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60 Abstract :A user friendly program in Pascal has ben developed for data acquisition and subsequent processing of time resolved spectra of transient species produced in pulse radiolysis experiments. The salient features of the program are (i) thiocyanate dosimetry and (ii) spectrum acquisition. The thiocyanate dosimetry is carried out to normalize experimental conditions to a standard value as determined by computing absorbance of the transient signal CNS_{-2} that is produced from thiocyanate solution by a 7 MeV electron pulse. Spectrum acquisition allows the acquisition of the time resolved data at 20 different times points and subsequent display of the plots of absorbance vs. wavelength for the desired time points during the experiment. It is also possible to plot single time point spectrum as well as superimposed spectra for different time points. Printing, editing and merging facilities are also provided.

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PROGRAMMING FOR TIME RESOLVED SPECTRUM IN PULSE RADIOLYSIS EXPERIMENTS

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Introduction

A transient species produced by the reaction of high energy electron pulse with a sample consists of a characteristic absorption band that can be monitored by absorption spectrophotometry. From the formation or decay trace of the species obtained on the scope of an oscilloscope, it's rates of formation and decay can be calculated. The unimolecular decay of the species may give rise to another species. In presence of another compound or solvent molecule in the vicinity, the transient may react bimolecularly to produce another species, the fate of which can be monitored spectrophotometrically if the spectrum of the original species is observed at different time scales covering that of the life and decay of the product species. In order to carry out investigations of such type of reactions , it is necessary to obtain spectrum of the transient species as a function of wave length at different time windows. Manual method for spectrum acquisition necessitates manual recording of absorbance values from maximum to final value at different time intervals on the decay or formation traces. The traces are recorded at different wavelengths and absorbance values at the same time intervals from these traces are noted down manually. This gives an array of wave length versus optical density at a different chosen time scales. This manual method is

very tedious and time consuming. Hence it has been made simpler by computerized spectrum acquisition program as described in the present report which gives description of a user-friendly software program written in Pascal language developed in our laboratory. The program has been in use for the last couple of years on our LINAC equipment and has made easy the acquisition and processing of time resolved spectra of samples in pulse radiolysis experiments.

The data obtained during pulse radiolysis experiments are in the form of oscilloscope traces which represent analog signals due to light absorption by transient species. The analog signal is digitized in the "IWATSU" transient digitizer (storage scope TS-8123). The data from this scope can be processed with help of an IBM PC. The necessary software has been developed for kinetic analysis of the data relating to decay or formation of the transient species[1].

Hardware interface:

IWATSU (TS-8123) storage oscilloscope samples the displayed waveform at 512 equally spaced points and stores the 512 ordinate values in it's internal memory. Two memory banks (A and B) are provided so that two waveforms can be stored simultaneously. It also has a built in GPIB interface through which the data stored in the two memories (A/B) can be processed. However,only memory bank 'A' was used throughout the experiment and corresponding arrangement in the software was made. To connect this scope to PC, a standard GPIB interface card was used. The procedure required to communicate with the GPIB bus are

supplied with the card as driver software. This resident software has to be loaded before operating the spectrum program. The digitized data (ordinate values i.e. digitized millivolts values) from the scope comes as 512 channel values each channel comprising of equally spaced time slots. To acquire data from the scope, the PC is first initialized as the controller on interface bus with address 'Ø'. All devices on the bus are then initialized and cleared. When the data is to be downloaded, a command is sent to the scope from PC and the data is read in accordance with the instruction code[2].

Software:

The flow chart for acquisition of data for spectrum is given in Fig.1. The scheme of the program is as follows.

1.Dosimetry:

Dosimetry is carried out to maintain the experimental conditions same from experiment to experiment and subsequently to normalize the readings to a standard thiocyanate value which is equivalant to normalizing to a constant absorbed dose of electron. For this purpose an aerated sample of thiocyanate solution (Ø.Ø5 N) is exposed to the electron pulse. This produces a transient thiocyanate ion (CNS^-_2) having maximum absorbance at 5ØØ nm. The experimental parameters to be input here are as follows:

i) DC level as read on the pulse radiolys control unit,

ii) Signal height in millivolts of thiocyanate transient.

O.D.thiocyanate (ODCNS) value is then calculated by using equation below and is displayed on the screen.

$$ODCNS = \log_{10} \frac{\text{DC level in mv}}{[\text{DC level in mv} - \text{Signal in mv (ordinate value)}]}$$

This ODCNS value is stored in the computer for spectral data normalization. In case the experiment is to be discontinued and resumed on some other day, the accelerator settings are so adusted as to give the same absorbed dose as obtained earlier. If the accelerator settings are not stable, subsequent optical density values of the transients, therefore, would also change. These changes in experimental values are taken care of by normalizing all observed O.D. values of the sample to a standard dosimetry value of thiocyanate solution taken on an earlier day.

The O.D.Normalized value (ODN) is calculated by the equation

ODN of the sample = K x O.D.(Observed) of the sample

where k is a normalization constant equal to [ODCNS,earlier value / ODCNS,later value].

Acquisition of time resolved spectrum and data normalization:

Block diagram of the twenty point spectrum acquisition program is given in figure 1. Figure 2 gives the different options available in the program.

Spectrum acquisition:

Trial run:

For acquiring time resolved spectrum of a sample, a

solution of the sample is taken in 1 cm quartz cell and is exposed to a 7 MeV electron pulse for a short duration of time. The transients produced in the solution are then spectrophotometrically analyzed by a crossed beam of xenon arc lamp and a photomultiplyer tube, output of which is supplied to a storage oscilloscope. Wave length is adjusted at a value where the transient is supposed to give maximum optical absorption. The digitized signal of the transient from the scope (which can be a formation or a decay type) is then transferred to a PC using GPIB interface bus. The millivolts vs. time signal is converted into an point vs. point graph as shown in fig.3.

On this trial signal, following parameters are fed :

i) base line values B_1 and B_2

ii) reference time T_0 and

iii) first time point T_1

Two values of baseline B_1 and B_2 are fed so that an average value of baseline between these two values are automatically recorded for each signal. This was to take care of a noisy base line. For a narrow pretrigger baseline, one may give the same value for B_1 and B_2.

Reference time T_0 indicates the end of the electron pulse and start of the signal.

The first time point T_1 is generally the point corresponding to maximum absorbance in case of a decay, and a minimum absorbance in case of a formation curve (Fig. 3).

The option is available here to input the values B_1 , B_2 , T_0 and T_1 either on the curve with the help of a cursor or by feeding the numerical values. The decay or formation trace

between T_1 and T_{last} i.e. T_{20} is then automatically divided into 19 equally spaced time points ($T_1, T_2, \ldots\ldots T_{20}$). The selected time points can be displayed in a table form as microseconds on the screen. At this stage, user has an option to change the time points or positions if necessary. (Fig.4)

Experimental run:

For an experimental run, a fresh sample is exposed to an electron pulse and following parameters are fed during the course of the experiment:

i) Wave length and

ii) DC level.

A starting wave length value is first adjusted on the monochromator and is fed to the computer. Next an electron pulse is given and DC level as read on the pulse radiolysis control unit is fed to the computer as a parameter. Here an option has also been provided to acquire DC level by incorporating an ADC card. This sequence of changing wave length, giving a shot of electron pulse, inputting wave length and DC level and transferring the data to the computer is repeated till a required wave length region is covered. From every trace obtained at a particular setting of a wave length, optical density values corresponding to 20 time points are calculated and the corresponding wavelength values are stored in the RAM along with wavelength and their serial numbers in the form of an array of the type given below.

Ser. Nos.	Wavelengths λs	Optical density values at time points in μ sec. T_1	T_2	T_3	T_4	T_{19}	T_{20}
1	λ_1	-	-	-	-	-	-
2	λ_2	-	-	-	-	-	-
.	.						
.	.	-	-	-	-	-	-
n	λ_n	-	-	-	-	-	-

From this array, 20 plots of wave length vs. optical density at desired time points are generated. User has an option to superimpose, save and view all 20 plots or selected 4 time point graphs.

As and when the data point is acquired, it is displayed as optical density vs. wavelength on the screen. The user is given a choice to select either a four window display (any four out of 20 time points) or a single window display with desired superimposed spectra of time points (Fig.5 and 6). During acquisition, it is possible to toggle between four window display and single window display. There is an option menu on the top of the display (Fig. 5 and 6) which is accessible to the user during data acquisition.

The options available here are as follows:

(1)During the experiment, it is possible to save any transient signal for kinetic analysis that can be carried out by using "IWAT" program[1].

(2) The limiting values of X axis representing wavelength in nanometers and Y axis representing absorbance can be changed at any time. At default, the Y axis is set by the maximum optical density value obtained from the trial signal. The X axis default

value is 300-800 nm. Smaller than 200 nm and bigger than 999 nm values are not acceptible and gives a beep when wrong wave length values are fed.

(3) During the experiment, the variable parameter 'wavelength' if wrongly fed, can be corrected immediately.

(4) It is possible to choose the time point spectra of interest by scanning through all 20 time point graphs either on a four window or on a single window.

(5) To avoid loss of data in the event of a power failure, the data is stored after each five shots in a temporary file (temp.dat) on the hard disk.

(6) At the end of the experiment, selected four time point data or twenty time point data can be stored on the hard disc or on the user's floppy.

Merging:

This option allows the user to break the experiment at any time and resume it later by recalling the saved data. Signal drift along the X and Y direction on the oscilloscope screen, if present, is compensated by taking a fresh trial signal and feeding new B_1, B_2 and T_0 values as described earlier.

Spectrum display:

Following facilities are available for display, editing, printing and plotting the saved spectral data (Fig.2b).

(1) **Display**:

Data from a named spectrum file can be recalled and

viewed for any time point selected out of the stored four or twenty time point data. Facilities to change the scale factors of X and Y axis at this stage are also provided. From a four or a twenty point data file, a single or a superimposed multiple time point data spectra can be viewed prior to printing.

(ii) **Editing and Printing**:

It is also possible to get a printout of data consisting of optical density (OD) and wavelength values for the chosen four time points as well as all the twenty time points in the form of a table. Optical density values can be obtained in the form of normalized values as well as observed values. The data corresponding to any time point can be edited by inputting the number corresponding to the wavelengths.

(iii) **Plotting**:

For better presentation of the plot, a program called "GPLOT" is written in Pascal language having following features.

GPLOT: The program allows the plotting of the different time point data of the same species or same time point data of different species on the same graph. For superimposition of different graphs, either the lowest and highest limits in the X and Y axis in different data sets are selected or one has the option to choose limits at will. In the latter case, two sides of the graph are used for one set of X, Y values and other two sides for another set. Finer adjustments and caption writing etc. are also possible in the program so as to make the graphs ready for presentation (Fig.7). A facility of opening a window

in a plot graph file and superimposing another plot of a smaller size in one of the corners of the graph is also incorporated in the program.

Acknowledgments:

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References:

1. M.S.Panajkar,P.N.Moorthy and N.D.Shirke, "Programming a microcomputer for on-line data acquisition and processing in pulse radiolysis experiment. Part 1: Kinetic Parameters". BARC-141Ø (1988).
2. Instructionmanual:Storage Scope TS-8123 Mainframe,IWATSU, E72Ø-625101(L).

Figure captions

Fig.1. Flow chart of the spectrum program.

Fig.2 (a). Acquisition menu

(b). Spectrum display menu

Fig.3. Chos ing parameters for acquisition of spectrum data in pulse radiolysis experiment.

Fig.4. Display of tabular time point data.

Fig.5. Four window time point data during spectrum built-up.

Fig.6. Superimposition of time point data during spectrum built-up.

Fig.7. Superimposition of decay and formation traces of transients produced in the pulse radiolysis of aqueous azobenzene solution.

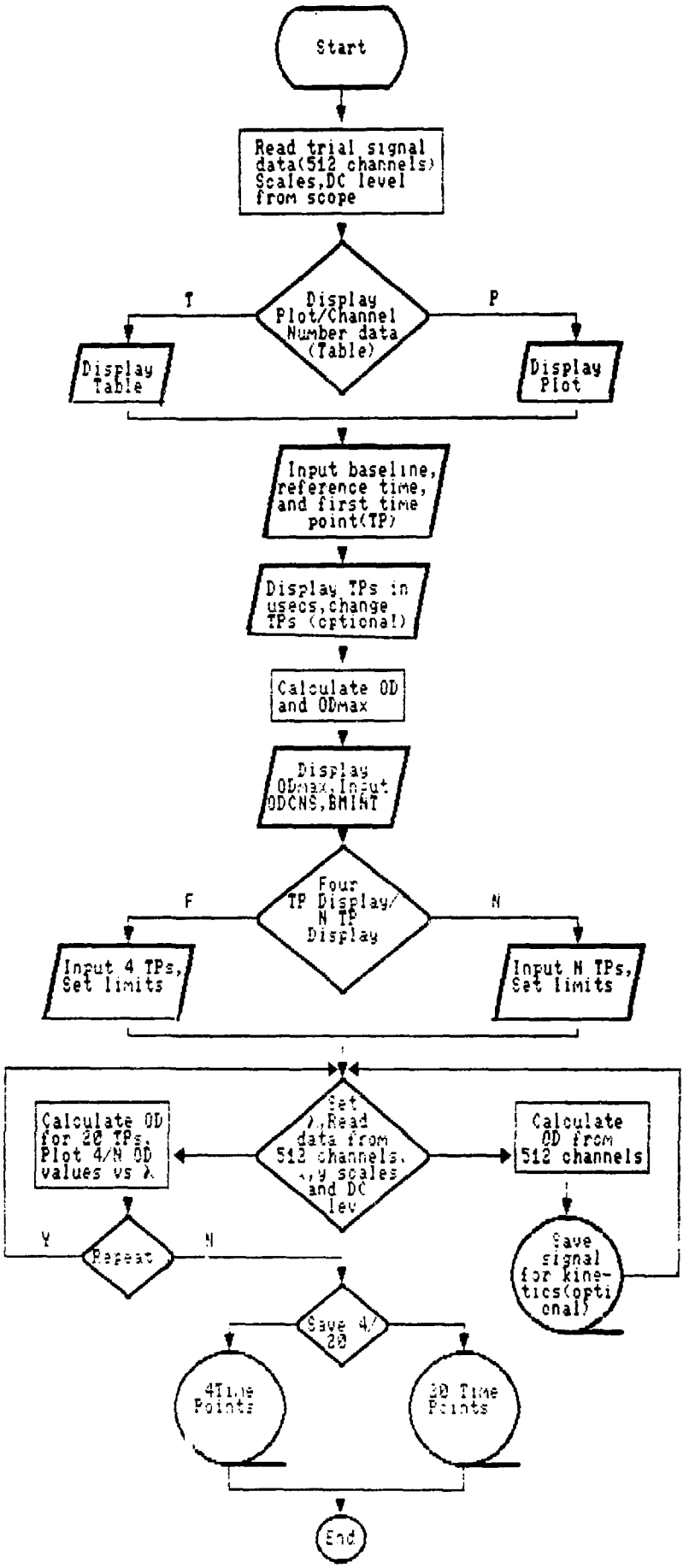
Start
Read trial signal data(512 channels) Scales,DC level from scope
Display Plot/Channel Number data (Table)
T
P
Display Table
Display Plot
Input baseline, reference time, and first time point(TP)
Display TPs in usecs,change TPs (optional)
Calculate OD and ODmax
Display ODmax,Input ODCNS,BMINT
Four TP Display/ N TP Display
F
N
Input 4 TPs, Set limits
Input N TPs, Set limits
Set),Read data from 512 channels, ,,y scales and DC lev
Calculate OD for 20 TPs, Plot 4/N OD values vs λ
Calculate OD from 512 channels
Y
Repeat
N
Save signal for kinetics(optional)
Save 4/20
4Time Points
20 Time Points
End

Figure 1

ACQUISITION MENU	
A	SPECTRUM ACQUISITION
C	CONTINUE FROM FILE (MERGING)
D	SPECTRUM DISPLAY
C	CHANGE USER DRIVE (NOW A:)
P	PRINTER ON. PRESS'P' TO PUT OFF
Q	QUIT PROGRAM

Fig.2 (a)

SPECTRUM DISPLAY MENU	
P	PLOT SPECTRA
E	EDIT SPECTRUM (ALL TIME POINTS)
L	PRINT SPECTRAL DATA
G	WRITE PLOT FILE (GPLOT)
A	ACQUISITION MENU
Q	QUIT PROGRAM

Fig.2 (b)

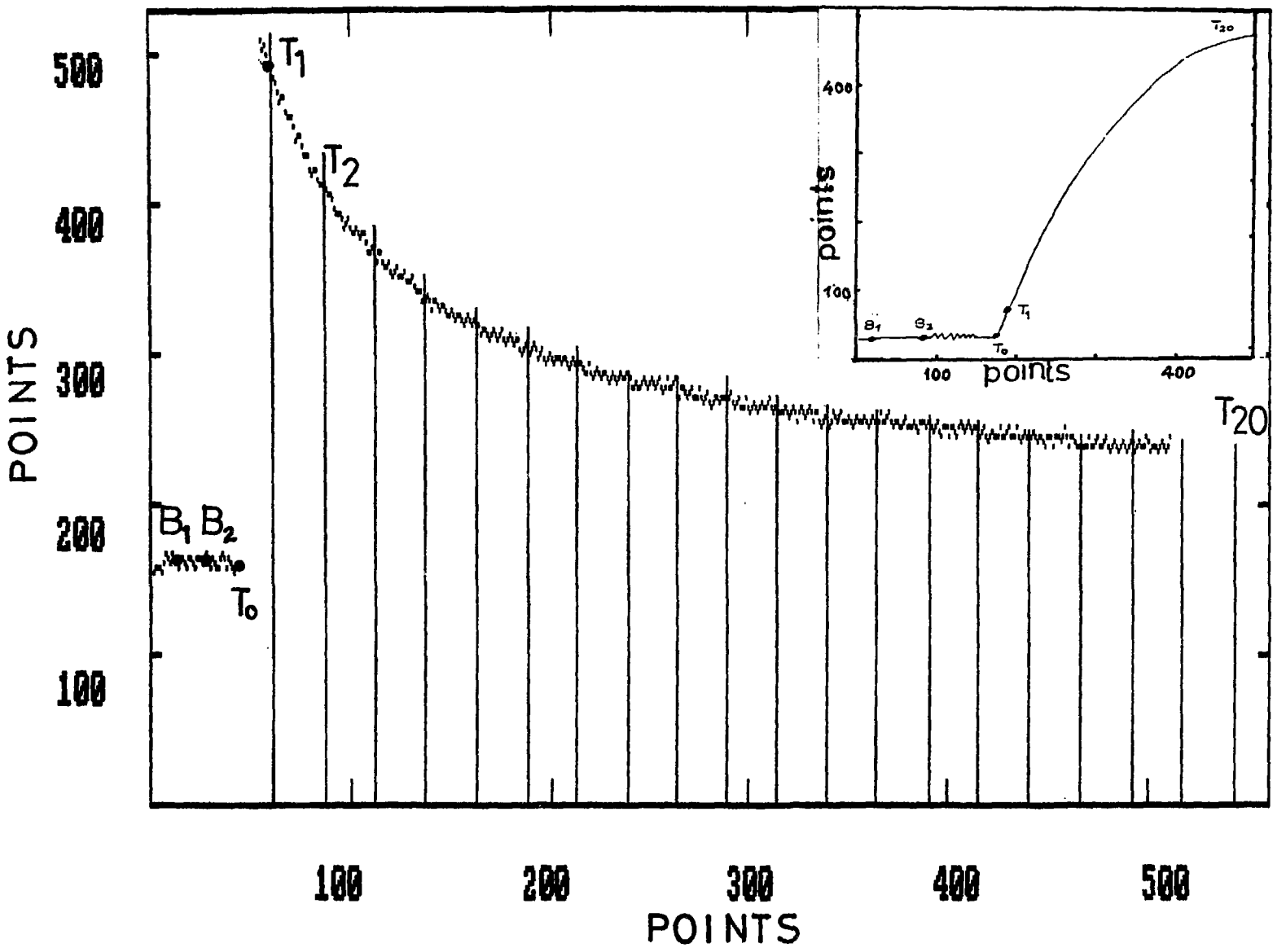
500
400
300
200
100
POINTS
T1
T2
T20
B1 B2
T0
100
200
300
400
500
POINTS
points
400
100
B1
B2
T1
T0
T20
100
points
400

Figure 3

Time pt. μsec	Time pt. μsec
1.TP[1] = 0	B.TP[11] = 94
2.TP[2] = 9	C.TP[12] = 103
3.TP[3] = 19	D.TP[13] = 112
4.TP[4] = 28	E.TP[14] = 122
5.TP[5] = 38	F.TP[15] = 131
6.TP[6] = 47	G.TP[16] = 141
7.TP[7] = 56	H.TP[17] = 150
8.TP[8] = 66	I.TP[18] = 159
9.TP[9] = 75	J.TP[19] = 169
A.TP[10] = 84	K.TP[20] = 178

PRESS ▶

Keys 1 - 9,A - K ¦ to change

Space ¦ to continue

Figure 4

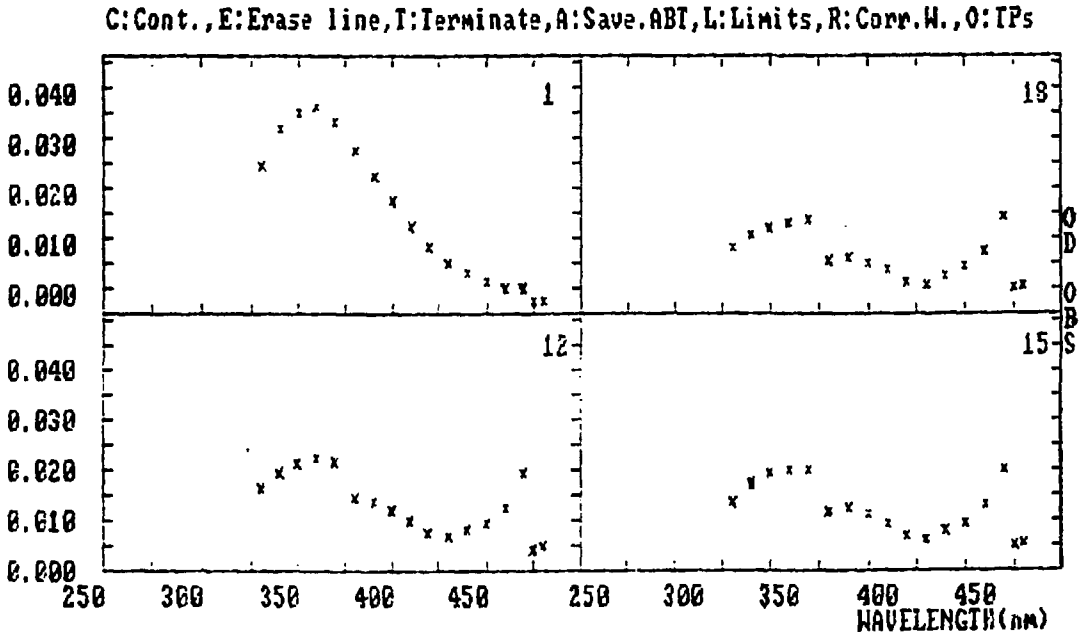
C:Cont.,E:Erase line,T:Terminate,A:Save.ABT,L:Limits,R:Corr.W.,O:TPs
1
18
12
15
0.040
0.030
0.020
0.010
0.000
OD
OBS
250
300
350
400
450
WAVELENGTH(nm)

Figure 5

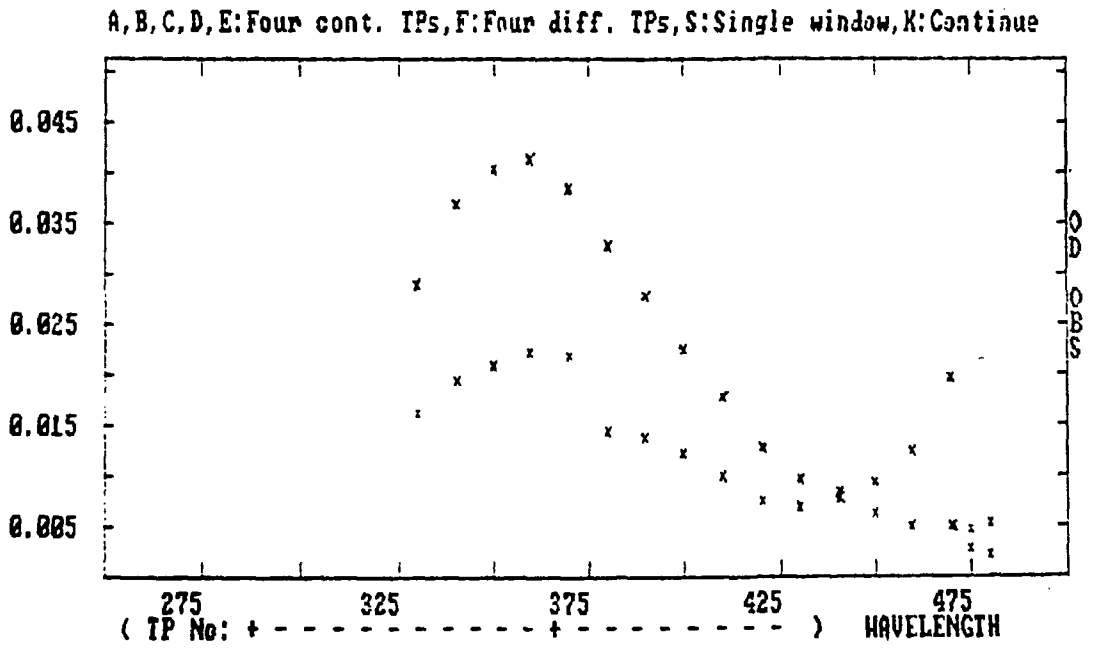
A,B,C,D,E:Four cont. TPs,F:Four diff. TPs,S:Single window,K:Continue
0.045
0.035
0.025
0.015
0.005
OD
275
325
375
425
475
(TP No: + - - - - - - - - - - + - - - - - - - - - -)
WAVELENGTH

Figure 6

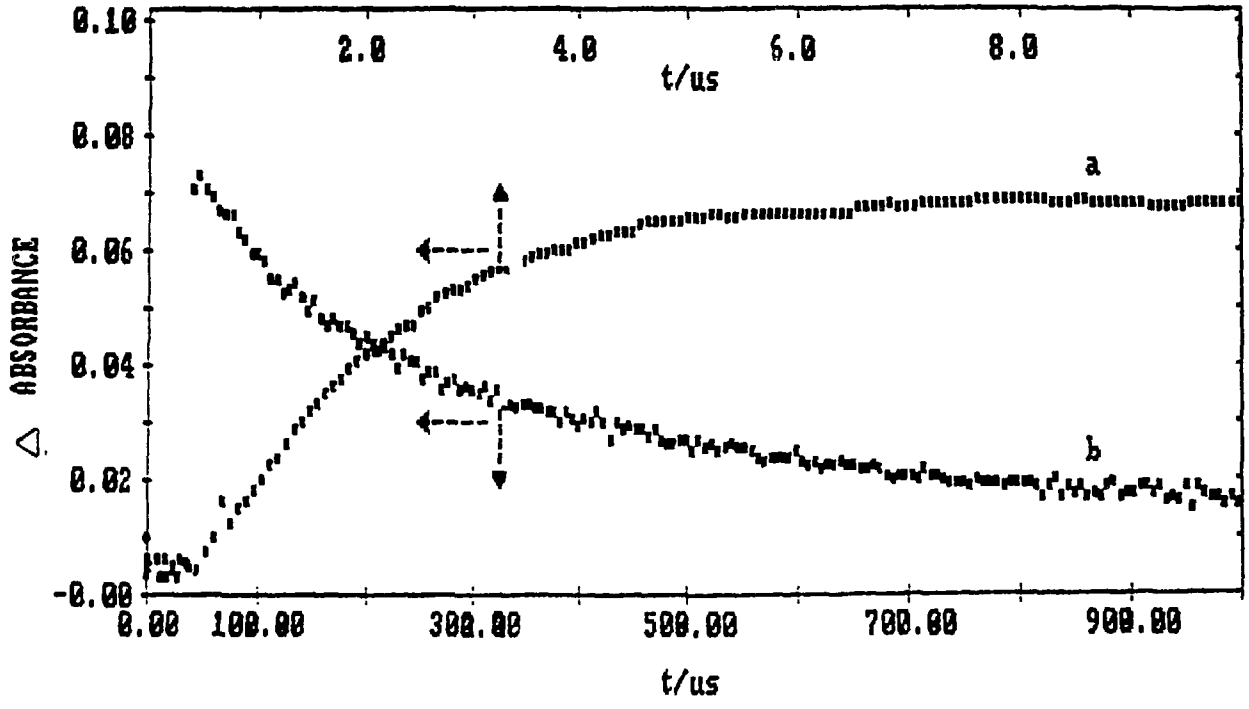
0.10
0.08
0.06
0.04
0.02
-0.00
ΔABSORBANCE
2.0
4.0
6.0
8.0
t/us
a
b
0.00
100.00
300.00
500.00
700.00
900.00
t/us

Figure 7

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