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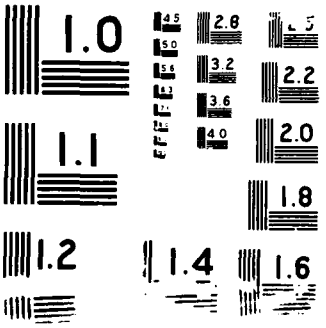
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Optical emission spectroscopic techniques play a wide role in modern chemical analysis. Over the years, these techniques have achieved new realms of sensitivity, selectivity, and accuracy. Early instruments employing photographic emulsion readout have been largely replaced with computer controlled systems. These systems either scan various wavelength regions or, in the case of direct reading spectrometers, contain banks of discrete photomultiplier tubes used to simultaneously observe a limited number of carefully selected wavelengths.

This "so called progress" has, without question, eliminated many laborious and time consuming tasks required to extract quantitative information from photographic emulsion. However, these time savings are costly because of the loss of the fantastic amount of information available when a large range of wavelengths are observed simultaneously. In atomic spectroscopy, most elements have several to hundreds of spectral lines; monitoring only one wavelength can lead to serious errors. Accurate background correction, source and system diagnostics and wavelength selection are often limited or compromised. Even with

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19. Abstract (continued)

these significant problems, direct readers generally outperform scanning instruments which suffer from their inherent need to observe each discrete wavelength separately, whether background or analyte line. Thus, the scanning approach is time consuming and highly susceptible to drift and stability problems.

Over the years, numerous investigators have realized these limitations. A variety of detection systems, including vidicons, image dissector tubes, othocons, and photodiode arrays have been examined in the quest for finding an electronic replacement for photographic emulsion. Until recently, all of these attempts have proven futile since each of these approaches suffered from one or more fatal limitation in the areas of sensitivity, wavelength coverage, dynamic range, number of resolution elements, cost, reliability, dark current, hysteresis and lag effects, or blooming. Recently, new spectroscopic systems employing advanced charge transfer device (CTD) solid-state array detectors have been implemented not only solving such problems, but offering new and exciting levels of performance. Characteristics of CTD detectors which make them ideally suited to both atomic and molecular spectroscopy include detector formats ranging in size from single elements to extremely large millions element arrays, photoactive areas from under 1 mm^2 to larger than 1000 mm^2, peak quantum efficiencies greater than 80%, dark count rates allowing many minute integration times, and read noises more than two orders of magnitude lower than commercially available photodiode array detectors[1]. The results of the evaluatic of the spectroscopically pertinent characteristics of several CTD detectors evaluated in our laboratories are presented.

The class of CTD detectors is divided into charge-coupled devices (CCDs) and charge-injection devices (CIDs). While both subclasses of CTD detectors, when properly operated, provide high performance, CIDs and CCDs possess differing capabilities suited to specific spectroscopic applications. Unique capabilities such as the ability of the CCD to alter the effective detector element size using the process of binning, and the ability of the CID to read the photogenerated charge information either destructively or nondestructively are described. Using these special abilities, several techniques for expanding the CTDs' operational dynamic range are discussed.

Using the special nondestructive readout mode of the CID, a special technique called random access integration (RAI) is used with a CID, allowing the integration time for each individual detector element to be independently optimized. The nondestructive readout allows the system to interrogate each detector element to determine the level of photogenerated signal during the course of an analysis. Before detector elements associated with bright spectral lines are overexposed, they are read and both the observed signal and the integration time are recorded. Detector elements found to be monitoring weak lines are allowed to integrate until sufficient charge has been collected. On extremely weak lines, multiple nondestructive reads are used to reduce the system read noise and further improve the signal-to-noise ratio. No prior knowledge is needed regarding line intensity; the system determines this during the course of the analysis. Background is also measured on both sides of each spectral line, allowing sophisticated background correction to be used as necessary[2]. When appropriate, multiple lines are observed for each element providing improved accuracy and enhancing detection capabilities.

While CTD detectors are available with a large range of formats and numbers of detecto elements, the larger arrays are rectangular instead of linear and are composed of relativel small detector elements ($\approx 25\mu$). The small size and format of these detectors are significa problems requiring ingenuity and imagination in an optical design in order to implement a system capable of providing appropriate resolution and spectral range for atomic emission spectroscopy[3]. The current CID echelle spectrograph uses an echelle grating for high dispersion, a quartz prism as a cross-disperser to separate the orders, and a telescope to reduce the two-dimensional spectral image to a size compatible with the CID detector. Data is presented describing the current CID-echelle system's detection limit and dynamic range performance in both simple and highly complex matrices. Detection limits for most elements are in the 1-20 ppb range. The analysis can be performed in complex matrices with almost no loss of sensitivity; for example, detection of < 5 ppb iron in the presence of 1000 ppm gadolimium is achieved.

19. Abstract (continued)

Using these concepts, the echelle-CTD system is able to utilize the wealth of spectroscopic information available during the course of the analysis to provide diagnostic information for improved accuracy and precision. The choices of spectral lines and background to be monitored is determined by the needs of the analysis, and includes such factors as the elements of interest, their concentrations (determined on-the-fly by the system), and possible interferences. Multiple wavelengths can be monitored for each analyte element while simultaneously observing adjacent background regions. This technology allows the concept of the truly "intelligent instrument" to be realized. Such an instrument is capable of selecting proper wavelengths and background correction methods for a given sample while the sample is being analyzed based on the specific composition of the sample.

(1) R.B. Bilhorn, J.V. Sweedler, P.M. Epperson, M.B. Denton, Applied Spectroscopy, (1987), 41, 1114.

(2) M.B. Denton, Analyst, (1987), 112, 347.

(3) R.B. Bilhorn, J.V. Sweedler, P.M. Epperson, M.B. Denton, Applied Spectroscopy, (1987), 41, 1125.

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by

M.B. Denton, R.B. Bilhorn, and J.V. Sweedler

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October 29, 1987

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Index Headings: Optical spectroscopy, multichannel detectors, atomic emission spectroscopy, molecular spectroscopy, charge transfer devices

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