(2)

ornl

ORNL/TM-7260

OAK RIDGE NATIONAL LABORATORY

UNION CARBIDE

A Digital TV-Echelle Spectrograph for Simultaneous Multielemental Analysis using Microcomputer Control

J. B. Davidson
A. L. Case

OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

HIGHLIGHTS

A digital TV-echelle spectrograph with microcomputer control was developed for simultaneous multielemental analysis. The optical system is a commercially available unit originally equipped for film and photomultiplier (single element) readout. The film port was adapted for the intensifier camera. The camera output is digitized and stored in a microcomputer-controlled, 512 × 512 × 12 bit memory and image processor. Multiple spectra over the range of 200-800 nm are recorded in a single exposure. Spectra lasting from nanoseconds to seconds are digitized and stored in 0.033 s and displayed on a TV monitor. An inexpensive microcomputer controls the exposure, reads and displays the intensity of predetermined spectral lines, and calculates wavelengths of unknown lines. The digital addresses of unknown lines are determined by superimposing a cursor on the TV display. The microcomputer also writes into memory wavelength fiducial marks for alignment of the TV camera.

Wavelength determination of ±0.02 nm can be made. A sensitivity improvement of 100X at 546 nm was demonstrated in a comparison with a standard, dc-operated photomultiplier at room temperature, using integration on the camera tube target. A rapid qualitative comparison of two stored spectra can be done by "blink testing" at one comparison per second. Preliminary results are given on a six-element standard containing Be, Cd, Hg, Pb, Sb, and Tl using a dc plasma jet for excitation.

CONTENTS

1. INTRODUCTION

1.1 General

An important trend in analytical spectroscopy in the last few years has been toward the replacement of the single-detector, single-recording-channel instruments with multidetector arrays and computer-based data collection and storage systems. The multidetector, multiwavelength approach eliminates the exit slit and projects a larger portion of the spectrum (up to several hundred nanometers) onto a linear or an area-imaging detector which acts as many hundreds or thousands of point detectors operating simultaneously. Data throughput can be increased by orders of magnitude. Contaminants which might go unobserved in a conventional single-channel system can be recognized. In addition, experiments involving transient spectra can be done.

The multichannel approach to nuclear spectroscopy has had a successful evolution over the last 35 y. Many of these nuclear electronics techniques have their counterparts in the so-called "optical multichannel analyzers." Present commercial development is concentrated on recording conventional linear spectra, using vidicon camera tubes or photo-diode arrays. Because of the small size of these detectors, the amount of spectrum which can be recorded at one setting of the optics is limited. The corollary situation is the loss of resolution which results from crowding the spectrum onto a detector 2-5 cm in width. The system to be described avoids this crowding through the unique spectrum format of the *echelle crossed dispersion spectrograph*, which was invented by Harrison,[1] saw service in the atomic energy program,[2] was revived in the rocket and space programs,[3] and lately in analytical instrumentation.[4-12] The echelle crossed dispersion spectrograph folds the spectrum into a two-dimensional raster whose length may be several meters and which preserves resolution and wavelength coverage. At the same time, the raster format fits into the TV-based area detectors.

1.2 Background of the Present System

Several years ago at Oak Ridge National Laboratory, Y. Talmi, P. M. Griffin, H. W. Morgan and G. K. Werner proposed to develop an echelle spectrograph for simultaneous multielemental analysis. A preliminary optical design to use a charge injection, area detector was completed[13] and some experience in applying detector arrays to linear spectra was gained.[14] Shortly thereafter there came on the market an improved echelle system with a 100 × 125 mm film output and a photomultiplier output. This improved optical system with its larger format suggested the use of a minifying image tube and a secondary electron conducting vidicon with a large, fast, digital memory to make a multiwavelength electronic recording system. Such a combination had been successfully used for a neutron counting camera.[15-16]

2. APPARATUS

A diagram of the overall system is shown in Fig. 1. Included are the excitation source, optics, and the three readout modes: photomultiplier, film, and the intensifier-digital TV system. The photomultiplier and film features are as supplied by the manufacturer. An externally operated lever was added for moving the mirror which directs the spectrum from the photomultiplier port to the film or TV port. In the standard instrument the mirror is operated when the film holder is pulled into the focal plane from its resting position against the main housing. The added lever makes it possible to change readout modes quickly without refocusing the TV camera.

2.1 Optics

The optical parameters and specifications* are shown in Table 1. The design of echelle grating spectrometers has been discussed by Harrison, Richardson, and others.[1,2,11,12,16-19]

The main parameters and equations governing the design and performance of an echelle grating are summarized in Fig. 2.[17]

2.2 Intensifier

The photographic format of the spectrometer as supplied is 10.0 × 12.5 cm (4 × 5 in.). To cover the actual area of the spectrum (∿7.5 × 7.5 cm), we used the central area of an image intensifier** having a 15-cm diameter fiber optic input. The tube is a single-stage, electrostatically focused, 6:1 demagnifying unit with a 2.5-cm fiber optic output screen. Its main specifications are shown in Table 2. The P15 output phosphor was selected for its fast decay (∿1 μs) to avoid afterglow when recording transient spectra or when used for event-counting applications. The fiber optic faceplate eliminates coupling lenses because it mates directly with the fiber optic faceplate of the camera tube. In addition to the overall flux gain, a brightness gain of 36 (the area reduction factor from input to output) improves the signal-to-noise ratio of nonpoint images.

Since the photocathode response of the intensifier (S20) does not extend to the ultraviolet, a wavelength converter is used. This is a thin layer of p-terphenyl deposited on quartz and placed in contact with the input faceplate.

---

*Spectrometrics, Inc., Burlington, Massachusetts.

**Manufactured by Machlett Corp., Stanford, Connecticut.

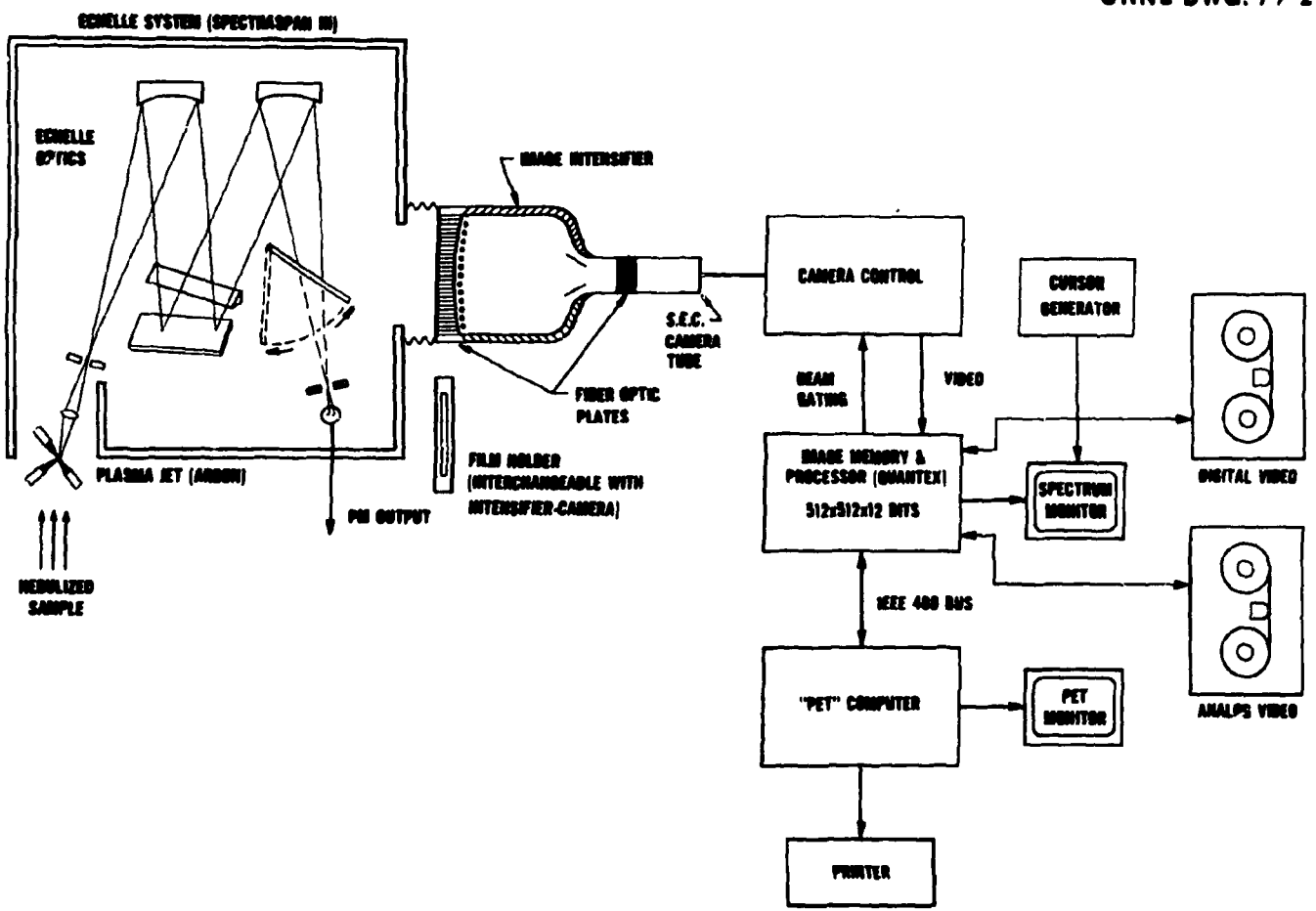


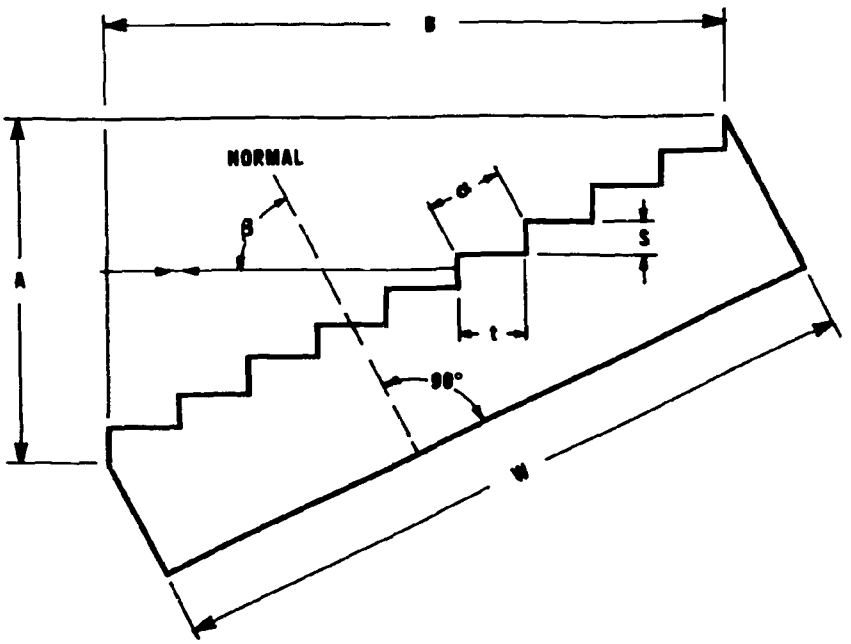
Fig. 1. Digital TV-echelle spectrograph: overall system.

Table 1. Spectra-Span III optical specifications

Focal length	f = 75 cm
F number	F = 13
Grating width	W = 9.6 cm
Grating height	H = 4.6 cm
Diffraction angle	β = 63°26'
Grating spacing	79 grooves/mm
Prism	30° quartz
Wavelength range	190 to 800 nm

Wavelength	Dispersion	Resolution (25 μ slit)
200 nm	0.061 nm/mm	0.0015 nm
400 nm	0.122 nm/mm	0.0030 nm
800 nm	0.244 nm/mm	0.0060 nm

ORNL DWG. 80-16710



$r = \frac{t}{s}$

λ = Wavelength

N = Number of Grooves

m = Spectral Order

P = Projection Distance

Free spectral range $F_\sigma = \frac{1}{2t}; F_\lambda = \frac{\lambda^2}{2t}$

Linear dispersion $\frac{dL}{d\lambda} = \frac{2rP}{\lambda}$

Resolving Power $\frac{\lambda}{d\lambda} = \frac{2B}{\lambda} = \frac{2Nt}{\lambda}$

Order $m = \frac{2t}{\lambda}$

Grating Equation $m\lambda = 2t = 2\sigma \sin \beta$

Fig. 2. Echelle parameters.

Table 2. Image intensifier tube specifications

Focus	Electrostatic
Stages	1
Input	150 mm diam fiber optic
Photocathode	S-20
Sensitivity	100 μA/lm
Gain	34 photons/photon (450 nm input light)
Output	2.54 cm diam fiber optic, P-15 phosphor
Resolution	5 live-pairs/mm referred to input (average)
Gain uniformity	50% edge-to-edge
Equivalent background illumination	6×10^{-12} lm/cm^2
Operating voltage	25 kV
Integral ion pump	

2.3 SEC Camera

The camera tube converts the brightened spectral image at the output of the intensifier to a charge image which can be read off by a scanning electron beam. The secondary electron conduction (SEC) tube* was selected for several important characteristics: sensitivity, minimum lag (∿90% read off in one scan), integrating capability, and extended dynamic range for point images (Table 3).

Table 3. Camera tube characteristics

Type	WL 30893 SEC Vidicon
Input	2.54 cm diam fiber optic
Photocathode	S-20
Sensitivity	146 μA/lm
Image section	Electrostatic focus
Reading section	Magnetic focus and deflection
Resolution	650 TV lines (325 line pairs) per raster height
Lag	At 50 na, signal is 11% in second frame
Uniformity	18%

The spreading of intense point images on the camera tube target ("blooming") can seriously affect the resolution and dynamic range in camera tubes.[20] Blooming on the SEC tube target is such that, although the center of a point-like image saturates, the light-produced charge in adjacent pixels (the "wings" of the charge distribution) can continue to increase in a nonlinear, but quantitative fashion. If the integral

*Westinghouse Corporation, Elimira, New York.

(volume) of the charge image is taken instead of the usual peak height, the dynamic range can be extended by an order of magnitude. These effects are shown in Figs. 3 and 4. Figure 3 shows the spreading effect on the peak as the signal is increased by the summing TV frames. Figure 4 shows peak height and volume vs concentration for a beryllium sample and the effect on dynamic range.

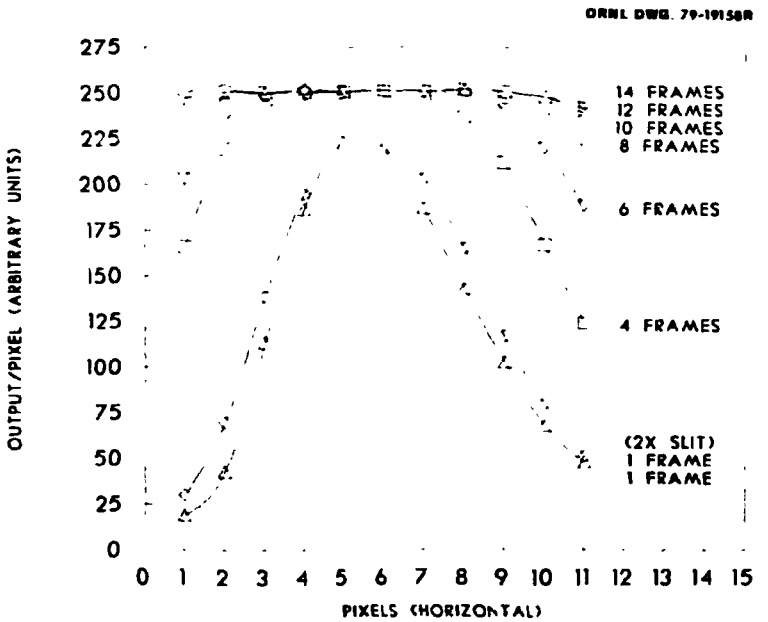


Fig. 3. Image spreading of point source on SEC tube target.

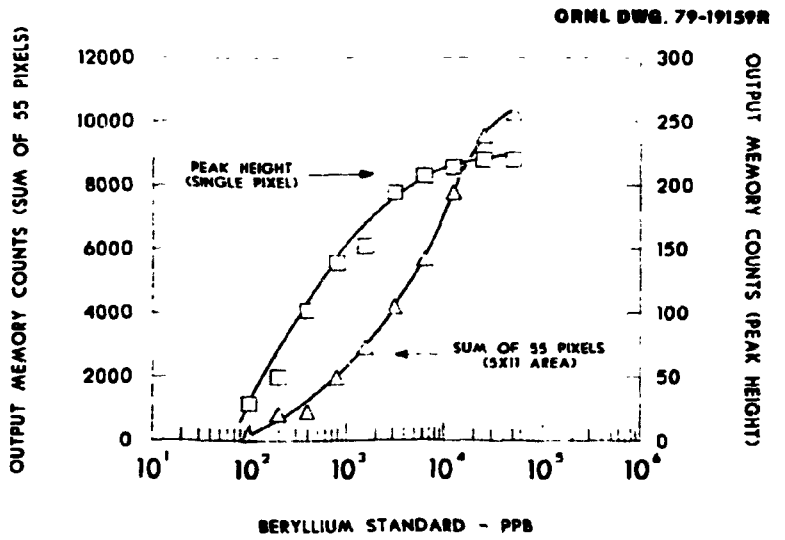


Fig. 4. Dynamic range comparison using a beryllium line: peak height (1 pixel) vs volume of peak (55 pixels).

The limiting resolution of the camera tube is about 600 TV lines horizontally and 400 vertically. This is less than that of the image intensifier, which is 750 TV lines. The resultant resolution approximately matches the 512 × 512 picture elements into which the image is digitized.

The camera controls were assembled from commercially available vidicon circuit boards* into a "6-wide" nuclear instrument module. Alignment, focusing, target, and suppressor voltages needed for the SEC tube were added. Circuits were added for turning off the scanning beam for signal integration. The synchronizing generator supplies the RS 170, standard signals (525 line, 30 frames per second).

2.4 Image Dissector

References 9 through 12 describe the use of the image dissector tube in echelle spectrographs. This tube is a photomultiplier whose photocurrent can be sampled at any small area (resolution element) by deflecting and focusing fields. It is inherently without memory and, hence, nonintegrating, thus precluding its use in simultaneous (parallel) recording of spectra. Only the signal from the selected resolution area (or spectral line) is measured. The signal from any other lines is lost. In multielemental analysis this means a loss of sensitivity, which depends on the number of lines N, each of which is to be measured for time t. The sensitivity is reduced to 100/N percent. The image dissector can be sensitive when measuring a single line (single photoelectrons can be counted), but its inability to integrate causes a drastic reduction in its overall sensitivity as a multidetector.

From the preceding discussion, it is apparent that the image dissector is different from the vidicon camera tube, considered as a type. Vidicons, such as the SEC tube used in the present system, can capture and store even instantaneously occurring spectra, which can be sampled (or scanned) while being integrated or later after the excitation is over.

2.5 Digital Image Memory and Processor

The spectrum is recorded by digitizing the analog video signal to 8 bits (maximum) as the charge image is scanned from the camera tube target and stored in the image memory processor** which holds 512 × 512 × 12 bits. The analog-to-digital converter and fast memory complete the digitizing and storage of the entire picture in 33 ms (one frame time). Other useful features of the memory-processor are:

1. Point-by-point digital subtraction of incoming video from information previously stored in memory (background, for example).

---

*Cohu Electronics, San Diego, California.

**Quantex Corp., Sunnyvale, California.

2. Summing of successive video scans. The memory contains 12 bits per pixel; therefore, a total of 4095 memory counts can be accumulated in a pixel before overflow and automatic shut off.

3. Continuous (sliding) averaging of input video.

4. Memory quartering.

5. Built-in microprocessor control of all functions, including a sequence-learning and execution mode.

6. IEEE-488 instrument bus control for reading and writing at any memory location. Instructions and data are transferred serially in single bytes.

7. Alternate parallel memory access via a 40-line port for reading and writing.

8. Analog video output for TV monitor.

These features are shown schematically in Fig. 5.

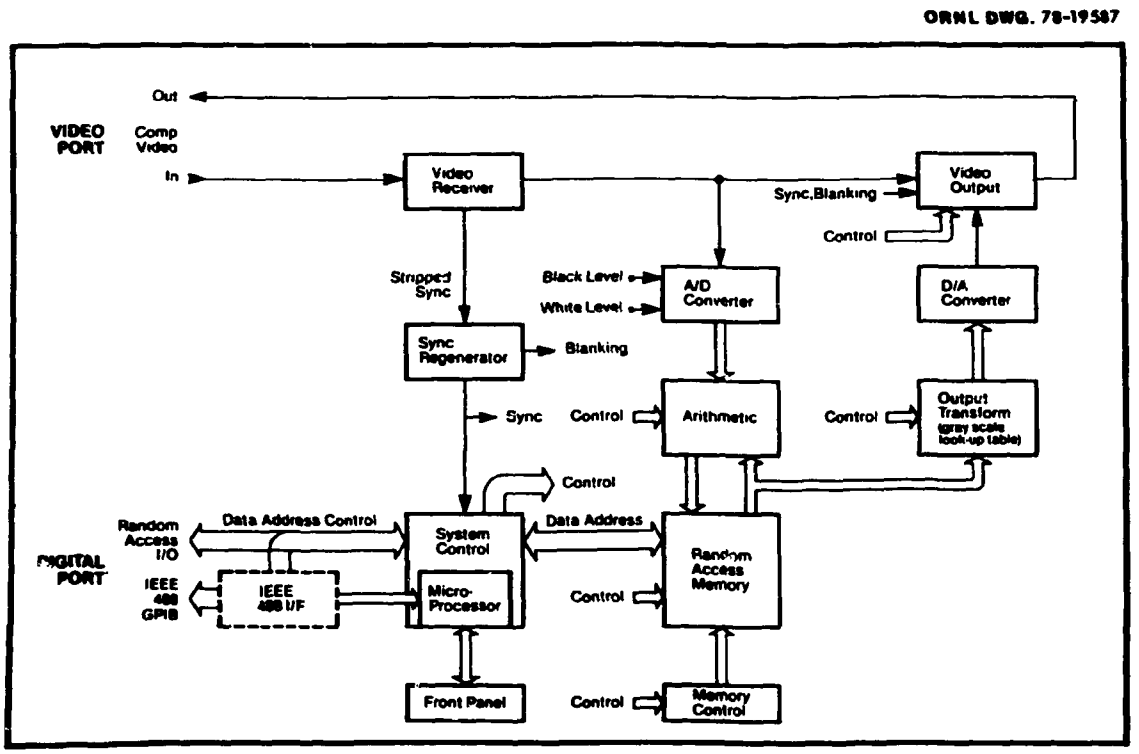


Fig. 5. Block diagram of memory-processor.

2.6 Microcomputer

Wavelength determination and spectral line intensity measurement are accomplished by means of an inexpensive microprocessor-based computer* connected to the memory-processor by the IEEE-488 instrument bus. The main functions performed by the microcomputer are:

1. Reading of any pixel, row of pixels, or pixel area; with totalizing, listing, and display by wavelength, element, etc.

2. Writing data from keyboard or program into any pixel. With this function, wavelength fiducials can be stored in memory for direct superpositioning on incoming video or previously stored video. This greatly facilitates the alignment of a calibration spectrum using TV positioning controls, so that the calibration lines match the computer generated calibration pattern.

3. Generating on the monitor screen a marker corresponding to a wavelength entered from the keyboard.

4. Calculating the wavelength of any point in the spectrum from the vertical and horizontal addresses. Addresses are determined by setting a separate digital cursor over the spectral line whose wavelength is wanted.

5. Controlling the push-button functions on the memory-processor, setting the spectrum integration time and camera beam gating.

6. Dividing the memory into quarters, and "blink" testing of spectra stored in two quarters.

In the blink test, the two spectra are alternately displayed on the full monitor screen at 2/second. Spectral lines which blink are not present in both samples in the same amount, thereby giving a rapid qualitative comparison over the complete uv-visible range.

2.7 Cursor Generator

After an unknown spectrum is digitized and stored, it is displayed on the monitor. Usually there are landmarks (argon, sodium, etc.) to indicate the wavelength region in which an unknown line lies. However, to obtain the wavelength of the unknown to 0.1 nm or less, its exact digital address must be determined. This is done by setting digital switches to position a cursor (one brightened pixel) over the unknown line while observing both on the monitor. The vertical and horizontal addresses from the digital switches are entered into the computer, which

---

*PET 2001-8, Commodore Business Machines, Inc., Santa Clara, California.

calculates and displays the wavelength. The reverse procedure of locating a given wavelength's position on the screen consists of entering the wavelength and setting the cursor at the addresses calculated by the computer.

The cursor generator consists of two digital delay gates* synchronized with the address clock in the memory-processor. One gate selects the horizontal line, and the other sets the position of a 50-ns pulse on the selected line. This pulse, mixed with the camera video to the monitor, superimposes a brightened pixel on the display.

2.8 Light Sources

For the development and testing of the TV readout system and for comparison with film and photomultiplier modes, various spectral lamps, hollow cathode lamps and the Spectra-Jet** argon plasma source were used. The characteristics of the plasma source as supplied by the manufacturer are shown in Table 4.

Table 4. Plasma-jet specifications

Spectra-Jet Plasma Jet, dc Arc	
Gas	Welder's grade argon
Typical flow rate	$\sim$10 m^3/s
Input power	115 V ac, 8 A
Sample uptake	$\sim$3 ml/min
Jet voltage	30 V

3. TEST RESULTS

Empirical expressions for locating wavelengths and for generating fiducials were derived from measurements made on the film and TV outputs using known spectral lines. One polynomial gives the spectral order that corresponds to any vertical address. The wavelengths corresponding to each pixel on an assumed vertical reference line are computed from a polynomial fitted to data from known lines. A third expression calculates the wavelength at any horizontal pixel along the order, using the reference wavelength and the known dispersion of each order converted to pixels per nanometer.

As a test, the computer was programmed to generate a point in memory every 0.1 nm from 220.0 to 809.6 nm. This pattern was stored and photographed from the monitor (Fig. 6). The superimposed spectrum, also stored in memory, is from a mercury lamp. The TV scan lines are just visible in

*TM 500 series by Tektronics, Inc., Beaverton, Oregon.
**Spectrametrics, Inc., Burlington, Massachusetts.

ORNL PHOTO 8391-80

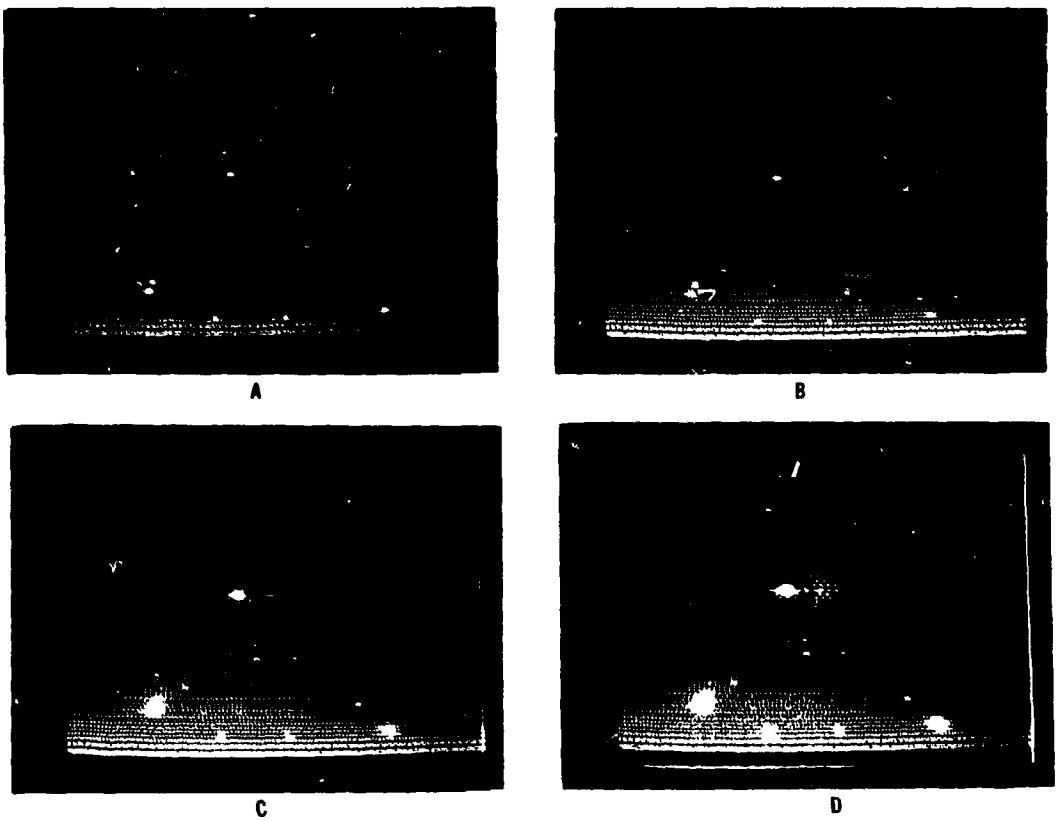


Fig. 6. Computer-generated echelle pattern with superimposed mercury spectrum. The separation of dots is 0.1 nm. Successive photographs show weak lines revealed by displaying lesser significant bits of data in memory (approaching background).

the background. Each order in this computer-generated pattern is separated by one or more scan lines. However, in an actual spectrum there could be ambiguity in determining the order in the long-wavelength region (>700.0 nm) where the vertical dispersion is less. This may produce large errors in wavelength determination. Selection of addresses above and below the apparent line, for comparison of the sample, can resolve the ambiguity. Selection of alternate lines of shorter wavelength is also a possibility. The four photographs in Fig. 6 illustrate that displaying successively smaller significant bits of the data in memory can make weak lines visible.

3.1 Wavelength Determination

A test of the ability of an operator to measure wavelength was made using eleven lines from a mercury spectrum stored in memory. The cursor was set on each line in turn, the addresses were written on separate sheets, and the process was repeated three times without reference to previous settings. The results shown in Table 5 indicate that the vertical position

Table 5. Wavelength determination

Handbook Value (nm)	Calculated Value (nm)	Δλ (nm)	Addresses	
			Vert.	Horiz.
253.652	253.648	-0.004	125	287
296.728	296.714	-0.014	163	310
313.169	313.162	-0.007	173	312
312.566	312.553	-0.013	173	356, 357, 357, 357
365.015	364.996	-0.019	195	227
404.656	404.046	-0.010	206	195
407.781	407.783	+0.002	209	430, 430, 430, 431
435.835	435.832	-0.003	213	191
546.074	546.039	-0.035	231	468
576.959	576.978	+0.019	235	352, 351, 351, 351
579.065	579.081	+0.016	234	269, 269, 269, 268

(order selection) was reproduced identically in the 44 settings. The horizontal locations were identical in 35. The wavelengths calculated by the computer from the cursor settings are shown in column 2, and the difference from the handbook value in column 3. Column 4 gives the vertical and horizontal addresses as read from the cursor generator dials. Except for the 546.074-nm line, the differences were less than 0.02 nm over the 300 nm covered by the lines.

3.2 Resolution

The overall resolution of the system is 0.05 nm (FWHM) at 260 nm (Fig. 7). The resolution varies over the spectral range as the dispersion changes (Table 1). The spatial resolution of the intensifier-TV camera is the limiting factor, since the inherent resolution of the optical system is an order of magnitude better, as may be seen in Fig. 8, which is a densitometer trace of the "iron triplet" taken on film.

Figures 9 and 10 show the appearance of the monitor of the memory contents for a six-element combined standard solution with and without background subtraction (distilled water blank). The excitation was by the argon plasma-jet. Since the position of the excitation region in which there was minimal background from the plasma was critical, micrometer adjustments were added. The results of reading the intensities of several concentrations of the combined standard are shown in Fig. 11.

ORNL PHOTO 1416-80

Fig. 7. PET computer plot of the overall system resolution at 260 nm.

ORNL DWG. 78-16481

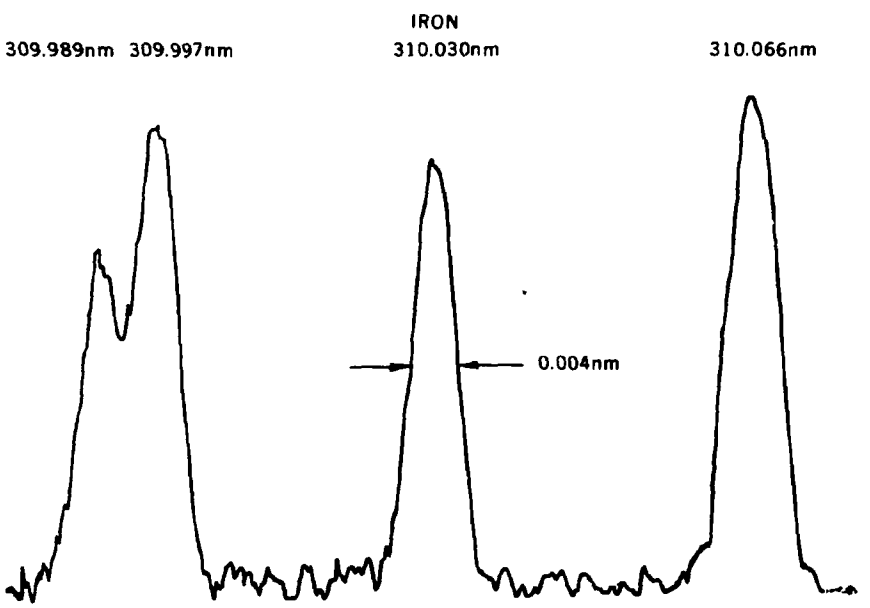


Fig. 8. Resolution of the spectrograph at the photographic port, using film.

ORNL PHOTO 2900-79

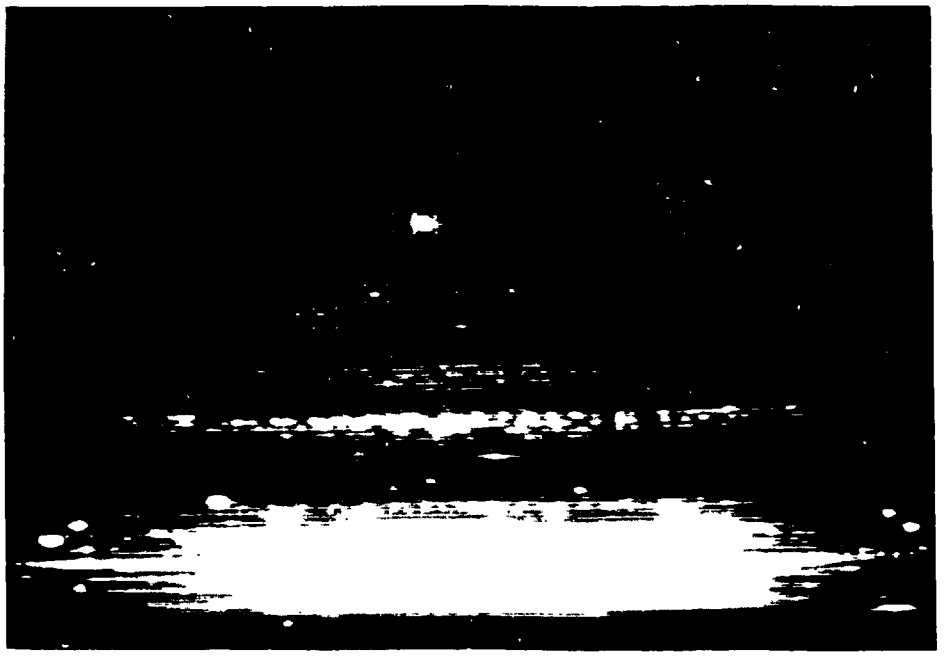


Fig. 9. Monitor display of a stored spectrum from a six-element standard without background subtraction. Rectangular, four-dot windows around selected lines were superimposed by the computer.

ORNL PHOTO 2899-79

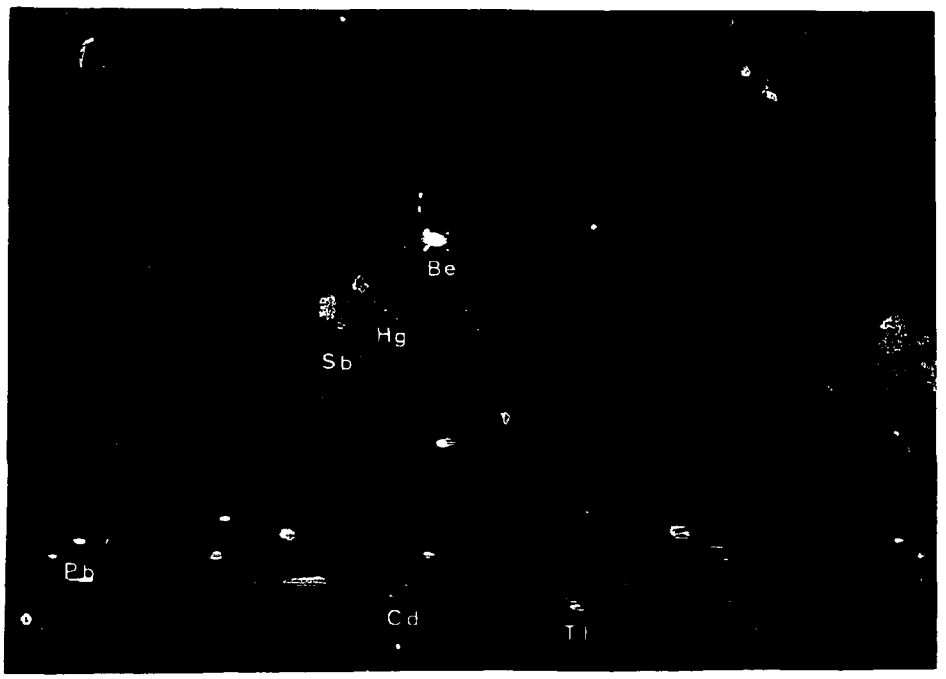


Fig. 10. Monitor display of spectrum in Fig. 7 with background subtracted (distilled water blank).

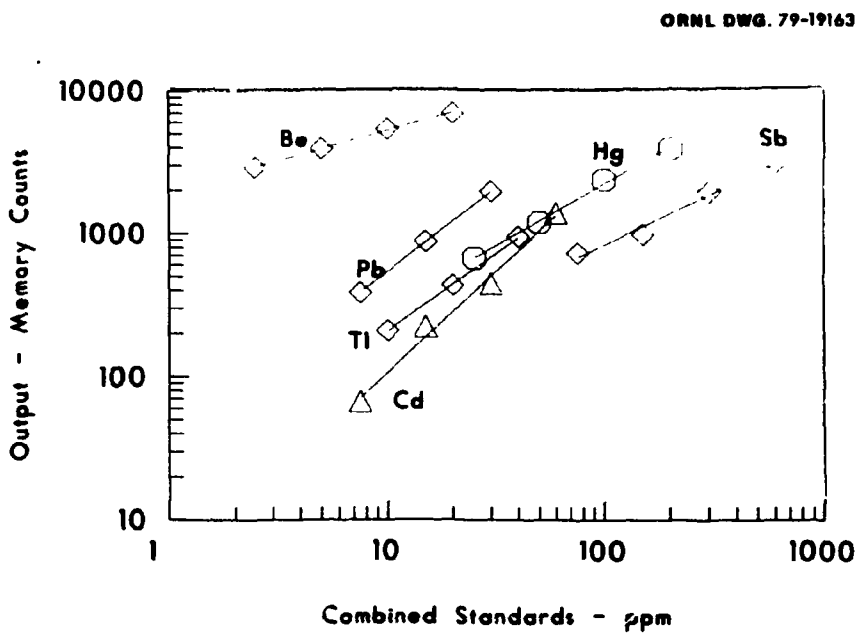


Fig. 11. Curves obtained from simultaneous analysis of a six-element liquid standard.

3.3 Sensitivity

The outputs from the TV and a photomultiplier (dark current ∿1 na) operating at room temperature were compared. The intensity of the spectral line was reduced by neutral density filters (Fig. 12). The sensitivity was extended a factor of 100 compared to the photomultiplier current as read on an electrometer (time constant ∿1 s).

Figures 13 and 14 show the complete system, with the exception of the plasma-jet assembly which is mounted in place of the hollow cathode lamp.

4. SUMMARY AND CONCLUSIONS

The development and preliminary testing of an echelle grating, crossed dispersion analytical spectrograph with digital TV readout has been described. The objectives which have been achieved are:

1. True, simultaneous spectrum recording and rapid analysis of 10 or more elements from a single sample.

ORNL DWG. 80-16711

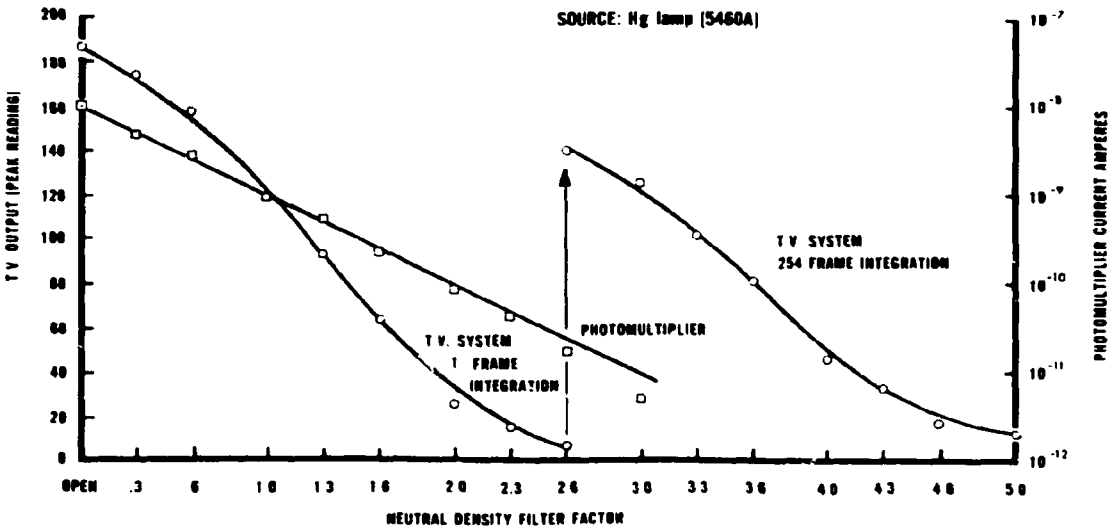


Fig. 12. Comparison of TV and photomultiplier sensitivity.

ORNL PHOTO 4837-78

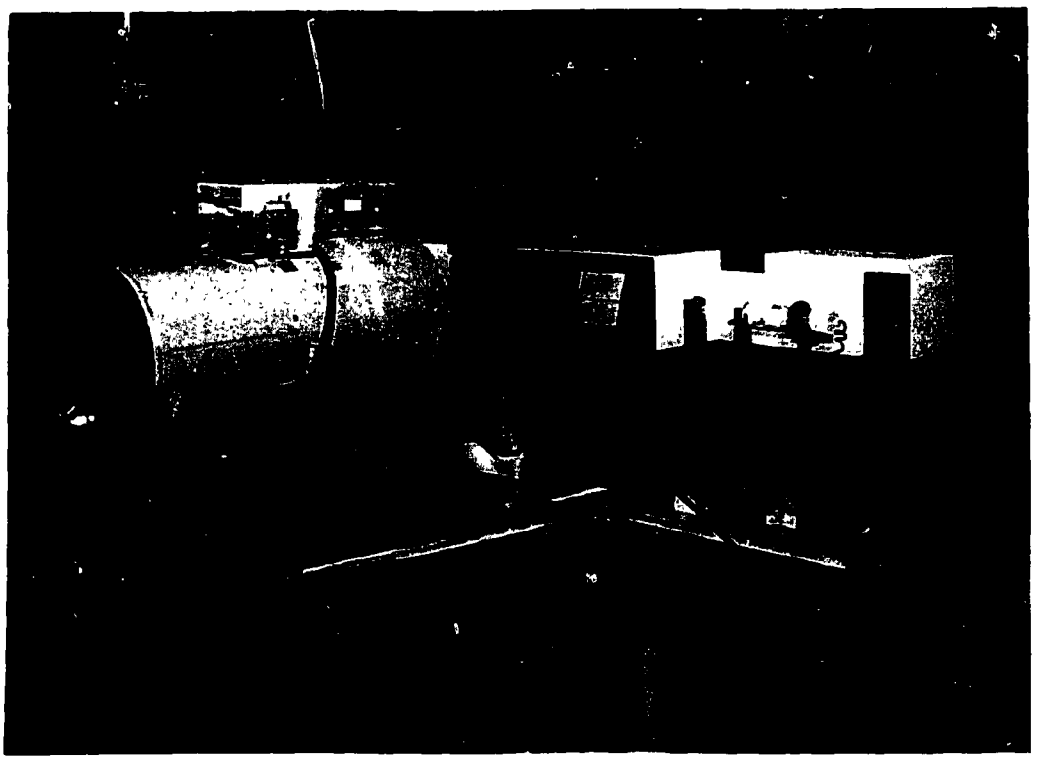


Fig. 13. Echelle optics and intensifier - TV camera mounted on table. The camera is moved back and the film holder is in place. A hollow cathode lamp is in place at the input.

ORNL PHOTO 3079-79

Fig. 14. Digital memory-processor, cursor generator, and monitor in rack, with computer to left.

2. Electronic readout of the spectrum from 200 to 800 nm in 33 ms (one TV frame time) without moving or changing the dispersing elements.

3. Digital conversion (a maximum of 8 bits per resolution element) and storage of 50K spectral data points per readout time (33 ms).

4. Capability of integrating time exposures of several hundred frame times before readout.

5. Sensitivity at each spectral point comparable to that of a good photomultiplier.

6. Real-time background subtraction at each spectral point.

7. Wavelength determination of 0.1 nm or better over the entire spectral range.

8. Real-time, point-by-point comparison of two spectra over the entire spectral range.

9. Transient spectrum-capturing capability in the subnanosecond range.

10. Mi[illegible]computer control and on-line data handling.

11. Det[illegible]mination of system limitation and future possibilities.

Initial tests indicate that the system will be useful for rapidly screening unknown solutions to detect many different elements. Quantitative analysis is possible with careful application of combined standards, use of matrix effect-reducing additives, internal standards, etc.

Initial testing has been done using atomic emission. Other techniques such as atomic fluorescence and atomic absorption (with multielement lamps or continuum) are readily adaptable. An interesting application to be tried soon is molecular fluorescence at low temperature of organic pollutants such as polynuclear aromatic hydrocarbons.

The system was developed around a commercial optical unit having photomultiplier and film readout features. In addition, it contains a complex mechanical dialing system for approximate wavelength selection and reading. The results indicate that a practical unit of greatly reduced mechanical complexity can be built using only TV readout with no moving parts. The design of such a system is being studied.

The speed with which a wide range (600 nm) can be monitored and compared with a standard or control spectrum using the blink test and other techniques, such as frame difference, opens the possibility of a continuous real-time system for process control, effluent discharge and environmental stream monitoring.

ACKNOWLEDGMENTS

The cooperation and assistance of T. Sliski in the mechanical design of the camera mount is gratefully acknowledged. We thank C. Fowler and E. Arakawa* who prepared uv phosphor layers, and C. Feldman** and M. Ferguson** for helpful discussions and standards preparation.

---

*Health and Safety Research Division.

**Analytical Chemistry Division.

REFERENCES

1. G. R. Harrison, *J. Opt. Soc. Amer.* 39, 522 (1949).

2. P. M. Griffin, R. A. Loring, G. K. Werner, and J. R. McNally, *Phys. Rev.* 87, 171 (1952).

3. J. D. Purcell, D. L. Garrett, and R. Tousey, *Space Research III*, Wolfgang Priester (ed.), John Wiley, New York, (1963).

4. D. L. Wood, A. B. Dargis, and D. L. Nash, *Appl. Spectros.* 30, 151 (1976).

5. P. N. Keliher and C. C. Wohlers, *Anal. Chem.* 48, 333A (1976).

6. M. S. Cresser, P. N. Keliher, and C. C. Wohlers, *Spectros. Lett.* 3, 179 (1970).

7. M. S. Cresser, P. N. Keliher, and C. C. Wohlers, *Anal. Chem.* 45, 111 (1973).

8. G. J. Matz, *Amer. Lab.* 3, 75 (1973).

9. H. L. Felkel, Jr., and H. L. Pardue, *Anal. Chem.* 49, 112 (1977).

10. H. L. Felkel, Jr., and H. L. Pardue, *Anal. Chem.* 50, 602 (1978).

11. A. Danielsson and P. Lindblom, *Phys. Scr.* 5, 227 (1972).

12. A. Danielsson, P. Lindblom, and E. Soderman, *Chem. Scr.* 6, 5 (1974).

13. G. K. Werner, unpublished report.

14. Y. Talmi and J. B. Davidson, *Pittsburgh Conf. Anal. Chem. and Spectros.* Paper 260 (1976).

15. J. B. Davidson, *Acta Cryst.* A25, S66 (1969).

16. J. B. Davidson, *J. Appl. Cryst.* 7, 356 (1974).

17. G. R. Harrison, J. E. Archer, and J. Camus, *J. Opt. Soc. Amer.* 42, 706 (1952).

18. D. Richardson, *Spect. Acta* 6, 61 (1953).

19. P. M. Griffin, *Encyclopaedic Dictionary of Physics*, Vol. 2, Pergamon Press, New York, 1961, p. 602.

20. R. R. Beyer, M. Green, and G. W. Goetze, *Advances in Electronics and Electron Physics*, 22A, J. D. McGee (ed.), Academic Press, London, 1966, p. 251.