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THE VACUUM ULTRAVIOLET

Part I. History and Instrumentation

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Introduction

Some months ago, I asked a well-known spectrographer for what purpose he had just ordered a vacuum spectrograph. "Well," he replied, "our company manufactures petroleum. Over the past decade, we have shown management that the infrared, ultraviolet, visible, x-ray and radio frequency spectra can pay off handsomely. Our studies in these regions have led directly to more and better products, cheaper production methods and increased sales. With this record, do you think I had any trouble convincing my boss that the *far* ultraviolet would eventually benefit the company, too?"

The odds are surely on his side as the technical hurdles are leaped one by one. Until recently, the region 10-2000A was the Antarctica of the electromagnetic spectrum—known for a long while but largely unexplored. Like Antarctica, too, its treasures were enticing but hard to come by. Now the picture is rapidly changing as the main problem—complete absorption by most atmospheres—is overcome. Today, vacuum equipment is out of the research stage permitting the spectrograph to be evacuated quickly, thus clearing the impenetrable fog of atmospheric air. Further, modern detectors, sources, windows and other accessories are reliable and readily available.

History

Before going into the potentialities of the vacuum ultraviolet, let us ponder the region as perhaps did Schumann in the 1890's. During those pioneering days, knowledge of the region was absolutely nil. Transparent optics had to be discovered and sensitive photographic plates had to be invented if the region was to be explored. Even the prism, commonly made of quartz and the heart of all spectrographs at that time, was found to block out radiation beyond 2000A in the ultraviolet.

Schumann's first task then was to find a suitable material for the prism. Years of systematically hunting through every natural mineral he could obtain, finally led him to calcium fluoride (fluorite). Attesting to his thoroughness, this is still used today down to 1200A, its cut-off point. But finding a prism aterial was only the first step. What the optics now transmitted, the photographic plate did not detect and the air in the spectrograph filtered out. The realization that these were three separate and distinct problems was, in itself, a tremendous achievement. We can imagine that when Schumann first discovered fluorite, he measured his success in terms of a tiny improvement in the spectrograms. Not until all three problems were solved, however, did he achieve spectrograms which really extended scientific knowledge appreciably. This collective achievement—this lifetime of work—is what has made Victor Schumann the most important contributor to vacuum spectroscopy.

After discovering fluorite, Schumann switched his efforts to the photographic plate—the second problem. The plate which he invented—if you can call the long series of trial-and-error experiments he conducted "invention"—is, like fluorite, still used today. The method of preparation which evolved is like an exotic food recipe, each step of which must be followed diligently if results are to be achieved. The plate must be stripped of most of its gelatin, heated gingerly, washed, dried and stored under just the right conditions. Even then, the emulsion produced is unstable, irreproducible and easily scratched. It has been, nevertheless, the basic photographic plate used in this region to the present time. Workers since Schumann have shown that it is sensitive to at least 50A.

His third, and perhaps most difficult problem, was absorption of radiation by the very air in the spectrograph. Vital to his success were a home-made vacuum pump and measuring equipment plus the ingenious gadgetry which he developed for changing wavelength and racking the camera while maintaining a vacuum. Were he not so ingenious, it is doubtful whether he would have had time—let alone patience—for his achievements.

Because Schumann laid the very foundations of vacuum spectroscopy, it is interesting to learn more of his life. Born near Leipzig in 1841, Victor Schumann became a designer and later a manufacturer of machinery. These formative years of engineering experience proved invaluable in his subsequent spectrographic studies. To appreciate this, we must think not of a modern, plug-in vacuum pump but of heavy, cumbersome pumps with leaky valves constantly threatening to squirt pumping oil of relatively high volatility into the spectrograph. We must think of his fragile mercury manometers rather than a neat electronic package containing a handy ionization and thermocouple gage combination. We must remember that Apiezon wax, silicone oils, stainless steel, Pyrex glass, fused silica, Teflon, neoprene o-rings and Kovar glass-to-metal seals were undreamed of miracles. Sealing a system vacuum tight was a major undertaking in those days when even the Tesla coil (not to mention mass spectrometer) leak detector was unknown.

To accomplish his extraordinary feats without these tools and

materials, Schumann had to make a painful choice in life: to devote full time to research or full time to his business. Fortunately for science, he chose the former, sacrificing his income altogether. From age 40, his decision made, he was to devote the rest of his active life to vacuum spectroscopy, sponsored and financed completely by himself.

Another contributor who should be singled out for his work in the far ultraviolet is Theodore Lyman. In 1906, Lyman first used a concave grating in place of the fluorite prism and so was able to make accurate wavelength measurements for the first time. Prior to that time, having no way of measuring the dispersion of fluorite, Schumann could only approximate wavelengths in this region. Lyman also extended the studies to 500A and developed a source bearing his name.

Using grazing incidence illumination of the grating, Compton and Doan (1925) were able to study soft x-rays, above 10A. They discovered that most materials have far better reflectivity below 500A using grazing rather than normal incidence. The discovery, an unexpected one, thus was not made until about 19 years from Lyman's first work with gratings. Within two years, Hoag used a similar grazing-incidence mounting for the vacuum ultraviolet and celebrated the "holing through" to the x-ray region.

A hot spark (sometimes referred to as a vacuum spark), originally discovered by Wood and rediscovered by Millikin in 1921, is significant historically. It was this source that permitted the merger of the x-ray and ultraviolet. In fact, the hot spark emits x-rays of such intensity that care must be taken in using it. In recent years, the source has not been used both because of its danger and because it is very unstable, eating away its electrodes at a rapid rate. The eroded particles of the electrodes, tungsten or other refractory metals, sputter against the slit jaws or even the grating with such force that they cause damage.

To shorten this historical account, permit a jump to the present. Advances were made during this interval, to be sure: the spectra of most of the elements were accurately charted; photographic and vacuum techniques were vastly improved; lithium fluoride was found to transmit further into the vacuum region than fluorite; the photomultiplier tube was invented which, with its attendant electronic amplifying and recording systems, is a tremendous improvement over the delicate, temperamental photographic plate.

Present Day Instrumentation

Now we are beginning to see a consolidation of this jig-saw puzzle. Instruments are available not only for dispersing light in the vacuum ultraviolet but also for exciting and detecting the spectra. The McPherson One-Meter Scanning Monochromator is a grating instrument with a 15,000 line/inch reflecting grating. Built into a cabinet about 5 feet high by 4 feet long, it is completely self-contained, with scanning drive, evacuating pumps and measuring instruments mounted below the spectrometer proper. Scanning speeds from 8 to 200A per minute are available merely by setting a quick-change gear box and the wavelength may be read directly to 1A on a counter. Entrance and exit slits are on turrets so that any of four different sizes from 40 microns to 1000 microns may be rotated into position without breaking the vacuum. With a two-stage mechanical pump and a diffusion pump, the instrument may be evacuated down to 10^{-6} mm Hg if necessary and the actual pressure may be continuously measured on a direct reading thermocouple or ionization gage.

Mention should be made of one instrument which offers considerable promise as an emission tool especially in the steel industry. It is the Quantovac manufactured by Applied Research Laboratories who claim that it may be used for the rapid determination of sulfur, carbon and phosphorus in steels. For this, the sample is placed in a nitrogen-flooded instead of an evacuated chamber which facilitates the analysis. Employing only a roughing pump, the instrument is a low-vacuum rather than high-vacuum one. In present form, its usefulness thus is limited to the region above 1600A, below which even minute traces of oxygen are opaque to radiation. But even if the instrument is capable of determining only sulfur, carbon and phosphorus in steels, its economic value will prove great. These three elements, the determination of which is often the bottleneck in production control, have defied the spectrographer for a long time.

Of course, the vacuum ultraviolet, like the near ultraviolet, has potentialities both in emission and absorption. Most of the work has been limited to absorption thus far because the instrumentation is so much simpler. For example, hydrogen discharge sources are being made to provide a continuum for absorption work in the region 1650-2300A. Such a lamp may be operated on direct current (Johnson, Watanabe and Tousey[1]) or, better, on 60-cycle 1800 vac (Jones and Taylor[2]). The latter permits the use of stable ac amplifiers and servo monitoring systems to keep the intensity of the discharge constant (Pondrum and Robertson[3]).

Thus far, a single discharge tube has not been discovered which will provide a continuum covering, say, 1000-2300A. The hydrogen continuum cuts off at around 1650A, beyond which it has a many-lined spectrum, not too useful for spectroscopic measurements. Below 1650A, the rare gases seem the most promising (Tanaka[4]). Best of these appears to be argon which, at a pressure of 200 mm Hg, emits a silent discharge covering the region 1066-1650A. In other words, the continuum of argon extends the hydrogen continuum to 1066A.

The other rare gases have continua in the vacuum ultraviolet and may be excited with the same discharge tube and electrical circuitry. Thus xenon has a strong but ever-decreasing continuum from about 1500 to 1900A; krypton from 1236 to 1850A.

The detector generally used in the far ultraviolet is a photomultiplier. The RCA-6903, with a fused-silica face plate, has excellent sensitivity down to 1540A. Generally, the output of the photomultiplier is amplified by ac stabilized amplifiers which are commercially available and recorded on a strip recorder. Below 1540A, the best detector is probably a phosphor-coated[5] photomultiplier. On receiving radiation in the far ultraviolet, the phosphor re-radiates at a longer wavelength which light can then pass through the fused-silica window. Watanabe[6] has shown that one phosphor, sodium salicilate, has a constant quantum efficiency in the region above 500A, thus facilitating intensity measurements. This phosphor is excellent physically in that it adheres to the window, does not sublime in vacuum and is stable.

Some of the special techniques required for absorption work in the vacuum region are of interest; for example, admitting a volatile organic material into an absorption cell at a fixed pressure without contamination. This has been nicely worked out by Jones and Taylor[2]. Samples are first evacuated into a manifold at a pressure of about 30 mm Hg. Noncondensable contaminants, such as oxygen and nitrogen, are pumped out after freezing the sample. The sample is then re-evaporated and the pressure once more measured. A known volume of the liquid is then transferred to a bulb and the rest of the system evacuated. The vapor is then expanded into both the absorption cell and a large bulb. In this manner, pressures as low as .05 mm are obtained reproducibly. Such low pressures reduce the possibility of absorption on the walls of the cell. The authors confirm the accuracy of pressure measurements by obtaining straight-line plots of absorbance *vs.* calculated pressure.

From the foregoing, it is obvious that vacuum spectroscopy has progressed quite far, especially in recent years. True, it has not reached the untrained technician level and in this respect lags way behind spectroscopy in the near ultraviolet. But interest and applications in the far ultraviolet are steadily increasing

tricks of the trade

TIME SAVER

Dayton R. Stoss of General Electric Materials and Processes Laboratory in Schenectady, N. Y., suggests a neat way of filtering lines in order to get a complete analysis in a single exposure. His is a grating spectrograph in which the second order and first order are photographed simultaneously. In the analysis of an alloy steel, he found that the normal exposure was too short to detect the tungsten in the steel. Yet, an increase in the exposure time would result in lines for the other elements which were far too dark. His solution was to use a glass filter over the slit after the first half of the exposure. Cutting out most of the ultraviolet, the filter thus acts as a curtain for those elements, whose lines are in the ultraviolet. The tungsten line at 4008A is, however, not filtered by the glass and so is exposed for a longer time. Stoss has devised an automatic shutter-operated filter for the purpose, this analytical problem being routine in his laboratory.

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FURTHER WIG-L-BUG NEWS

The Wig-L-Bug is still finding applications not only in the spectrographic laboratory but also elsewhere. Here are two unusual uses in the electron microscopy laboratory.

1) Electron microscopists mount many of their specimens on grids, consisting of screens of exceedingly fine wire. Mr. J. G. Sayre of the Owens-Corning Fiberglas Corporation has developed a method for cleaning such grids. A 1" long (cat. no. 3111) plastic vial is first half-filled with -320 mesh carborundum powder. About 50 of the tiny grids are then added and the vial is 3/4 filled with water. The contents are shaken for 2-3 minutes in the Wig-L-Bug and then emptied into a container covered with a fine mesh screen which is next placed under a faucet and washed for 15 minutes. Finally, the grids are dried on filter paper. Mr. Sayre reports that grids so cleaned are "entirely free of any previous samples and electron diffraction patterns from these grids show no lines."

2) Another use by electron microscopists of the Wig-L-Bug is the production of particles in the sub-micron range. In this application, samples are ground in a steel vial (3114 or 3117) with water or another suitable liquid for 2-10 minutes. The vial is allowed to stand for about a half hour and the smallest particles, floating because of surface tension, are removed with an eye-dropper.

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and, with these, techniques and instrumentation are sure to progress.

The next article on this subject will discuss actual as well as possible applications of the vacuum ultraviolet.

References

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4) Tanaka, Y., *J.O.S.A.* 45: 710 (1955).
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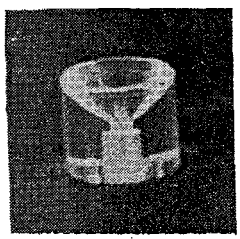
6) Watanabe, K., Inn, E. C. Y., *J.O.S.A.*, 43: 32 (1953).

ELECTRODE FUNNELS

We were indeed gratified to hear that our suggestion to use 1/8" diameter lower electrodes has actually resulted in greatly improved precision in many laboratories. The narrow electrode minimizes arc wandering, the goblin of the dc arc. Recommended is an electrode (cat. no. 4020, $19.00 per hundred) having a 0.096" diameter hole drilled 1/4" deep in a straight 1/8" diameter rod. But one solution creates another problem. Now spectrographers have asked us for a funnel similar to the ones which we supply for 3/16" and 1/4" electrodes in order to facilitate filling of the 1/8" electrodes. We are happy to announce that the funnel is now available. Made of clear, highly-polished Plexiglas, it mounts on top of the electrode. It may be cleaned in mineral acids and electrostatic sticking of some substances in dry weather may be eliminated by using the Staticmaster Brush (cat. no. 3900 at $4.95).

3001 Funnel for 1/4" diameter electrodes
3002 Funnel for 3/16" diameter electrodes
3003 Funnel for 1/8" diameter electrodes
Each .....$ 2.50
Per Dozen (specify how many of each size).....**$24.00**



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POROUS CUP ELECTRODES

Most porous cup electrodes have a bottom wall thickness of 0.025". Although perfectly suitable with most discharges, a high-intensity spark discharge will occasionally pierce the floor and possibly cause spattering of a corrosive chemical inside the electrode. An electrode with a 0.040" floor will often prevent this. The National Carbon Preform L 4048 ($22.00 per hundred), which we stock, meets this specification. In addition, it is squared off inside and outside, again serving to prevent perforation by the spark.

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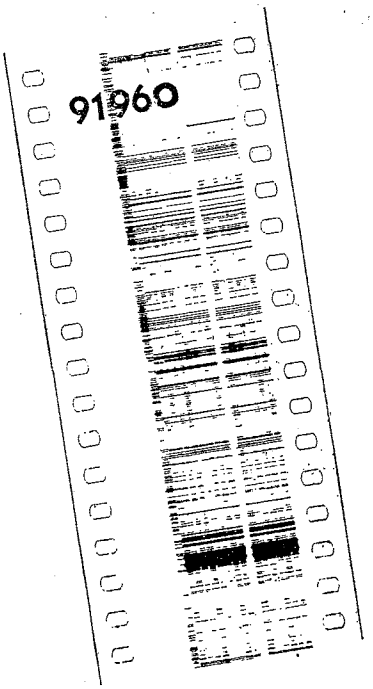
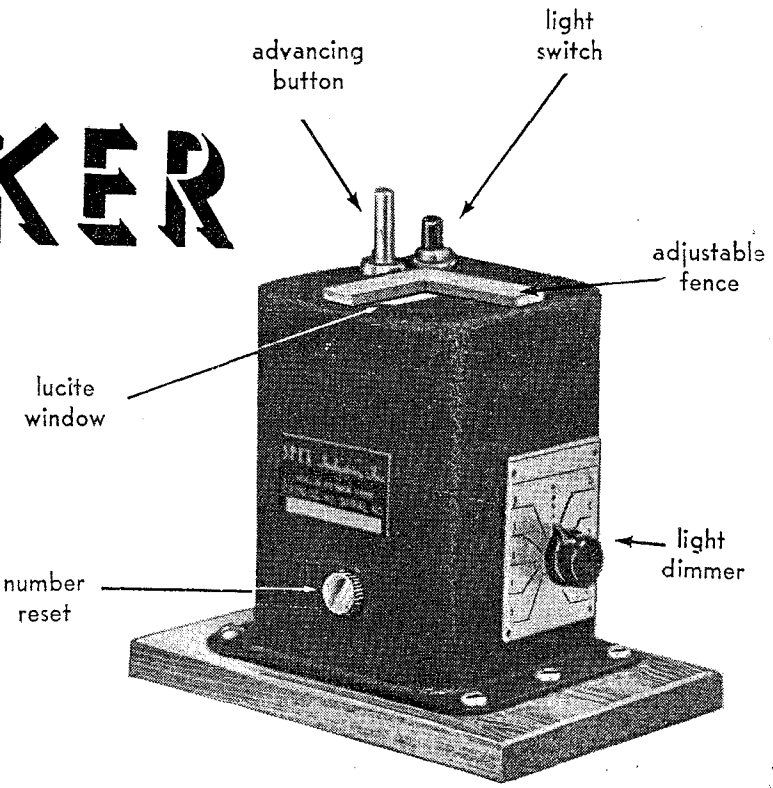
GRAPHITE POWDER

The novice is often bewildered by the choice of so many grades of graphite powder. Two types are available, one for briquetting use and the other for use as a diluent and buffer. Both of these may be purchased in particle sizes of -100, -200 and -300 mesh. We recommend the use of the buffer grade, UCP-2, -100 mesh not only in conjunction with our semi-quantitative G standards but also as a general purpose material. The coarser -100 mesh material has little tendency to fly out of the cup during arcing. Further, especially when mixed with the sample for a few seconds in the Wig-L-Bug, the graphite does not smear and the particle size remains sensibly unchanged. Particle size variations are one of the significant causes of poor reproducibility which may be nicely controlled by following the above suggestions.

New Model

SERIAL MARKER





for | **SPECTROSCOPY, X-RAY DIFFRACTION, ELECTRON DIFFRACTION METALLOGRAPHY, NUCLEAR PHYSICS, MICROSCOPY AND PHOTOGRAPHY**

The Opto-Mechanism Serial Marker photographically assigns a 4 or 5-digit number to any light sensitive emulsion. In the darkroom, before development, the film or plate—of any size—is held against a Lucite window through which a number is projected by pressing a switch. The number is advanced by pressing a second button. Resetting, if necessary, is accomplished by rotating the side knob.

Three models of the SERIAL MARKER are now available. No. 3700 prints a 4-digit number; 3701, 5 digits; 3702 prints a 5-digit number and has a built in attenuator for controlling the exposure. The 3702 is particularly useful in those laboratories where several emulsions, differing in speed, are used. The instrument is first calibrated for each emulsion. This is done by determining the proper position of the attenuator for the emulsion with, say, a 2-second exposure. Once calibrated, the SERIAL MARKER will consistently print a correctly exposed number on any emulsion.

All three models are now equipped with an adjustable gate so that the identifying number may be printed in the same relative place on each film or plate.

The housing is of steel, finished in black crinkle which will resist attack by photographic chemicals. The base is finished mahogany. A household "nite-lite" supplies the illumination and is readily replaced.

3700 **Serial Marker,** prints a 4-digit number approx. 3/16″ x 5/8″; complete with 6-watt, 115-v, ac or dc, candelabra-base bulb.
Each **$54.00**

3701 **Serial Marker,** prints a 5-digit number approx. 3/16″ x 3/4″; complete with 6-watt, 115-v, ac or dc, candelabra-base bulb.
Each **$60.00**

3702 **Serial Marker,** same as 3701 but with built-in attenuator for controlling light intensity.
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