one element superimposed on one of another element. It might seem that, since optical spectra contain so many more lines than the x-ray spectra of the same element, the possibilities of interference would be correspondingly greater in the former. Quite the opposite is true, however. With so many lines to choose from, the technician is usually able to find at least one completely free of interfering lines. In fact the rule-of-thumb is that, when a survey is made of a complete unknown, at least two lines of every element should be studied before that element is reported. In optical spectroscopy, there are, nevertheless, occasional interferences. The determination of silicon in stainless steel is a good example. Here only one line is detected, that at 2881A. Within a few tenths of an angstrom of it is a strong chromium line. Where the determination of silicon in high-chromium steel is required, a spectrograph with a dispersion at least 3 A/mm is called for. The determination of traces of silicon in the presence of tungsten is another example, a strong tungsten line blocking the 2881A line.

Thus optical spectroscopy relies on improving resolution to eliminate interference. To do this, larger spectrographs may be used; the slit may be narrowed; a grating spectrograph may be shifted to higher orders.

X-ray spectroscopy, too, has devices for minimizing interference². Again, the primary one is resolution. But obtaining higher resolution is somewhat simpler than with the optical spectrograph. The dispersing crystal is changed, lithium fluoride being one with a small lattice spacing and consequently a high dispersion and resolution. Three other ways are available for improving resolution and so preventing overlapping lines: 1) The excitation of certain lines can be prevented by lowering the voltage of the x-ray tube to a value below the excitation potential of the particular line; 2) a thin foil of metal may be used as a very narrow band-pass filter; 3) a pulse height discrimination detector may be used, serving to resolve two lines electronically.

Applications

Perhaps the best way of showing how the two analytical tools complement each other is by giving typical examples of each in various industries.

In the steel industry low-alloy steels are routinely handled by optical spectroscopy (with an assist from the wet chemist on carbon, sulfur, phosphorus). The high-alloy steels such as the stainlesses, the tool steels and the high-temperature alloys are best analyzed by x-ray spectroscopy for the major constituents. Again optical spectroscopy is called upon for the minor additives as well as impurities.

In the lead industry, purity has always been a requirement for storage battery and anti-corrosion applications. Here the optical spectrograph has made its impact. The x-ray spectrograph is

now showing its colors in the analysis of lead alloys such as solders, bearing metals, antimonial leads and type metals.

In the copper industry, optical spectroscopy is an essential tool. It has been stumped, however, by the direct determination of copper in major concentrations and sometimes by segregation problems. X-ray spectroscopy is taking up the trail here nicely. At least one organization now uses x-rays for assaying scrap metal for copper on which basis it is sold. X-rays may overcome the difficulty of determining nickel in nickel silvers (70% copper, 15% nickel, remainder zinc).

The light metals, aluminum, magnesium and zinc are particularly nice to analyze by optical spectroscopy. Many of the elements determined are below aluminum in atomic number. X-ray analysis is thus precluded. Optical spectroscopy deserves almost full credit for the hard-to-match production control of these metals and also for the development of many new alloys.

The petroleum industry employs optical spectroscopy for the analysis of used lube oils. This art has been developed to such an extent that most railroads use the spectrograph as a regular check on their diesel engines. Spotting lead from a failing bearing permits preventive maintenance with huge money savings. On the other hand, x-ray spectroscopy has found regular jobs, too. It is used to control the lead and bromine content of gasolines. It appears to offer the best way of assaying cracking catalysts for such poisons as vanadium and nickel. Although traces of these elements are sufficient to destroy a catalyst, x-rays can distinguish between good and poor batches³.

Atomic energy applications of both tools are numerous. Taking an example at random, iron and aluminum traces are neatly

controlled in zirconium by optical means. For the determination of uranium, thorium and the rare earths, x-ray spectroscopy is more sensitive than optical spectroscopy and consequently has found wide application.

Conclusion

In summary, the article above can be concluded in a manner terse and to the point: get both!

Acknowledgments

May I express my sincere thanks to Dr. R. H. Bell of Lucius Pitkin, Inc., who spoke on the above topic recently before the Society for Applied Spectroscopy. The enthusiastic response he received on delivering that address prompted and inspired this article.

References

- 1 Campbell, W. J. and Carl, H. F., *Norelco Reporter*, March-Sept. 74 (1956).
- 2 Parrish, William, *Norelco Reporter*, March-Sept. 35 (1956).
- 3 Dryoff, G. V. and Skiba, P., *Anal. Chem.*, 26: 1774 (1954).

NICKEL-BASE STANDARDS

A series of 4 nickel, 4 Inconel and 3 Monel secondary spectrographic standards is now available from the International Nickel Co. The standards are rods 1" in diameter by 2" long and cost \$5.00 apiece. Further information may be obtained from International Nickel Co., 67 Wall Street, New York, N. Y., Att.: Mr. P. J. Doyle.

X-RAY FLUORESCENCE STEEL STANDARDS

We offer an extremely useful set of steel standards for x-ray spectroscopy. These are the low-alloy steels of the British Bureau of Analysed Samples which we have mounted and prepared especially for x-ray spectroscopy. The standards themselves have been described previously. They are eight in number and contain 11 elements graded in small concentration steps as follows:

Al	0.027-0.057%	Mo	0.007-1.41%
C	0.1% nominal in each	Ni	0.048-5.15
Co	0.006-0.018%	Si	0.013-0.81
Cr	0.044-3.07	Sn	0.004-0.012
Cu	0.090-0.49	V	0.034-0.64
Mn	0.016-1.42		

The standards have proved excellent for the analysis of alloy steels in the AISI 2000, 3000, 4000, 6000 and 8000 as well as the 1000 carbon steels. They are invaluable to the analyst who runs occasional steels without prior knowledge concerning alloy type. To minimize matrix effects, the iron content in each standard has been kept constant. For example, a standard with high nickel contains low chromium.

The x-ray standards are buttons 1/2" in diameter by 3/16" thick. Like metallographic specimens, they are mounted in Lucite 3/8" thick by 1" in diameter. After being molded, the surface is ground flat and smooth. It is recommended that before use the standards be polished in the same fashion as the unknowns.

These standards were tested on a General Electric XRD-3 instrument through the courtesy of Dr. C. Manning Davis of the International Nickel Company Research Laboratories, Bayonne, N. J. The following were the exposure conditions:

Target	Tungsten
Potential	50 KV
Current	45 ma
Crystal	LiF for all determinations except Mn where Topaz was used to resolve Cr line nearby
Exposure	10 seconds
Mask	1/2" diameter
Line	K-alpha for all elements
Detector	Geiger counter

Although no attempt was made to achieve the ultimate sensitivity, straight-line working curves were obtained over the following ranges:

Cr	0.2-3.1%	V	0.12-0.67%
Ni	0.05-5.1%	Mo	0.19-1.4%
Mn	0.17-1.5%	Cu	0.1-0.46%

In all instances, the actual threshold of sensitivity was well below the minimum figures given above. For vanadium, further work was done with a helium atmosphere bringing the sensitivity down to 0.03%. Silicon may be determined to around 0.1%.

1200	Steel Standards, Low Alloy Series, rods, 1/2" dia. x 6" long, for optical spectroscopy.	
	Set of 8	\$92.00
1201	Steel Standards, Low Alloy Series, discs, 1/2" dia. x 3/16" thick, mounted in Lucite 1" dia. x 3/8" thick, for x-ray spectroscopy.	
	Set of 8	\$92.00
1202	Steel Standards, Low Alloy Series, turnings, 100 grams each, for wet chemical analysis.	
	Set of 8	\$102.00

tricks of the trade

MORE ABOUT SPEX MIX

A number of questions about Spex mix have been repeated often enough for us to supply the answers in these columns. Why were 43 elements chosen? How did we arrive at the figure 1.34% for each element? What compounds were used in its preparation? How was it prepared?

To answer the first, the 43 elements chosen are the most common ones. It seemed wise not to add the rare earths or the platinum group because of the myriad lines of these elements at 1.34%. Paradoxically, at the concentration level where they would be used in semi-quantitative work (0.0001%-0.1%), most of these elements would go undetected.

The 1.34% figure is a calculated one. Enough silver oxide was weighed out to yield 1.00g of silver; enough calcium carbonate was weighed out to yield 1.00g of calcium. At the end, the total weight of the material was divided by 43 (the number of elements) to give 1.34%.

This helps answer the question about the form of the elements. In general, oxides were selected in order to avoid anion effects. Certain oxides—calcium for example—are hygroscopic or otherwise unsuitable. In these instances, other compounds such as the carbonate were used.

The individual compounds were first ground by hand to -200 mesh. After being weighed, they were mixed by passing them through sieves in a device similar to our hour-glass mixer, but on a large scale. The mixture was then ground in a ball mill for several hours. No evidence of contamination or segregation was found after milling.

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WORK SHEETS

In order to convert raw transmittance data to percent concentration, most spectrographers use a work sheet. Such a sheet permits the data to be assembled orderly and neatly with a minimum of confusion. We have helped design a Work Sheet which is not copyrighted so that you may have it photo-offset in your own organization. The Work Sheet is already in use in dozens of laboratories and has been modified several times to make it nearly universally applicable. If you want a few of the sheets to try and later copy, jot us a line and we shall cheerfully mail some to you.

CLEANING SLITS

On a stigmatic spectrograph a dirty slit is readily detected upon examination of the spectra. One or more narrow streaks appear across the lines. On a non-stigmatic instrument, the chief effect may be a loss of precision. The line will not be uniform along its length so that, if the microphotometer is set for one region and then another, different readings will result.

Unfortunately, there is no single remedy for a dirty slit because dirt may consist of a whole host of substances. In any event, it's best to use the gentlest treatment first and proceed to more drastic ones. Accordingly, the first attempt should be with air alone. Sucking with a rubber bulb often works and, if not, blowing with a rubber bulb. If these fail, a Staticmaster brush (cat. No. 3900) will often prove effective, especially if there is an electrostatic attraction holding the dirt. Finally, a piece of non-splintery wood such as a tooth pick should be used. Gently stroke one jaw but once with a smooth stick. Use a new surface for each stroke.

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FILTERS FOR INDIVIDUAL LINES

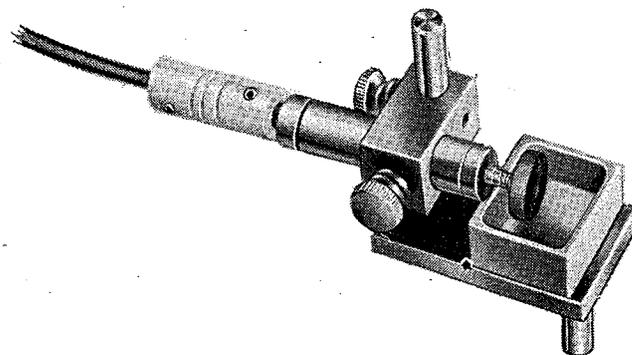
Very frequently in a routine analysis problem, it is found that all of the lines except one or two are of the proper intensity. The "hold-outs" are just too dense to read on the microphotometer. The spectrographer may then either resort to two exposures or he may be lucky enough to find a material which will properly filter those particular lines. Such a filter is, of course, placed directly in front of the line image on the plate. The quest for a filter may find the spectrographer asking the microscopist for cover glasses or he may salvage pieces of window glass or fogged film for the job. Mr. Seymour Hackman of J. R. Elkins Co., Brooklyn, N. Y., suggests Plexiglas (Lucite does not transmit as well in the ultraviolet). He takes an exposure without the filter, then a series of others with Plexiglas sheets of varying thicknesses in front of the slit. In this manner, he finds one which attenuates the line of interest properly. Once found, a piece of the Plexiglas sheet is cut and mounted with pressure sensitive tape at the camera in front of the line image. To determine this position, he first marks the line on the film and then places it in position without the cassette. Hackman has reported that the technique has enabled him to prepare several filters for various problems in a short time. For example, he is able to determine in one exposure all of the elements in zinc base alloys through suitable filtering.



Preforms and rods of National Carbon Company and United Carbon Products Company available from stock. Make us your headquarters for ALL spectrographic supplies — electrodes, plates, film, photoprocessing chemicals, etc.

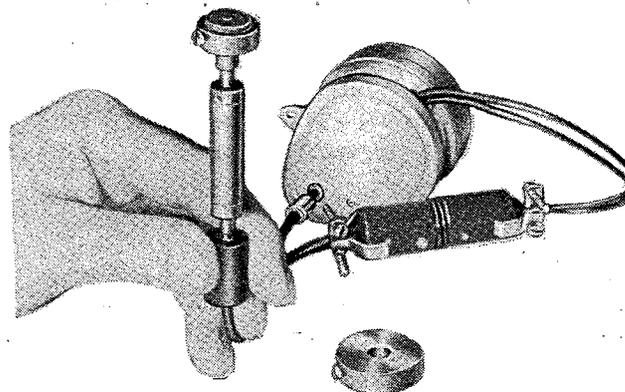
COMBINATION ANALYZER

The Combination Analyzer is designed to operate either directly on solutions or as a rotating platform for the analysis of dried liquids. Powered by a 10-rpm synchronous motor, the instrument is positioned simply by placing it in the jaws of the arc-spark stand clamps. If desired for a permanent set-up, the motor may be mounted on the outside of the arc-spark stand. A specially annealed flexible cable connects the instrument shaft to the motor. This turns the shaft vertically or horizontally smoothly and without whipping. A grooved Teflon coupling insulates the cable and motor from the high voltage of the spark. Constructed of 18-8 stainless steel, the instrument will withstand corrosive chemicals and may be cleaned in mineral acids. It may be assembled for left-hand or right-hand operation depending on which way the door of the arc stand faces. Set screws are provided for ease in disassembly; thumb screws for rapid positioning in the optical path.



No. 3400 Combination Analyzer as set up for solution analysis.

The first photo shows the instrument as set up for solution analysis in which the shaft turns on a horizontal axis. In this application, a measured amount of liquid is placed in an aluminum or porcelain boat. A disc electrode is placed on the shaft, split to furnish the required tension. The instrument is lowered against an adjustable stop. As the disc rotates through the liquid, a spark is directed to it from an upper electrode which may be a $\frac{1}{8}$ " rod broken at the end.



No. 3400 Combination Analyzer shown as it would be used for platform electrode analysis.

Also shown is the Table Adapter No. 3402.

As a Rotating Platform, the main section of the Combination Analyzer is slipped out of its support and placed alone in the electrode jaws. An adapter is screwed on the end of the shaft and a loaded platform electrode is dropped into the adapter. The instrument is offset vertically a few degrees so that the spark from the upper electrode is directed to the channel in the disc electrode.

A Table Adapter is available as an accessory. This is used for $\frac{1}{4}$ " or 1" diameter briquets or other specimens. Continuously rotating, the specimens are sampled over a great area, improving reproducibility of elements not homogeneously dispersed.

3400	Combination Analyzer, complete with 10-rpm Motor (115 vac), glazed porcelain boat, aluminum boat, line cord and feed-through switch.	
	Each	\$195.00
3401	Porcelain Boat, for above, glazed, 60-mm long.	
	Per Set of 12	\$10.00
3402	Table Adapter, for $\frac{1}{4}$ " diameter or 1" diameter samples, such as briquets or discs.	
	Each	\$12.00
3403	Aluminum Boat, spare, for solution analysis.	
	Each	\$5.50
4011	Graphite electrode, high-purity, for solution analysis, UCP 106.	
	Per 100	\$14.00
4012	Graphite electrode, high-purity, for rotating platform, UCP 1907.	
	Per 100	\$16.00

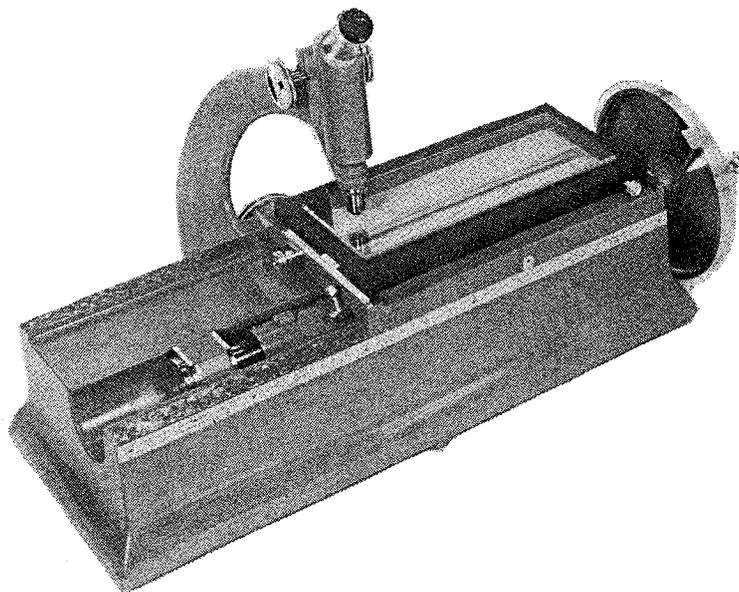
McPHERSON MEASURING COMPARATORS

High-dispersion spectroscopy is placing renewed emphasis on wavelength measurement. Complex molecular bands, isotope spectra, the spectra of the rare earths and trans-uranium elements all are being measured to better than 0.001A. Such precision requires not only a spectrograph having a linear dispersion of at least 2A/mm but a measuring instrument built to the rigorous specifications of grating ruling engines. Fitted with an aged, hand-lapped screw and made by optical engineers rather than machinists, the McPherson Measuring Comparators are guaranteed to yield the accuracy called for.

The Model 100 instrument may be modified in several ways to serve other uses. For example, one modification incorporates a photodetector. Using this attachment, it is possible to measure the exact density center of a diffuse line.

Another modification is an instrument designed to measure distances along two perpendicular axes and angles to 1 minute of arc. Ballistic computations frequently need information of this nature. A typical instrument in this series is the Model 111.

If your requirements are along the lines of this instrumentation, a letter explaining your problem will permit our engineers to submit prompt quotations.



Model 100—Measuring Comparator for precise linear measurements in one direction.

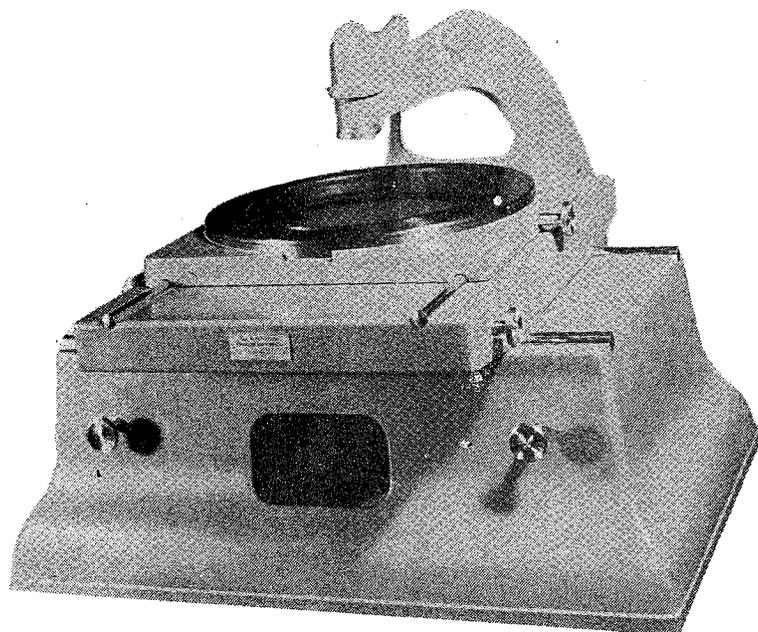
MODEL 100 OUTSTANDING FEATURES

General Specifications:

Height	14 inches
Length	24½ inches
Depth	12 inches
Weight	90 pounds
Longitudinal stage motion	
255mm reading to 1/1000mm	
Cross slide motion..	102mm reading to 1/10mm
Accuracy	1 micron in 255mm
Finish	All parts corrosive resistant

Graduated Dial: rotates with the precision screw permitting readings to a fraction of a micron.

Precision Screw and Nut: guaranteed to be accurate to one micron in 255mm (10 inches). A straight line corrector bar is used with this screw and nut combination to obtain perfect calibration at a specific temperature. The instrument will be adjusted for operation at 68°F unless otherwise specified. **Please Note:** We consider a screw to be unfinished if local corrections have to be made as such corrections can only mean short-lived accuracy.



Model 111—Measuring Comparator for precise linear measurements along two perpendicular axes and angular measurements.