

Advantages of Photodiode Array

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Preface

All products are continuously being improved for better performance. Spectrometers have developed in many ways since the introduction of simple and moderately priced spectrophotometers which were commercially available from the mid 1950's.¹ Such improvements have enabled SCINCO to manufacture PDA type UV-Vis. spectrophotometers.

The scope and performance of conventional single channel detector type UV-Vis. spectrophotometers were found to be somewhat limited. This encouraged a search for novel techniques which could be applied to the development of UV-Vis. spectrophotometers.^{2,3} Dispersed light is focused directly onto the detector array, saving considerable time and greatly reducing instrument complexity. The combination of dispersing element and detector array is employed in most spectrophotometers today.⁴

The introduction of multichannel detectors such as the linear photodiode array (PDA), charge coupled device (CCD) and vidicon enabled new detection systems to be developed for UV-Vis spectrophotometers and encouraged the rapid development of polychromators from the 1970s^{5,6,7}. As indicated in the diagram in **Figure 1** (PDA), a polychromator is an enhanced monochromator. With monochromators, wavelength scanning necessitates mechanically rotating

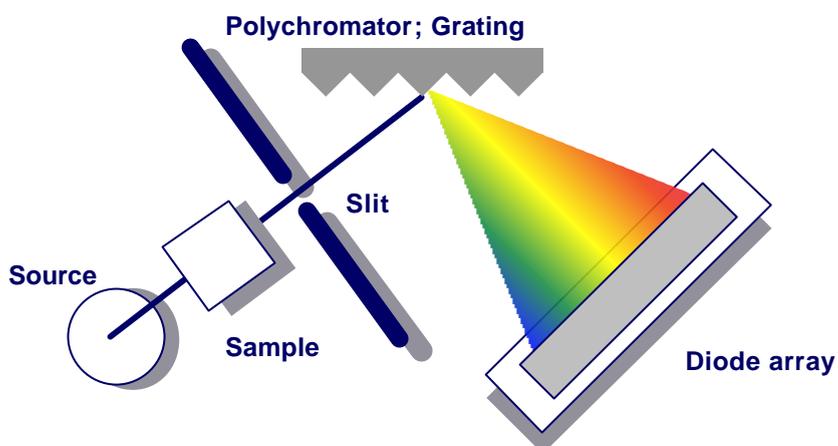


Figure 1. Schematic of photodiode array spectrophotometer

the dispersing element about its vertical axis; in a polychromator, it is accomplished by electronic scanning of the multichannel detector.

Multichannel detectors such as the photodiode array, charge coupled device or vidicon are usually flat and are best used with a dispersing arrangement which yields a flat focal plane. Under optimum conditions, they can detect as many wavelengths simultaneously as their number of individual diodes, resolution elements or pixels. Stray light and background per element are of course not lessened by the fact that they are arrays, but charge transfer devices have very low dark currents.

CCD requires less of an electrical charge than PDA and also has higher charge-to-voltage conversion efficiency, making CCD ideal for low-light-level detection such as Raman and Luminescence.^{8,9} PDA, on the other hand, is more suited for applications where the light level is relatively high. Because the photon saturation charge of CCD is small, if this saturation level is reached then the light intensity will be saturated. But for PDA the photon saturation charge is greater than CCD so the detection range of PDA is larger than CCD. Furthermore, PDA delivers lower noise than CCD. So we recommend using PDA in applications where higher output accuracy is needed.

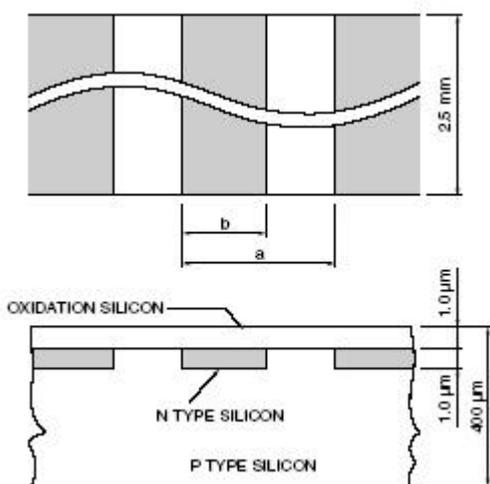


Figure 2. Simplified schematic diagram of self-scanning photodiode array, a : 25 mm, b: 13 mm

converts light into electrical signals and temporarily stores them. These signals are then read out as time-series signals via the output line by sequentially turning on the switch array connected

What is Photodiode Array (PDA)?

Diode arrays having numbers of elements ranging from 128 to 1024 – and even up to 4096 – are available. This multichannel detector makes an ideal sensor for an entire spectrum in a UV-VIS dispersive spectrophotometer. With that application in mind, newer arrays have been made with adjacent diodes 25.6 mm long and spaced 25 μm on centers. Each diode is defined by a p-doped region 13 μm by 2500 μm (2.5 mm) that serves as the cathode (**Figure 2**).

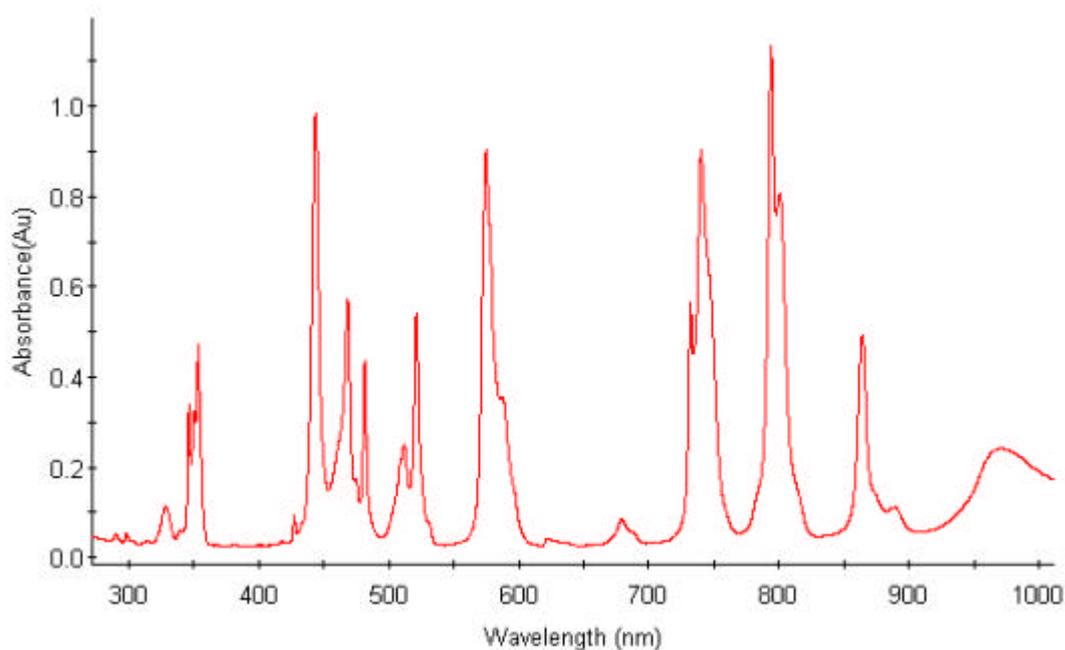
A polychromatic beam from the source is irradiated onto the inlet slit of the polychromator after passing through the sample compartment. The polychromator disperses the narrow band of the spectrum onto the diode array. The photodiode

to each photodiode with address pulses generated from the shift register.¹⁰

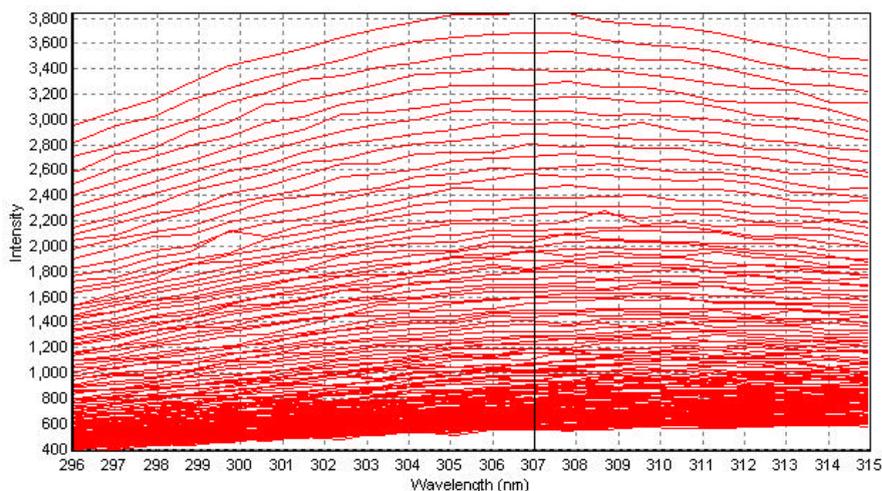
Simultaneous Multiwavelength Measurement

A spectrum for the whole wavelength range should be acquired for best results. The correlation between wavelengths and particular detector channels in a polychromator facilitates nearly simultaneous measurement of the intensities of the various wavelengths.

Only one specific datum point can be acquired at a time with the conventional UV-Vis. spectrophotometer since it only has one detector. But data for many wavelengths can be acquired with the photodiode array spectrophotometer simultaneously since there are several hundred or a thousand detectors present. **Figure 3** is the total wavelength spectrum of Didymium solution which can be obtained within 1 second.



**Figure 3. The spectrum of didymium solution: S-3150, SCINCO,
measuring time: 1 s**



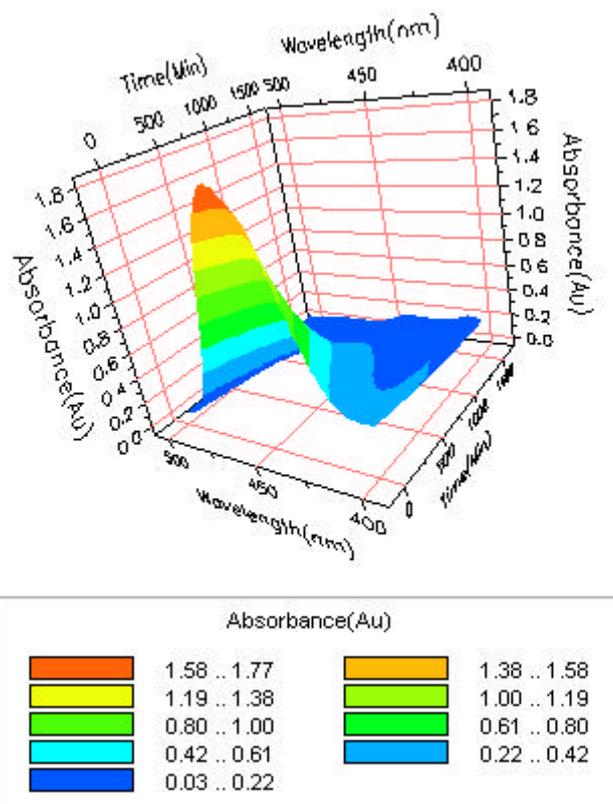
**Figure 4. Ultra kinetic mode; Fenton oxidation reaction, S-3130, SCINCO.
Measuring interval time : 69 ms, minimum scan time: 20 ms**

Fast Scan Speed

Fast spectral acquisition makes diode array spectrophotometers the first choice for measurement of fast chemical reactions and denaturing materials.¹¹ For example, **Figure 4** shows spectra measured at intervals of 69 ms during an oxidation reaction of an ferrous ion. With this data, the disappearance of the reactant and appearance of the product can be monitored simultaneously.

Figure 5 displays a kinetic reaction in 3D graphics mode which enables the reaction to be viewed at a glance. This mode shows the wavelength, absorbance and time (or temperature) axes. Such a function is rarely available in a conventional type instrument and the measurement would take a long time to accomplish.

Before the advent of multichannel



**Figure 5. 3D Graphics of kinetic data;
Decomposition of ascorbic acid (S-3130,
kinetic mode)**

detectors, all rapid spectral scanning was performed using a monochromator in which a scanning mirror could be rotated quickly. The mirror determined the angle at which radiation impinged on the dispersing device and thus the wavelength appearing at its exit slit.

By employing a polychromator, some distinct advantages in rapid scanning are gained. In addition, fast reading (about 10 μ s per channel) of the output is possible. From 5 to 900 ms may be taken to sample the output of all the elements. These times are short enough for fast spectrometric measurements.

High Signal to Noise Ratio

The duration and intensity of illumination determine both the final S/N ratio and the exposure interval needed to acquire a spectrum. This interval is also the integration time for the signal. A longer integration time allows a higher S/N since the signal will be larger and noise averaged more completely towards zero.

There is no Integration function in the conventional UV-Vis spectrophotometer which accumulates the signal. For example, the total required time will be 1000 sec. for 1000 data points and it takes 1 sec. to measure one datum. In this case, all 1000 data have the same signal to noise ratio (S/N).

But in a PDA instrument which has a 1000 photodiode array, 1000 data points can be measured in 1 sec. and it would take 1/1000 sec. to achieve the same result obtainable in 1 sec. in a conventional instrument. Therefore, when the same sample is measured for 1000 sec in a PDA instrument, the signal is accumulated and is 1000 times greater than when measuring for 1 sec. The noise will be $1000^{1/2}$. This means that the S/N ratio is improved by $1000^{1/2}$.

This resulting benefit of fast data acquisition is termed Fellgett's S/N Advantage or Multichannel Advantage.

Wavelength Precision

In a conventional UV-Vis spectrophotometer mechanical movement is required to select a specific wavelength, either manually or by using a stepper motor. But a photodiode array UV-Vis spectrophotometer acquires data at each wavelength by electrical scanning. In this way, the wavelength reproducibility of a PDA instrument is much better than the conventional mechanical scanning UV-Vis spectrophotometer.

Minimal Stray Light effects

In addition, a photodiode array type spectrophotometer has a reversed optic structure which minimises stray light problems, a serious issue in conventional UV-Vis spectrophotometers. (Figure 6)^{10,11}

In actual fact, the S-1100 or S-3100 Series PDA UV-Vis spectrophotometer is not affected by outer stray light and therefore an experiment can be performed with the sample compartment cover open.

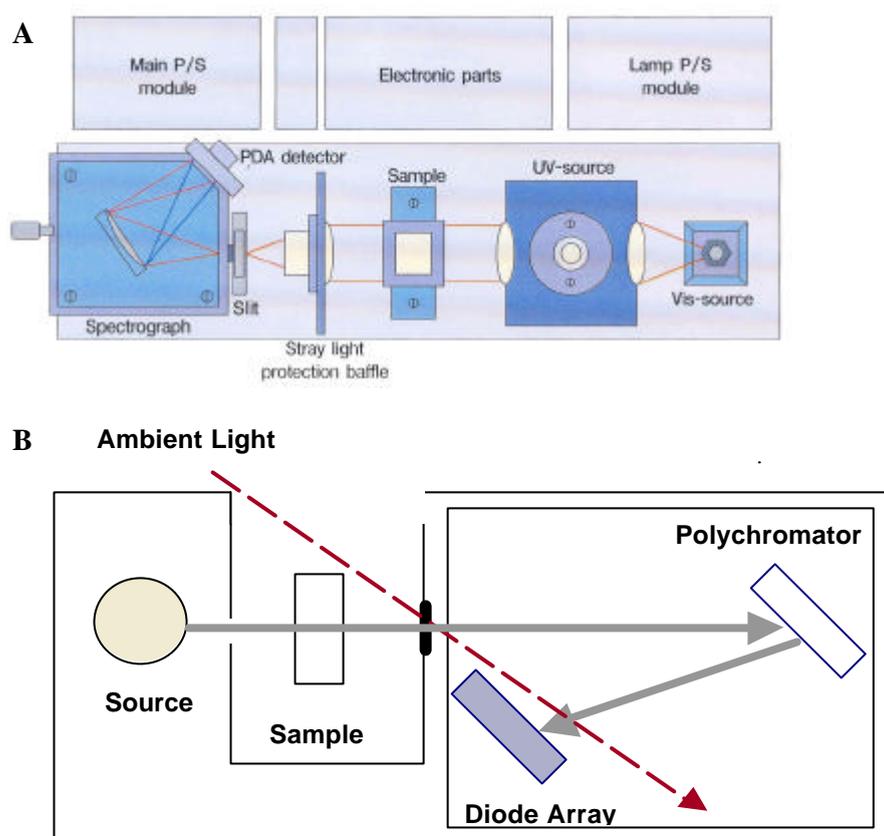


Figure 6. Some schematics of a PDA spectrophotometer

A. Schematic of S-3100 PDA spectrophotometer, reversed optic

B. Reasons for minimal stray light effects

Ruggedness

A PDA is a solid-state device and is more secure and reliable than a PMT (photomultiplier tube). There are fewer alignment/registration problems since the grating (or prism) is locked in position. Furthermore, a polychromator avoids the variations in optical performance with wavelength and time that are introduced in a scanning monochromator by moving the grating.

Indeed, in a polychromator no mechanical movement is required except perhaps the opening of a shutter at the entrance slit. The PDA type UV-Vis spectrophotometer has no moving parts and is therefore much less prone to mechanical problems or defects compared with a conventional instrument. After-sales service is also easier to perform.

Market Analysis

The Spectroscopy Market can roughly be divided into 3 sections: mass spectrometry, atomic spectroscopy and molecular spectroscopy. The Markets for all 3 sections have been growing steadily, e.g. the expected growth rate for molecular spectroscopy is 4% during 2003.¹²

UV-Vis, FT-IR, Fluorescence, Raman and NIR spectroscopy instruments are in the Molecular group. Our main interest, UV-Vis, is the largest category, 39.9%, in this section.¹³

UV-Vis spectroscopy finds applications not only in traditional Chemistry but also in newer markets such as pharmaceuticals & life science, environment, agriculture, energy and the petrochemical Industry.

Techniques for UV-Vis spectroscopy have been developed to keep pace with the expansion of applications and, as a result, there is a whole variety of UV-Vis instruments available on the market.

The low priced market has experienced stiff competition as there are so many manufacturers of low priced and simple UV-Vis spectrophotometers. But sales of these instruments are declining because of the demands in various applications which require more sophisticated functions.

Faster and more powerful instruments, at marginally higher prices, are rapidly replacing these lower performance instruments.

At present, the PDA market stands at approx. 10~15 % of the global UV-Vis market and approx. 12% (US\$23 million) of the US market.¹⁴ In the Japanese market, there are not so many PDA systems installed as in the US market. The Japanese UV-Vis market is largely shared by Shimadzu, Hitachi, Jasco, Perkin-Elmer and Varian. But we are expecting a growth in PDA in Japan in the near future.

Summary & Future Developments

The PDA UV-Vis spectrophotometer has a multi-channel detector, controlled by a microprocessor, which can collect spectral data for many wavelengths simultaneously, while a conventional UV-Vis spectrophotometer has a single channel detector which can collect data for a selected wavelength. The PDA UV-Vis spectrophotometer is much faster and gives more

reproducible results than a conventional UV-Vis. spectrophotometer because the latter has moving parts, such as a grating or prism, which are operated by a stepper motor for selecting a specific wavelength. These moving parts can affect the reproducibility.

The S-3100 Series systems of SCINCO are multi-channel spectrophotometers with 1024 channels in a 1 inch photodiode array and have optimum wavelength resolution. A PDA detector has an integrating function which accumulates individual measurements to enhance the signal. The benefit of having the integrating function is known as Felgett's S/N advantage or multi-channel advantage.

Many analytical instruments other than Spectrophotometers are now utilising Multichannel Detectors such as PDA and CCD. The use of PDA is growing 10~15% annually. In order to satisfy such a market demand and customer requirements, the current S-3100 Series PDA UV-Vis spectrophotometer will be developed further. We shall introduce new analytical methods for various applications in addition to our current techniques. We shall achieve greater user satisfaction and our Research and Development programme will be continuously expanded.

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