QUANTITATIVE ANALYSIS WITH THE ATOMPROBE

GEORGE CHAPLENKO

PREVIOUS reports on the Atomprobe dwelled on its qualitative capability and for much work a simple identification of a micro-constituent is all that is needed. For instance, when we detected chromium in a non-ferrous alloy, the metallurgist was immediately suspicious that some of the remelt scrap in the particular heat had not been stripped of its chrome plating. Similarly, detection of iron in particles imbedded in the surface of non-ferrous articles was an indication of improper shot-blasting.

Often, however, qualitative data must be augmented with percent concentration figures to be meaningful. When a discrete inclusion is found in a heat-treated metallurgical sample, a knowledge of its composition will help verify the effectiveness of the heat treatment or indicate whether the proper heat-treatment procedure had been followed.

A bottleneck in quantitative spectrochemical analysis of micro samples is lack of standards in which small areas of 5-50 microns, commensurate with the grain size of many alloys, are guaranteed to be accurately representative of the homogeneity over the entire surface. How then can such microscopic areas be analyzed quantitatively without resorting to bracketing through known standards? Of the many possible approaches we shall describe and illustrate three examples.

For the first technique a graded series of additive references is "manufactured" directly on the surface being analyzed. Each reference is prepared by reacting a small measurable area of the sample with a reagent containing a known amount of the required element. When reaction is completed, the element becomes — well, almost becomes — an integral part of the sample. The reacted area is then treated as a **bona fide** concentration standard.

In technique B, the total number of all the different phases (three in the specific example) that constitute the entire sample, must be known. The contribution of each individual phase toward the gross composition of the sample is proportional to its relative abundance and to its specific composition. The former is readily ascertained by direct microscopic measurement of phase areas. Then the distribution of each particular element among all the phases is determined as the ratio of intensities of its analytical line, measured in spectra obtained by sparking individual phases. Local concentrations of the element are finally calculated by dividing average (gross) concentration in proportion to the element distribution and the phase abundance figures.

Method C is based on the assumption that, since an inclusion is dimensionally dwarfed by the bulk of the sample, it contributes little or nothing to the gross analysis; macro analytical data are accordingly taken to represent the matrix composition only. Micro analysis is performed by determining the concentration ratio of the element in the inclusion and the matrix, and then calculating element percentage in the inclusion from the concentration ratio and the gross concentration figure.

All work described was performed with the Spex-Mallinckrodt Atomprobe (Spex Cat. 1900 and 1901) equipped for both photographic and photoelectric readout and previously described in detail (1, 2, 3). Additional pertinent specifics will be given whenever appropriate.

Example A: Application of "in-situ" standards.

Problem: Establishing detectability level of sodium in an aluminum alloy.

Samples: Aluminum specimens, mounted and metallurgically polished.

Sample preparation: All plastic mounts were drilled to allow electrical connection to specimen; Na reference spots applied to surface as described later.

Excitation Conditions:
    Voltage ....1750V dc
    Capacitance 20μμF
    Resistance 10Ω
    Inductance 100μH
    Analytical Gap 30μ
    Counter-electrode .... Tungsten

Grating: 1200 grooves/mm, blazed at 7500A, set to the first order.

Readout: Photographic, with 4" x 5" Kodak 103-F plates, exposed for 12 seconds; 70μ entrance slit.

Preparation of "reference spots":
    Sodium concentration reference standards were prepared directly on the surface of the specimen, each made by depositing a single 0.002 ml drop of solutions containing 5.0%, 0.5%, 0.05% and 0.005% of NaOH. The solution drops were allowed to react, then were air dried. Resultant spots, about 3 mm in diameter, especially those produced by the two lower concentrations, tended to have a discernible outer ring about 70μ wide,

apparently caused by a higher concentration of the reagent in that area. Both the assumedly "rich" ring and the "poor" center of all spots were sparked, as well as a "blank" area of the specimen. All spots produced discernible Na spectra showing Na 5990A and Na 5896A lines even in the exposures from the 0.005% NaOH spot; no sodium lines were detected in the spectrum of the "blank" sample area.

Interpretation of data:

The detectability limit of the method for Na was computed as being equal to at least the quantity of Na present in the area covered by the spark burn. Since in the case of the 0.005% NaOH solution the total "reference spot" was produced by 2×10^{-3} ml of solution, it contained not more than 6×10^{-8} g of Na. Assuming that all of this was concentrated in the outer "rich" band (70μ wide and 3 mm in diameter) the quantity of sodium present in any 70μ dia. burn crater within the band was computed on the basis of the ratio of the two areas as equal to 3×10^{-10} g. Thus, the detectability limit for sodium is 0.3 ng or lower. Since previous experience indicates an average burn penetration of about 1μ, this corresponds to a local concentration of sodium of about 0.04%.

The validity of this interpretation, as well as all others presented, is largely dependent upon the matrix effect being absent or negligible and upon sodium, if present in the matrix, producing spectral lines at the same rate as the surface sodium at the synthetic "reference spot."

Example B: Micro-analysis based on macro-analytical data.

Problem: Estimation of relative local boron concentration in ductile iron.

Samples: Ductile iron specimens, metallurgically polished and etched.

Sample preparation: None

Grating: 1200 grooves/mm, blazed at 5000A, set to the second order.

Readout: Photoelectric and photographic

Method and Interpretation: For the photoelectric readout, a dc amplifier (Spex ER-1) recording console and a photomultiplier were operated under the following conditions:

Photomultiplier voltage ....1250 V dc
RC constant ....0.3 sec
Sensitivity ....10^{-9} amp FS
Entrance & exit slits 15μ
Wavelength scan speed ....stationary
Recorder chart speed ....1 inch/min.
Excitation voltage ....1750 V dc
Capacitance ....$20\mu\mu F$
Resistance 10Ω
Inductance ....$100\mu H$
Analytical gap 40μ
Sparking time ....3 sec

The B 2498A line was identified by scanning across the 2490-2510A region while sparking first a sample of pure iron, then a sample of boron carbide. The spectrometer grating was then locked in such position that B 2498A emerged at the exit slit. Three typical phases of sample were sparked: ferrite, pearlite and a white triangular phase with black dots, surrounded by pearlite. After the intensity of the boron line was recorded, the three phases were sparked again, this time with grating position adjusted to record the intensity of the background adjacent to the boron line.

Charted peaks, representing intensity of B 2498A and the adjacent background were measured to obtain intensity in terms of peak height. Line/background intensity ratio and the relative boron concentration were computed.

	Ferrite	Pearlite	Triangular
Peak, height, B 2498A, mm	23	27	68
Peak height, bkgd., mm	19	15	24
Line/background ratio	1.2	1.8	2.8
Relative boron concentration	1	1.5	2.3

The average boron concentration, based on macro-analysis of the sample, was known to be of the order of 0.01%; from this value and the relative concentration figures above, concentration of boron in all three phases could be estimated:

Average line/intensity in terms of relative concentration factors = (1 + 1.5 + 2.3)/3 = 1.6

Boron Concentrations:
Ferrite $0.01 \times (1/1.6) = 0.0062\%$
Pearlite $0.01 \times (1.5/1.6) = 0.0094\%$
Triangular phase $0.01 \times (2.3/1.6) = 0.0144\%$

For the photographic readout, spectra were recorded on 4" x 5" Kodak 103-0 plates, exposed under the following conditions:

Excitation voltage ....1750V dc
Capacitance ....residual
Resistance ....residual
Inductance ....residual
Analytical gap 40μ
Entrance slit 50μ
Exposure ....15 sec
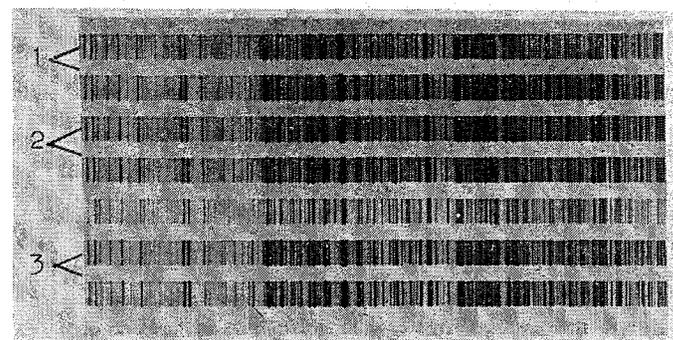
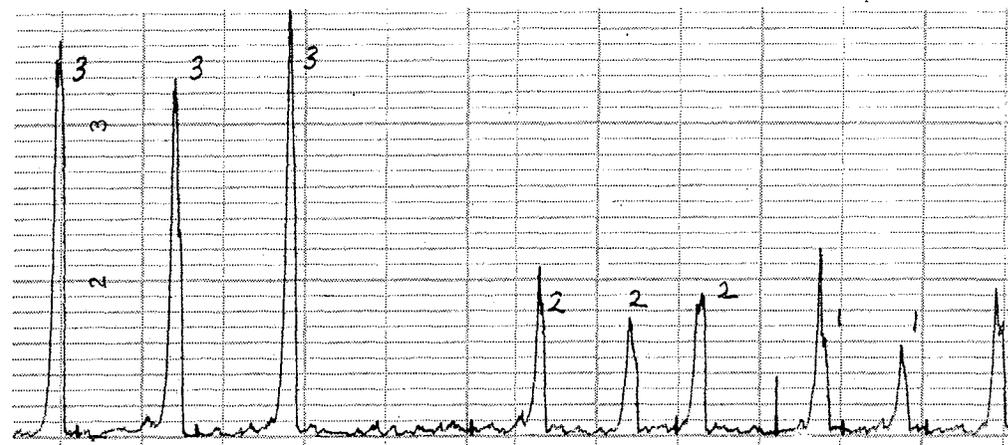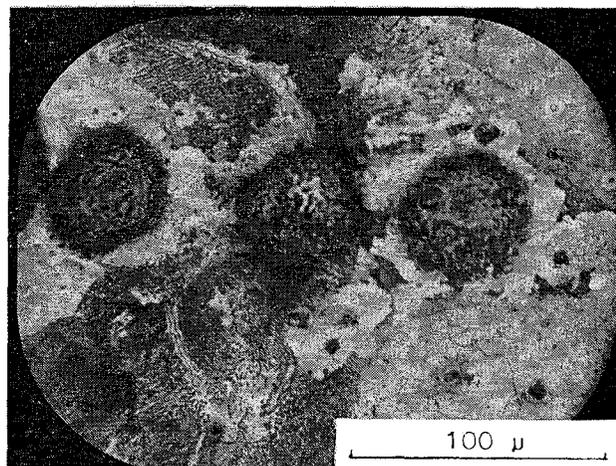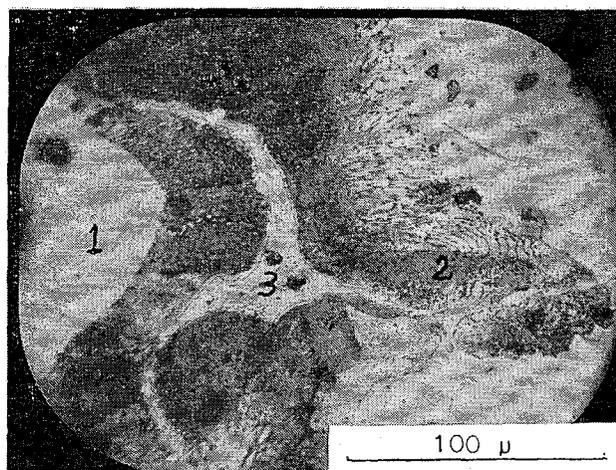

Fig. 1   Boron in Ductile Iron, Photographic Readout
1 - ferrite,   2 - pearlite,
3 - triangular areas with black dots
Note the 2497/2498 boron doublet in reference spectra (two bottom exposures)

Three phases of the sample were sparked in duplicate. To facilitate line identification, two additional boron carbide exposures were juxtaposed. Lines were identified with a Spex master plate.

Intensity of boron B 2497A line and of adjacent background was measured on a microphotometer in order to calculate first line/background, then the relative concentration of boron in the three phases.
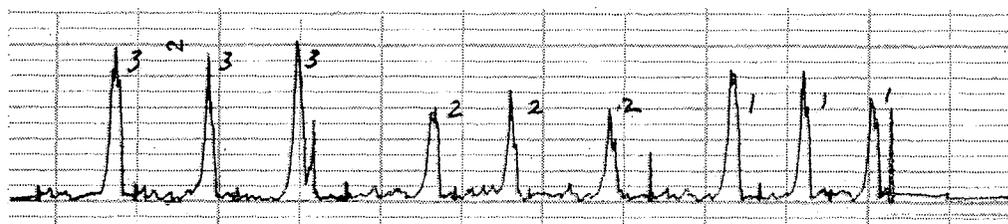
	Ferrite	Pearlite	Triangular
Transmittance, B 2497A, %	46.6	46.7	35.3
Transmittance, background, %	61.5	60.5	72.5
Line/background	0.76	0.77	0.49
Relative B Concentration	1	0.99	1.57

FIG. 2 DUCTILE IRON

ABOVE: 400x PHOTOMICROGRAPHS, TAKEN BEFORE
   AND AFTER THE SPARKING

ON THE RIGHT: INTENSITY OF B 2497.73 LINE
   AND ADJACENT BACKGROUND, RECORDED FOR
   DIFFERENT MICROCONSTITUENTS
   1 – FERRITE, 2 – PEARLITE,
   3 – WHITE TRIANGULAR PHASE WITH BLACK
   DOTS, SURROUNDED BY PEARLITE

INTENSITY OF B 2497.73

INTENSITY OF B 2497.73

INTENSITY OF THE BACKGROUND AT 2497.25

From these values and from the average concentration of boron, 0.01%, local concentration could be computed:

Average concentration, in terms of relative concentration factors = $(1 \times 0.99 \times 1.57)/3 = 1.22$

Local concentrations:

Ferrite	$0.01 \times (1/1.22)$	$= 0.0082\%$
Pearlite	$0.01 \times (0.99/1.22)$	$= 0.0081\%$
Triangular Phase	$0.01 \times (1.57/1.22)$	$= 0.0129\%$

We then see that photoelectric and photographic data sets differ by between $\pm5\%$ and $\pm14\%$. Considering that the two determinations were not conducted at exactly the same sample location, the agreement is remarkably good. The validity of computed local concentrations is limited by the assumption that all three areas are present in the sample in the 1:1:1 ratio.

Example C: Matrix Composition as a Reference Standard.

Problem: Determine concentration of several elements in an inclusion surrounded by matrix of known chemical composition.

Sample: Copper-base alloy, metallurgically polished and etched.

Sample Preparation: None

Excitation Condition:

Voltage	1750V dc
Capacitance	$10\mu\mu F$
Resistance	200Ω
Inductance	$200\mu H$
Analytical Gap	40μ

Grating: 1200 grooves/mm blazed at 3000A, employed in first order.

Readout: Photoelectric, ER-1 recording console and a photomultiplier, working under the following conditions:

Photomultiplier Voltage	1150V dc
RC Constant	0.3 sec
Sensitivity	10^{-9} amp FS
Wavelength Scan Speed	Stationary
Entrance and Exit Slit	25μ
Sparking Time	3 sec

Method: Appropriate analytical lines were selected by a scanning run on samples of pure Zn, Mn, B, Fe, Al, and Cu. Then the sample was sparked and intensities of analytical lines for both the matrix and the inclusion were recorded; peak heights were measured and inclusion/matrix concentration ratios calculated. This when multiplied by the known elemental concentration of the matrix material yields the concentration in the inclusion directly.

Element	Analytical Line, A	Inclusion Peak, mm	Matrix Peak, mm	Ratio Inclusion/ Matrix	Composition, % Matrix (nominal)	Composition, % Inclusion (estimated)
Zinc	2558	2	43	0.05	27	1.3
Manganese	2576	35	16	2.2	3	6.6
Boron	2497	52	2	26.0	0.27	7.1
Iron	3021	135	7	19.3	3	58.0
Aluminum	3093	22	12	1.8	5	9.0
Copper	3248	23	80	0.29	62	18.0

Boron was not listed in the composition of the matrix but was definitely detected in both the matrix and the inclusion. Since no other elements were detected, it seemed appropriate to calculate boron in the inclusion by difference and then estimate boron in the matrix from this figure and the boron line intensity ratio.

Ⓡ EFERENCE standards are a must in quantitative analysis. However, a cunning spectroscopist may obtain reasonably close results even when his standards cupboard is bare. Actually, in such cases determinations are usually based on "ersatz" references of some kind, and the above exemplifies several ways of applying such substitute standards in emission micro-analysis.

Our illustrative examples indicate that photoelectric readout is potentially more sensitive, but is more "wasteful" than photography since the sample must be sparked separately for every single element (when the size of analytical burn is to be kept to a minimum) or sparked for a long time, while a spectrum is being scanned (when a reasonably large burn size can be tolerated). The photographic presentation has the important advantage of direct integration.
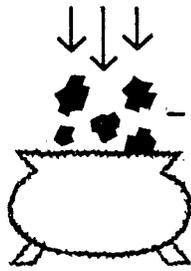
References:

1. G. Chaplenko, D. O. Landon, A. J. Mitteldorf, "The Atomprobe at Work," Spex Speaker, Vol. XI, No. 3, Oct. 1966.

2. G. Chaplenko, D. O. Landon, "Microspark Spectroscopy in Trace Analysis," NBS Symposium on Trace Characterization. (Preprint), p. 16, Oct. 1968.

3. G. Chaplenko, D. O. Landon, A. J. Mitteldorf, "The Atomprobe—A Progress Report," Proceedings of XIV Colloquium Spectroscopicum Internationale, p. 879, Debrecen, Hungary, Aug. 1967.

4. R. D. Schelleng, "Boron Contamination in Ductile Iron," Modern Castings, p. 70, Oct. 1967.

SHATTERBOX NEWS DEPARTMENT

For people who would like to utilize our Shatterbox but cannot always gather anywhere near 100 ml of sample yet cannot squeeze what they do have into the 15 ml capacity #8503 vial, we have come up with a new set of grinding vials and a rack which will hold three of them for simultaneous grinding in the Shatterbox. With a grinding capacity of about 25 ml each these should fill the bill for the "just betweens."
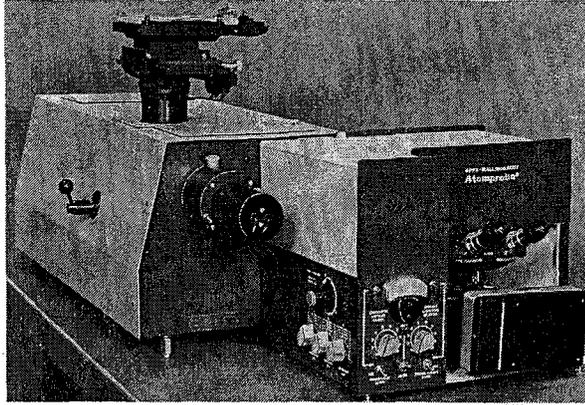
8507 Grinding Vial, hardened steel, 25 ml grinding capacity, the Shatterbox will hold three of these in one 8507R Rack ....Each **$ 75.00**
Set of three **$210.00**

8507R Rack, for holding three 8507 vials ....Each **$ 90.00**

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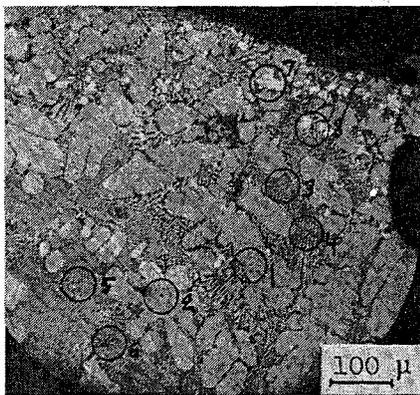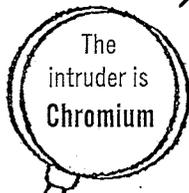
Atmospheric Ozone

One test we never thought of applying to our spectrometers —the effects of altitude—was performed **in situ** last month, when a Spex Model 1700 3/4-Meter Czerny-Turner Spectrometer was lofted in a balloon and successfully transmitted back to earth data related to the ozone concentration of the atmosphere.

Performed under the sponsorship of the National Environmental Satellite Center of the Environmental Science Services Administration in Suitland, Md., the experiment was carried out by Dr. R. T. Bettinger and Mr. J. R. Bohse of the Atmospheric Physics Group, Department of Physics and Astronomy, University of Maryland, College Park, Md. After three years of elaborate planning, exquisite optical, mechanical, electronic and computer programming design followed by exhaustive laboratory testing—and then an insulting 7-day wait for the weather to cooperate—the instrument package was finally sent aloft as Oct. 11 dawned in Palestine, Texas. There the National Center for Atmospheric Research launched the 250-foot diameter balloon, sending its payload up to its "float level" 117,000 feet above the ground. Prevailing winds at this altitude drove the balloon eastward and, after cut-off, the payload parachuted to a comparatively soft landing some 300 miles away, about 10 miles south of Yazoo City, Mississippi.

The purpose of the experiment was to determine the feasibility of eventual satellite monitoring of the ozone distribution in the atmosphere. Already, Tiros satellites are televising the cloud cover below to provide a continuous mapping of the changing weather patterns and thus help in long-range weather forecasting. It is hoped that additional monitoring of ozone in the atmosphere will furnish further helpful data to improve forecasts. The basis of the monitoring is the well-known absorption of ozone in the 2000A-3000A region which protects us earthlings from being burned to an ultraviolet crisp.

Ozone in the upper atmosphere results from a complex equilibrium loop of chemical reactions. First atmospheric oxygen, O_2, struck by the intense ultraviolet and x-ray emission from the sun, is converted to ozone, O_3. The ozone then develops the intense absorption band in the ultraviolet which not only brakes the reaction but causes dissociation back to O_2 to complete the cycle.

In the lower atmosphere, ozone in lesser concentrations than at higher altitudes is produced over areas of air pollution. Nitrous oxides are dissociated by sunlight into O_3 among other reaction products.

Interest in ozone stems from two reasons. In the upper atmosphere, the oxygen-ozone-oxygen cycle is accompanied by the generation of huge quantities of heat as the absorption of kinetic energy at 3000A is transferred to the atmosphere. Great convective swells develop; turbulence and movements of broad masses of air sweep across the sky. The determination of ozone concentration gradients in four dimensions—along the three coordinates and in time—will, it is thought, provide continuous and immediate clues regarding the development of weather conditions on the ground.

Secondly, it is thought that ozone can serve as a "tracer" to spot motions of the atmosphere in lower regions. Hopefully, smog movements may then be followed, smog warnings issued.

The experiment incorporated a Model 1700 spectrometer inside of a framework housing suitably insulated with polyurethane foam. A plane mirror was so oriented on a turret that, when indexed to five positions, the spectrometer viewed first downward, next the sun through a quartz diffusion plate, then a Hg calibration lamp to correct for any unforeseen wavelength errors, then upward and finally in an "anti-solar" direction. The detector chosen was an Ascop solar-blind photomultiplier with a CsTe cathode. Photon counting was the amplification system decided upon because of the ease with which information could be digitized for telemetering to the ground-based CDC 160 computer.

The spectrometer was set to scan first in a forward direction the region 2600-3300A as it was pointed downward. Scan rate was 1 A/sec and an event marker signal was fed to the computer for wavelength calibration every 0.5A. Slits were opened to achieve a resolving power in the order of 5A. After directing the look downward, the turret-mounted mirror swung to a position where direct sunlight could be studied and the scanning direction was reversed, 3300-2600A.

J. R. Bohse, at the University of Maryland, examines the almost totally recovered equipment after its 117,000 foot-high rendezvous with ozone in the earth's upper atmosphere. Most evident here is the housing framework and polyurethane foam sheathing which insulated the spectrometer and related instrumentation from the debilitating cold.

The initial experiment was not wholly successful for one of those simple but unforeseen reasons that plague all space research: the horizontal aiming system went haywire. To obtain the required data, the spectrometer had to be constantly oriented toward the sun. This was to be accomplished through an "aspect eye" sensor which controlled a small motor below the swivel joint connecting the payload to the balloon. Great care was taken to make sure that the aspect eye would operate at temperatures up to 100°C because, constantly facing the sun, it was expected to heat up considerably. On launching, however, the aspect eye never locked itself into the direction of the sun. It got colder and colder as the balloon rose and finally failed before ever starting its orientation operation.

Despite the lack of data in the fore and aft directions to and away from the sun, all other data were taped and are presently being processed. Final reduction of data will be in an IBM 7094. Sneak previews of the data indicate that results are in the right "ballpark."

Surpassing the Unsurpassable

A self-imposed function of our SPEX SPEAKER has been to resurrect from obscure literature those articles which, because of their cosmopolitan interest, might be welcomed by our readers. An example is a technical note describing the excellent research by Profs. Boye Ahlborn and A. J. Barnard of the University of British Columbia in Vancouver, which until now has been secreted from most of their fellow spectroscopists in the Journal of the American Institute of Aeronautics and Astronautics (p. 1136, June, 1966).

Ahlborn and Barnard accomplished what appears to be the impossible. They showed convincingly that they could make wavelength-shift measurements better than the theoretical resolution of their spectrometer. Specifically, working with a Spex Model 1700 Spectrometer having a theoretical resolution at 6328A of 0.05A, they demonstrated Doppler shifts of around 0.003A.

Their clever technique involves two identical variable neutral density wedges. One wedge is placed over the top half of the exit slit of the spectrometer; the other, oriented so its increasing density is in the opposite direction, is placed over the bottom half of the slit. Through mirrors, light from each half of the exit slit is directed to separate photomultipliers. When the output signals (S_1 and S_2) are measured, the investigators calculated that the wavelength shift of a line is equal to:

$$\Delta\lambda = [(S_1 - S_2)/(S_1 + S_2)]\ [t_0/b(dx/d\lambda)]$$

where t_0 is the initial transmittance of the filter and b is the change in transmittance at a distance x across the wedge.

Assuming the exit slit of the spectrometer to be equally illuminated over its length, when the line whose profile is under study is centered in both wedges, they transmit identically. Now cause a slight shift of the line, in this case by a refractor plate placed inside of the entrance slit of the spectrometer. The peak of the line then shifts to one side, let us say to the right where the upper wedge is getting more dense and the lower wedge is getting less dense. Now the two photomultipliers receive differing amounts of light and a calculation based on the equation above will furnish the amount of the shift.

The work was done in connection with Doppler shifts in plasmas. But other applications are sure to come to the minds of our readers.
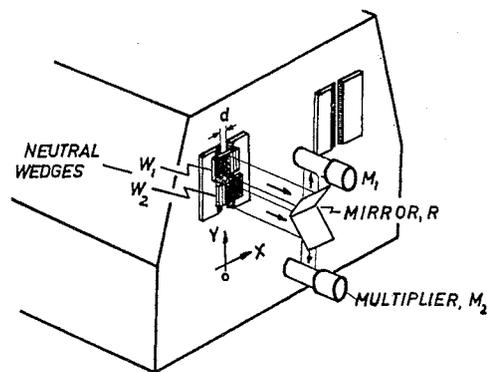
The Action Spectrum of Erythema Induced by Ultraviolet Radiation

OK, what causes sunburn? The title above encapsulates a recent study by Drs. Daniel Berger, Frederick Urbach and Ronald Davies of Temple University's Skin and Cancer Hospital in Philadelphia.

The last definitive work on the subject of sunburn having been done in Germany in 1927 by K. W. Hausser, the present investigators felt that it should be updated especially in view of the fact that prism spectrometers of that vintage suffered from scattered light ailments. Was the 1% or more of scattered radiation, wavelengths other than those supposed to be there, largely responsible for skin reddening? That was the question that new techniques and instrumentation could answer.

Modern technology provides access to far more sophisticated and powerful equipment than that known in 1927. Starting with a 2500-watt Xenon lamp, a source that yielded 2 mW/cm² after passing through the spectrometer, scattered light levels were reduced to an estimated 0.00001% of the peak radiation with a Spex Model 1400 Double Monochromator. It was modified with slits opening to 6.5 mm in order to get enough throughput to cause sunburn in a reasonable time. With slits opened wide (bandpass 35A), a mild dose of sunburn was produced in 9 seconds at 3000A, the peak of sunburn activity. At 2450A, 84 seconds were required; 13 minutes at 3150A; 25 minutes at 3200A.

Armed with filters, densitometers and thermocouples, Berger et. al. were able to characterize their observations further. Thus 2540A radiation produces a pale pink-red sunburn which appears in 4-5 hours, peaks in 8-12 hours and starts to fade in 24 hours. The color of sunburn from 3000A radiation, by contrast, is red-purple; it peaks in 24-48 hours and persists for 3-5 days.

The capability of setting the double monochromator to single-mode operation encouraged a study of the effects of scattered light. At the intermediate exit slit position, scattered light was estimated to be 4000 times worse than at the final exit slit. By exposing the abdomens of subjects to identical levels and bandpasses of radiation from the exit and intermediate slits, they found that the stray light from a single monochromator could introduce an error of over 50%.

IN MEMORIAM, MAURICE F. HASLER

The unique career and active life of this internationally known scientist came to an end on July 16, 1968 with an untimely accidental death at 61. The car he was driving was struck at a grade crossing by a railroad switch engine.

In more than 34 years devoted to research, design, development and production of spectrochemically-oriented analytical instrumentation Dr. Hasler had accumulated a distinguished collection of awards, society memberships, patents and published scientific papers. Relative newcomers to spectroscopy may not remember that Dr. Hasler pioneered the instrumental package, putting together source, spark stand, spectrograph, microphotometer, photoprocessor and calculator equipment to provide accurate, speedy and efficient production laboratory service.

A co-founder of Applied Research Laboratories, he was Chairman of the Board, as well as Director of Research and Development. The company became a wholly owned subsidiary of Bausch & Lomb, Inc. in 1958 and subsequently Dr. Hasler was appointed to the Bausch & Lomb Board of Directors, achieving his most satisfying goal upon the opening of the Hasler Research Center, Goleta, California in 1963. Mutual friends and associates, we are sure, will agree that this living legacy remains as a most fitting memorial to Maurice Hasler.