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Design and assembly of a fast spectrophotometer system for monitoring chemical reactions

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In this work we report the design and assembly of a fast spectrophotometer to monitor fast chemical reactions. The system incorporates coupled charge detector (CCD) technology, enabling the instantaneous capture of complete optical spectra in a time scale as short as few microseconds. For demonstration purposes, the degradation of one of the pesticides (benomyl) was monitored using this system.

1. Introduction

During the past three decades dramatic changes have occurred in the experimental procedures employed to obtain optical spectra. The changes were linked with the fast developments of two major fields, namely laser and computer technology. The laser, as an ideal light source, was quickly adopted by spectroscopists because of the radiation's high power, coherency, and monochromaticity. The fast developments in laser technology were the main cause for the foundation of many new fields in spectroscopy such as nano-, pico-, and femtosecond time resolved spectroscopy besides the many applications of Raman spectroscopy [1], [2]. The developments in electronics in general and more specifically in computer and computer control, enhanced the efficiency as well as the speed of optical spectrometers [3]. Historically the prism spectrograph was the only tool for recording the optical spectra, which can be considered as a preliminary multichannel spectrometer. Advances in technology introduced monochromators and photomultiplier detectors in optical spectrometers. Such systems offered an ultra high resolution and sensitivity approaching single photon detection [4]–[6]. One of the disadvantages for such a system as compared to the spectrograph is the exposure time. While in the case of the spectrograph the exposure time can be very short because all the wavelengths are approaching the detector at the same instant. In the case of the monochromator the wavelengths are approaching the detector sequentially and therefore the sample will be exposed to light for long periods

depending on the scan range and some other factors. There are cases where the single channel detection system is impractical, such as high intensity light sources (lasers) and optically unstable samples. For such cases the ideal solution would be to use an arrangement similar to the old spectrograph/photographic plate system, *i.e.*, multichannel detection system. The main idea in this system is to replace the classical photosensitive glass plate with a multichannel detector and to remove the exit slit of the monochromator. The first detector of this type was the vidicon [7]. The sensitivity of the vidicon was much lower than that for the photomultiplier tube, therefore the uses of such detector were limited to applications having high optical yield [8]. The second generation of multichannel detectors was the self-scanned diode array. In this work, a CCD is used. Such detector offers sensitivity approaching the PMT, in addition to many other facilities, such as gating, pixel grouping, imaging, *etc.* The assembled system enabled fast spectral acquisition with which chemical fast changes in chemical reactions could be easily monitored.

2. Experimental arrangement

A block diagram for the system is shown in Fig. 1**a**. It consists of four major units, light source, spectrograph, optical 2D detector, control electronics and data station.

The light source consists of two main blocks, deuterium lamp (190–350 nm) and tungsten (350–900 nm). The deuterium light beam is focused into the middle part of the sample cell using a quartz lens. The power supply that ignites and supplies the deuterium lamp with constant current was designed and built in our laboratory.

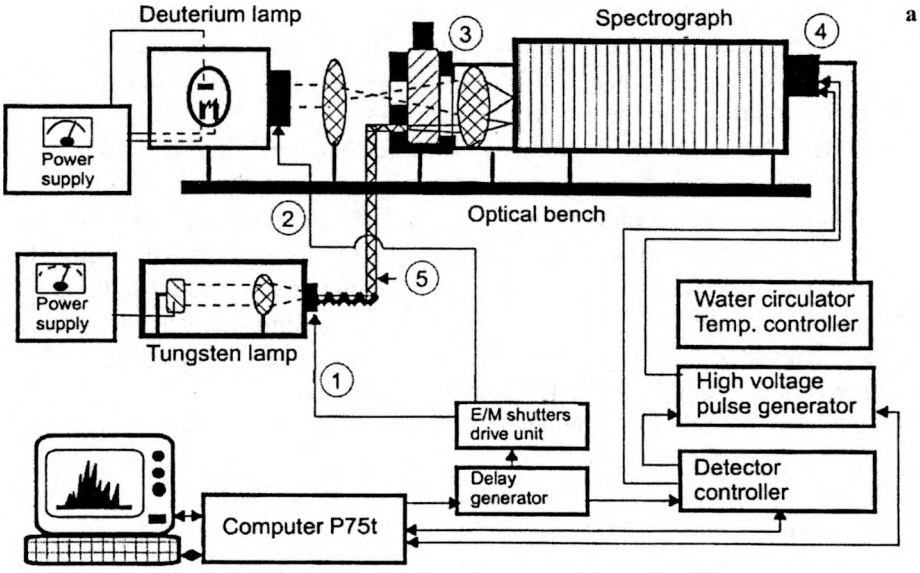
A 100 watts tungsten lamp operated by a DC stabilized power supply (Ealing, model 021/026) is used as the visible radiation source. An optical fiber cable is used to transfer the visible light beam to the lower part of the sample cell. Electromechanical shutters (1 and 2) are used to control the exposure of the sample to any of the light beams.

The sample holder block was fabricated in the machine shop of the faculty. It is designed to accept standard ($10\times10\times50$ mm^3) sample cells. It can be used for absorption as well as fluorescence applications. Excitation light beam is introduced from a side perpendicular to the detection path using an optical fiber.

The spectrograph used in this setup is Chromex model 5001. It contains 3 gratings (75, 150, 300 grooves/mm) enabling the selection between 3 different resolutions. All spectrograph operations such as the selection of grating, slit width as well as wavelength calibration are fully controlled by Windows software.

The CCD detector, Princeton Instruments model ICCD, consists of 512×376 elements. It has a broad spectral response (200–900 nm) with gating facility to a minimum of 2 ns. It is equipped with a thermoelectric cooler that maintains the detector at a temperature of –30 °C for minimizing the dark current. A detector controller (model ST-38) driven by Windows 3.11 software is used to control and transfer the data to the computer.

A programmable delay generator model (DG-535) Stanford Research systems INC is used to synchronize the trigger of the diode array detector with the electromechanical



1, 2 – electromechanical shutters, 3 – sample cell holder, 4 – CCD optical detector, 5 – optical fiber

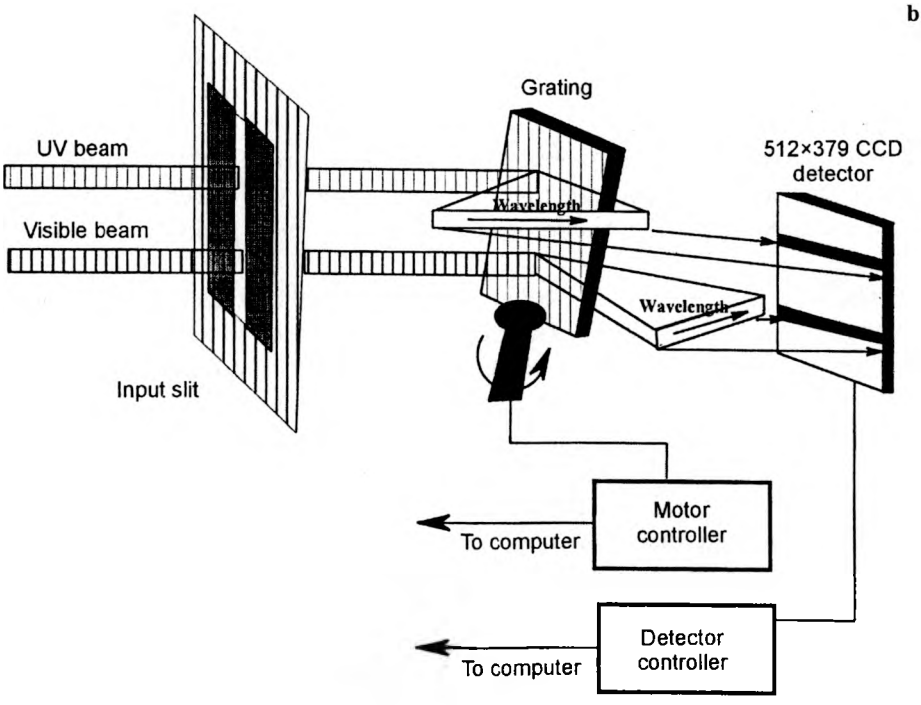


Fig. 1. Block diagram for the experimental setup (**a**). Optical paths of the UV and visible beams inside the spectrograph (**b**).

shutters. Upon the reception of an input pulse it outputs, as many as, 4 pulses with a programmable time delay between each of them. This is extremely important for synchronization due to the large difference in response times between the electromechanical shutters and the electronic detectors.

The computer, DELL (P75t), includes a fast interface card driven by windows software. To start data acquisition, the computer triggers the detector controller via the fast interface card installed on the computer motherboard. The detector controller outputs a trigger pulse that is fed into the programmable delay generator unit. The latter outputs two pulses with different time delays, the undelayed pulse is fed into the electromechanical controller unit to activate the mechanical shutters while the delayed pulse is used to trigger the detector. The detector can be operated in two modes. The first is the free running mode in which the detector stays always alive. The second mode is the gated mode, in which the detector becomes live only when it receives a high voltage pulse from a high voltage pulsar. For this purpose, a programmable high voltage pulsar Princeton model (PG-200) is used.

The software fully controls all the functions of this generator, *i.e.*, the gate pulse width, pulse delay, as well as the external or internal pulse trigger.

The type of grating selected determines the spectral window, *i.e.*, the width of the spectrum. For example, the 75 G/mm grating offers a spectral window of 150 nm, while the 600 G/mm grating offers 35 nm spectral width. The wavelength selected by the monochromator is always the middle part of the spectrum. The whole spectrum is collected during the selected exposure time of the detector. Exposure times as short as few nanoseconds are possible, therefore a complete 150 nm spectrum can be obtained in this time scale. The main benefits of this setup are:

– The short time during which the sample is exposed to probe light, this time can be as short as the detector exposure time. Since we are using electromechanical shutters, we are limited to the shutter response time, which is in the order of milliseconds.

– As is shown in Fig. 1**a**, the UV beam is interring to the sample from an area different from that for the visible. The two beams travel into the spectrograph in two different planes and therefore can reach the CCD detector at two different heights.

Using the grouping facility in the detector control, we can assign the upper one, for example, for the UV spectra and the lower one for the visible spectra as is shown in Fig. 1**b**. This advantage eliminates the need for changing lamp position each time we need to change the spectral wavelength range from UV to visible or *vice versa* as it is found in classical spectrophotometers. In fact, this facility enables the detector to act as if it were two separate diode array detectors.

3. Data processing

The system is designed as a single beam spectrophotometer where a reference spectrum should be acquired and stored as a data file in the computer. Before that a background file should also be recorded and stored. This data file contains the dark current from

the elements of the detector elements. The system automatically subtracts this data file from any acquired spectrum. The dark current value is dependent on temperature, therefore the CCD detector is cooled down to –25 °C in order to reduce the dark current level down to few counts per photodiode. The computer uses the three data files on the basis of Beer's law to calculate and display the absorption spectrum.

4. Results and discussion

Figure 2**b** shows the UV spectrum 0.73 mg/L of anthracen in cyclohexane recorded by the new system. This result is compared with that found in the spectral atlas of polycyclic aromatic hydrocarbons for the same concentration, Fig. 2**a** [9]. The spectrum in Fig. 2**a** was recorded using Model-555 Perkin–Elmer spectrophotometer, which requires several minutes for the mechanical scanning of the monochromator. It is clear that the spectrum in Fig. 2**b** has a better resolution and is also recorded in a time scale as short as 5 microseconds.

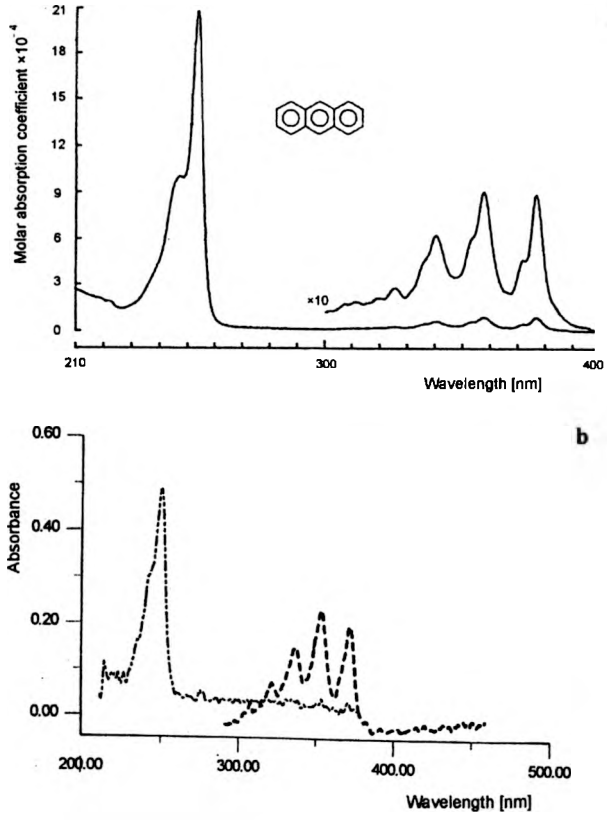


Fig. 2. Absorption spectrum of 0.73 mg/L anthracene in cyclohexane as obtained in reference [8] using Perkin–Elmer Model 555 instrument – **a**, absorption spectrum of the same concentration as in **a** obtained by the new system – **b**.

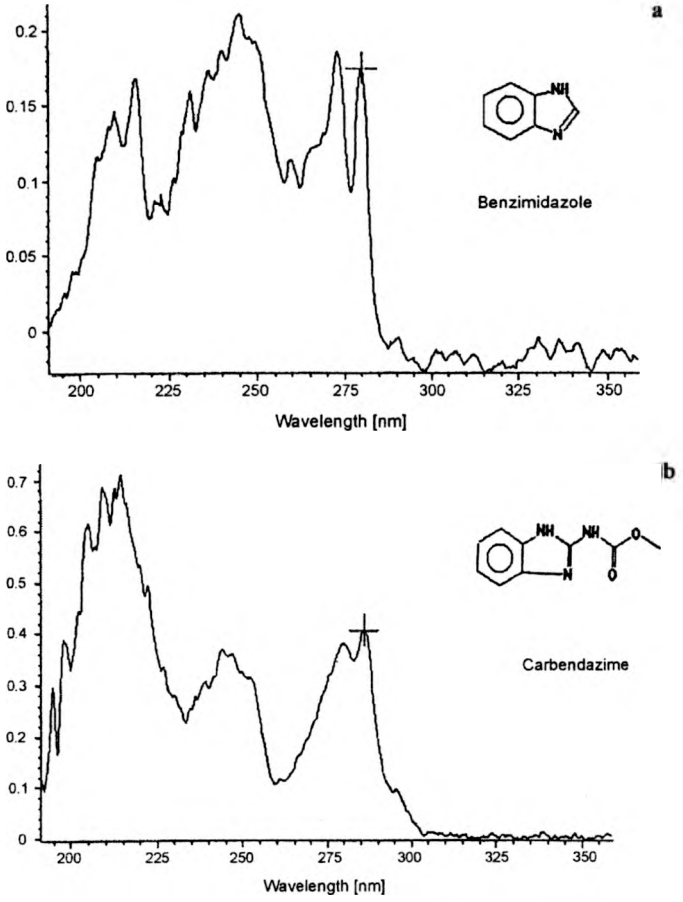


Fig. 3. The UV spectra of: 0.5 mg/L benzimidazole in CH_3CN (**a**) and 0.7 mg/L carbendazime in CH_3CN (**b**).

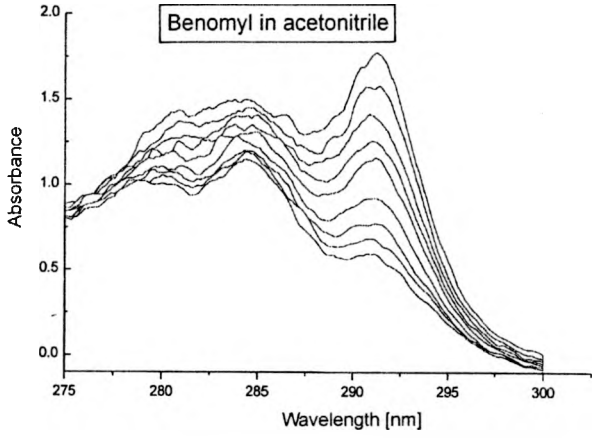


Fig. 4. The 2D UV spectra of 0.65 mg/L benomyl in CH_3CN for different periods of time.

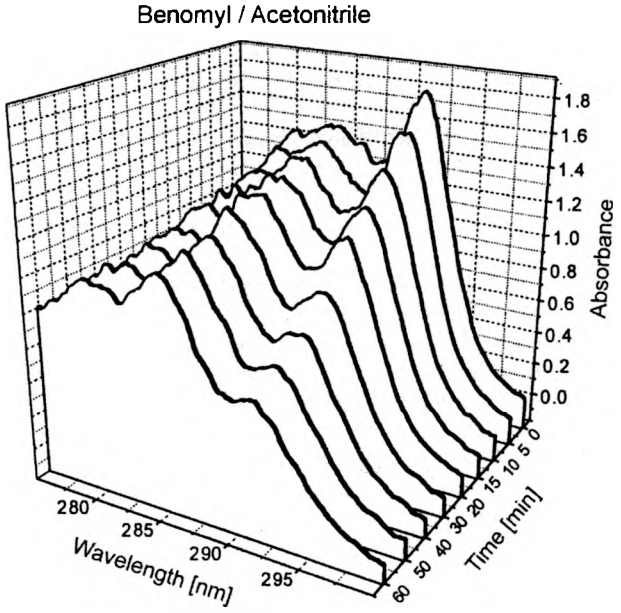


Fig. 5. The 3D UV spectra of 0.65 mg/L benomyl in CH_3CN and versus time (0–80 min).

To illustrate further the capabilities of the new system, the degradation of benomyl, a benzimidazole based pesticide, to form carbendazime, another benzimidazole based pesticide [10], was monitored by the new system. Figure 3**a** shows the UV spectrum of 0.5 mg/L benzimidazole in CH_3CN solvent, while Fig. 3**b** shows the UV spectrum of 0.7 mg/L carbendazime in the same solvent. The difference between the two spectra is the broadening of the peak near 284 nm due to the methylcarbamate group attached to the parent molecule (benzimidazole). The addition of a second methylcarbamate group to benzimidazole molecule for the formation of benomyl causes a new peak at 293 nm to appear in the spectrum of benzimidazole. Such peak enables the differentiation between carbendazime and benomyl. Benomyl is found to be unstable in polar solvents, it starts to degrade to carbendazime immediately after preparing it in solution [10]. Using the new system we could monitor the continuous drop in the intensity of the peak at 293 nm, which indicates the continuous degradation. The result is clearly shown in Figs. 4 and 5. Figure 4 shows a 2D plot of the UV spectra taken after several periods of time. Figure 5 shows a 3D plot of the absorption versus wavelength and time indicating the fast acquisition and display capabilities.

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