New Developed Data Treatments for the Characteristic Linear Array Ayah 5SX1-T-1D-CFI Analyser Segment Response Profile & Generalization

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Abstract

Derivative spectrophotometry is one of the analytical chemistry techniques used in the analysis and determination of chemicals and pharmaceuticals. This method is characterized by simplicity, sensitivity and speed. Derivative of Spectra conducted in several ways, including optical, electronic and mathematical. This operation usually be done within spectrophotometer. The paper is based on form of a new program. The program construction is written in Visual Basic language within Microsoft Excel. The program is able to transform the first, second, third and fourth derivatives of data and the return of these derivatives to zero order (normal plot). The program was applied on experimental (trial) and reals values of sulphate determination in the form of barium sulphate by a Linear Array Ayah 5SX1-T-1D-CFI Analyser. The data was collected through an Array M3500A 6.5Digit Digital Multimeter linked between the spectrometer and computer.

Keywords: Derivative spectra, Back return of derivative spectra, Visual Basic, data treatment.

معالج بيانات جديد ومتطور لمعالجة هيئة الإشارات المسجلة من جهاز Linear Array Ayah 5SX1-T-1D-CFI Analyser

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الخلاصة

تعُد المشتقات الطيفية من التقنيات المستخدمة في الكيمياء التحليلية في تحليل وتقدير المواد الكيميائية والدوائية. اذ تتصف هذه الطريقة بالبساطة والحساسية والسرعة في التقدير. وتجرى المشتقات الطيفية بطرائق عدة منها الضوئية والالكترونية والحسابية وعادة تكون ضمن جهار المطيافية المستخدم. يعتمد البحث على بناء برنامج مكتوب بلغة الفجوال بيسك ضمن برنامج الاكسل يقوم باشتقاق البيانات كمشقة أولى وثانية وثالثة ورابعة وإرجاع هذه المشتقات الطيفية الى المشتقة الصفرية. تم تطبيق البرنامج على قيم تجريبية وأخرى حقيقة عند تقدير الكبريتات على هيئة كبريتات الباريوم باستعمال جهاز -Linear Array Ayah 5SX1-T-1D) (CFI Analyser وتم جمع البيانات من خلال جهاز Array M3500A 6.5Digit Digital) (Multimeter الرابط بين المطياف والحاسوب الالكتروني.

Introduction

Derivative spectrophotometry is one of the advanced modern spectrophotometric technique. It is based on so called derivative spectra [1,2] which are generated from parent zero-order ones.

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The concept of derivative spectral data was first introduced in the 1950s [3, 4], when it was shown to have many advantages. However, the technique received alittle attention primarily because of the complexity of generating derivative spectra using early UV-Visible spectrophotometers. The introduction of microcomputers in the late1970s made it generally practicable to use mathematical methods to generate derivative spectra quickly, easily and reproducibly. This significantly increased the uses of the derivative technique.

Derivative spectrophotometry involves the conversion of a normal spectrum (fundamental, zeroth order spectrum) to its first, second or higher derivative spectrum by differentiating absorbance (dA) of sample with respect to "wavelength (dλ) or time (dt)" versus wavelength (λ) or time (t) [5] as shown in table 1.

Table 1- Calculation of Derivative Spectrum

A = Absorbance		A = Attenuation of incident light
Zero order	$A = f(\lambda)$	$A = f(t)$
First order	$\dfrac{dA}{d\lambda} = f'(\lambda)$	$\dfrac{dA}{dt} = f'(t)$
Second order	$\dfrac{d^2A}{d\lambda^2} = f''(\lambda)$	$\dfrac{d^2A}{dt^2} = f''(t)$
Third order	$\dfrac{d^3A}{d\lambda^3} = f'''(\lambda)$	$\dfrac{d^3A}{dt^3} = f'''(t)$

The derivatisation [6] of zero-order spectrum can lead to separation of overlapped signals, elimination of background caused by presence of other compounds in a sample. This method allows one to realize the ability of detection of small differences in spectral outlines.

Figure 1 shows a computer simulation of the effects of derivatization on the appearance of a simple Gaussian absorbance band. Derivative spectra are always more complex than zero-order spectra.
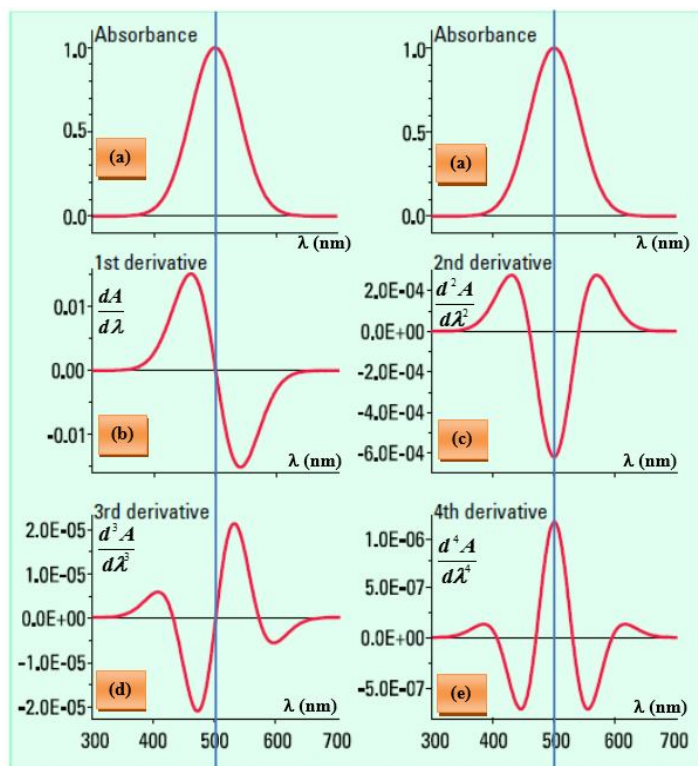

Figure 1-Normal scan plot and computer simulation of zero order (a) first (b), second (c), third (d) and fourth (e) derivative plot and changing in peak height of these plot

The Main Advantage of Derivative Spectrum [7,8] is to enhance resolution permitting identification of analyte with close λ_{max} (i.e. might be an impurity in an expected pure compound). This is very important in pharmaceutical industry. It also eliminates baseline shift effect arising from instrument or sample handling. (This falls in the area of improving of Signal to Noise ratio). It eliminates scattering effects thus helpful for analyte present in turbid solution.

In our work, a new approach was used to interpolate the obtained responses which have no similarity what so ever in any previously published works. It nearly draws a segment profile for the measuring sample segment. It widen the horizons of using derivative spectroscopy as applied in this research work.

This paper describes a new developed data treatment for the derivatisation and return back via building a new program. The program has been built in a Visual Basic language within Excel program to deal with the data obtained from Linear Array Ayah 5SX1-T-1D-CFI analyser [9]. The program is treatment the response according to kinds of response peak.

The new program is capable for deriving 1st, 2nd, 3rd, and 4th derivative in general. Also returning the data of higher derivative order to a lower derivative order was also considered.

Obtaining Derivative Spectra [2]

Derivative spectra can be obtained by optical (First-derivative spectra may generated by a dual wavelength spectrophotometer, it's generated by scanning with each monochromator separated by a small constant wavelength difference), electronic (electronic delay signals one before another using analog resistance capacitance devices), or mathematical methods (software for obtain data treatment). Optical and electronic techniques were used on early UV-Visible spectrophotometers but have largely been superseded by mathematical techniques (the work conducted in the project based on this point). The advantages of the mathematical techniques are that derivative spectra may be easily calculated and recalculated with different parameters.

Analytical Application of Derivative Spectrophotometry

Derivative spectrophotometry has found a wide application in chemical analysis, the following some one of these applications:

- Qualitative Analysis.
- Confirmation of identity.
- Discrimination of Broad Bands.
- Background elimination.
- Matrix Suppression.
- Derivative Analysis of Hyperspectral Data.

Microsoft Excel Visual Basic Program for Data Treatment

The program has been built in a Visual Basic language within Excel program to deal with the data obtained from Linear Array Ayah 5SX1-T-1D-CFI analyser. The program is treatment the response according to kinds of response peak.

The program derive and return back to original peak profile. The new program is capable for deriving 1st, 2nd, 3rd, and 4th derivative in general. Also returning the data of higher derivative order to a lower derivative order was also considered.

Figure 2 show the kinds of profile peaks obtained from our system 5S-1D-1T-flow injection analyser when different parameters applied.

The program is divided into two parts the first deals with how the data can be extracted (derivatized) while the second part deals with how these derivatized data return back to its original.

The program that was initialized was based on eleven data sheet.

- The first sheet is an outline for the program and how to use it.
- The second sheet is the introduction of data to new program.
- The third sheet is the transfer data sheet for choose treatment function (derivative or return back) of data.
- The fourth sheet is the first order derivatisation of transferred data.
- The fifth sheet is the second order derivatisation of transferred data.
- The sixth sheet is the third order derivatisation of transferred data.
- The seventh sheet is the fourth order derivatisation of transferred data.

- The eighth sheet is the return back of first order derivative to zero order derivative (normal plot).
- The ninth sheet is the return back of second order derivative to zero order derivative (normal plot).
- The tenth sheet is the return back of third order derivative to zero order derivatives (normal plot).
- The eleventh sheet is the return back of fourth order derivative to zero order derivative (normal plot).
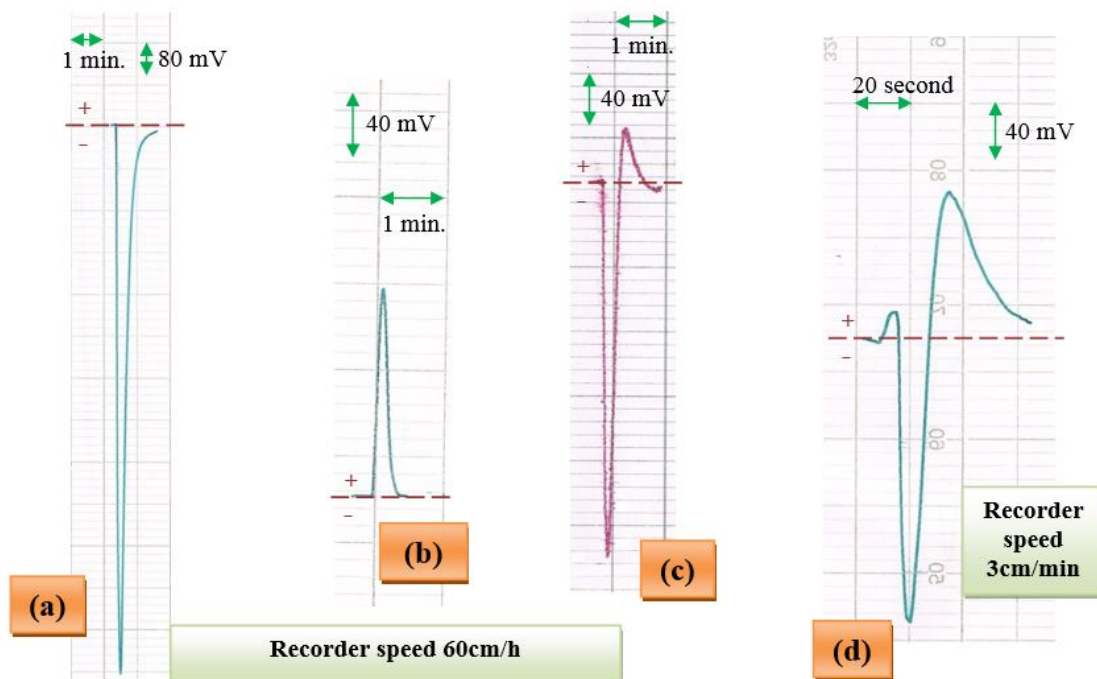

Figure (2): Kinds of obtained peaks profile.
(a) 8-Hydroxy quinoline (7 mM)-CH_3COONH_4 (20 mM)-Fe^{+3} (10 mM).
(b)$K_4[Fe(CN)_6]$ (0.7 mM) – Chlorpromazine.HCl (10 mM).
(c) $K_3[Fe(CN)_6]$ (5 mM)-HCl (100 mM)-Chlorpromazine.HCl (10 mM)
(d) $BaCl_2$ (400 mM) – Na_2SO_4 (50 mM)

First Part: Derivative of Data
First Derivative
   Assuming that there is a set of values (x, y). The attenuation of the incident light that is on the y-axis and time values on the x-axis. First Derivate of data is done by drawing the values of (dy/dx) versus (x) values. This process done through the following steps:
   First: find the values of (dx), where it represents time difference between the two readings one after the other by the following equation:
$dx_n=(x_{n+1})-(x_n)$……..(1)
when $dx_1 = x_{2(sec.)} − x_{1(sec.)} = \Delta x_{2-1}$
   Second: find the values of (dy), which represents the difference attenuation of incident light expressed mV between the two readings within the same response but with a time difference that represented by dx to give the y values. These process are done by the following equation:

   $dy_n=(y_{n+1})-(y_n)$……..(2)
   when n=1 then $\rightarrow$ $dy_1=y_2-y_1$

Third: find the first derivative by dividing the dy values on dx values as shown below:

Derivative-1 = dy_n/dx_n ....(3)

Then draw the (dy/dx) values with the (x) values. These operations are carried out through use of the commands in appendix A:

For example, assume experimental (trial) values (x,y) to plot high symmetry response as shown in figure 3. First derivative function was applied on experimental values.
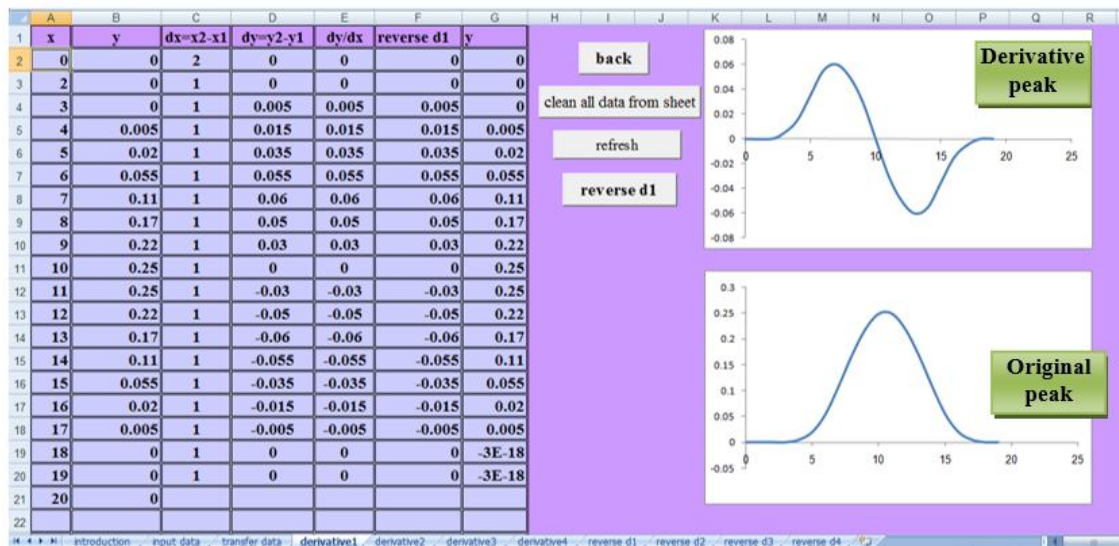
Figure 3-Derivative1 sheet contain data, plot of original peak and first derivative for experimental values

The comparison with other programs in the world that available on the Internet. CHEMIX School-Chemistry software for Students Teachers Chemists and Scientists, version 3.60, product from Arne Standnes company is available on website http://www.chemix-chemistry-software.com/chemistry-software.html. The software includes a set of functions compacted within the program, one of these tasks is the spectral derivatives of the first, second degree only.

The same experimental (trial) values that used in the established new program to plot high symmetry response as shown in figure 4. First derivative function in CHEMIX-School software was applied on experimental values.

Figure 4-Zero and first order derivative for experimental value by using CHEMIX-School software

When taking real values obtained from reaction of sulfate (50 mmol) with barium (400 mmol) the plot is asymmetry. The first derivative was applied on real value and the output plot is asymmetry as shown in figure 5.
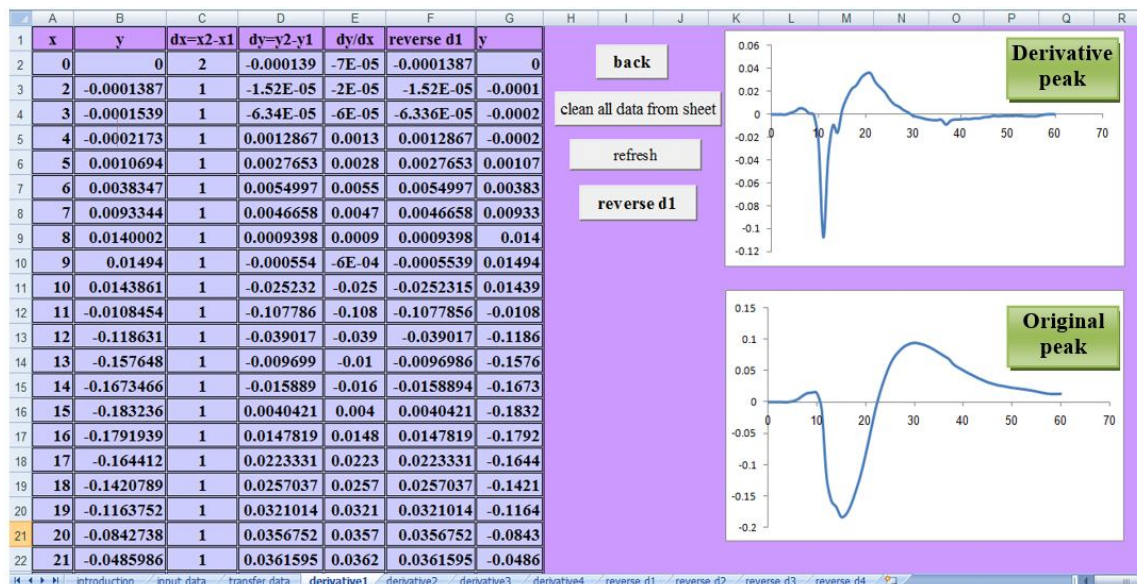
Figure 5-Derivative1 sheet contain data, plot of original peak and first derivative for real values for barium sulphate

The same real values obtained from reaction of sulphate (50 mmol) with barium (400 mmol) that used in established new program. The first derivative was applied on real value by using CHEMIX-School software as shown in figure 6.

Figure 6- Zero and first order derivative for real values by using CHEMIX-School software

Second Derivative

Assuming that there is a set of values (x, y). The attenuation of the incident light that is on the y-axis and time values on the x-axis. Second Derivate of data is done by drawing the values of $[(dy/dx)/dx]$ versus (x) values. This process done through the following steps:

First: find the values of (dx), where it represents time difference between the two readings one after the other by the following equation:

$$dx_n=(x_{n+1})-(x_n)........(1)$$

Second: find the values of (dy$^\backslash$), which represents the second difference of attenuation of incident light expressed mV between the two readings within the same response but with a time difference represented by dx to give the y values. These processes done by the following equation:
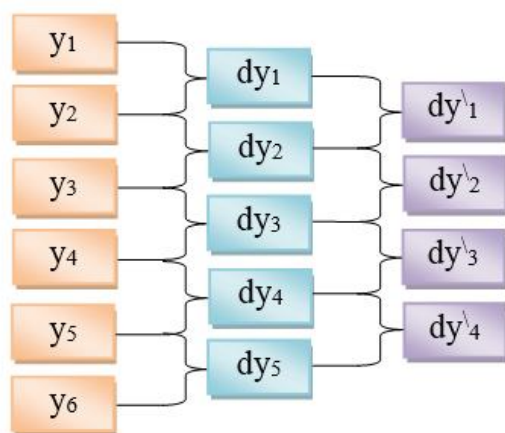
$$dy^\backslash_n = (dy_{n+1}) - (dy_n) \ldots \ldots (2)$$

when n=1, then →dy$^\backslash_1$ = (dy$_2$)-(dy$_1$)

Third: find the second derivative by dividing the dy$^\backslash$values on dx values twice time as shown below:

Derivative-2 = [(dy$^\backslash_n$/dx$_n$)/(dx$_n$)] ……….(3)

Then draw the [(dy$^\backslash$/dx)/dx] values with the (x) values. These operations are carried out through using of the commands in appendix A.

For example, assume experimental (trial) values (x,y)to plot high symmetry response as shown in figure 7. Second derivative function was applied on experimental values.
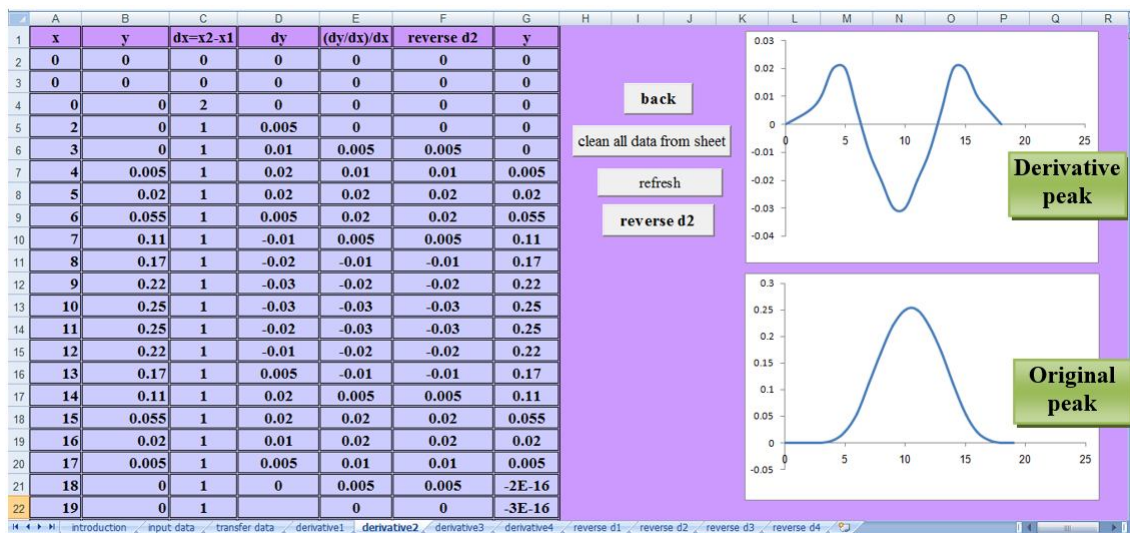
Figure 7-Derivative2 sheet contain data, plot of original peak and second derivative for experimental values

The same experimental (trial) values that used in the established new program to plot high symmetry response as shown in figure 8. Second derivative function in CHEMIX-School software was applied on experimental values.
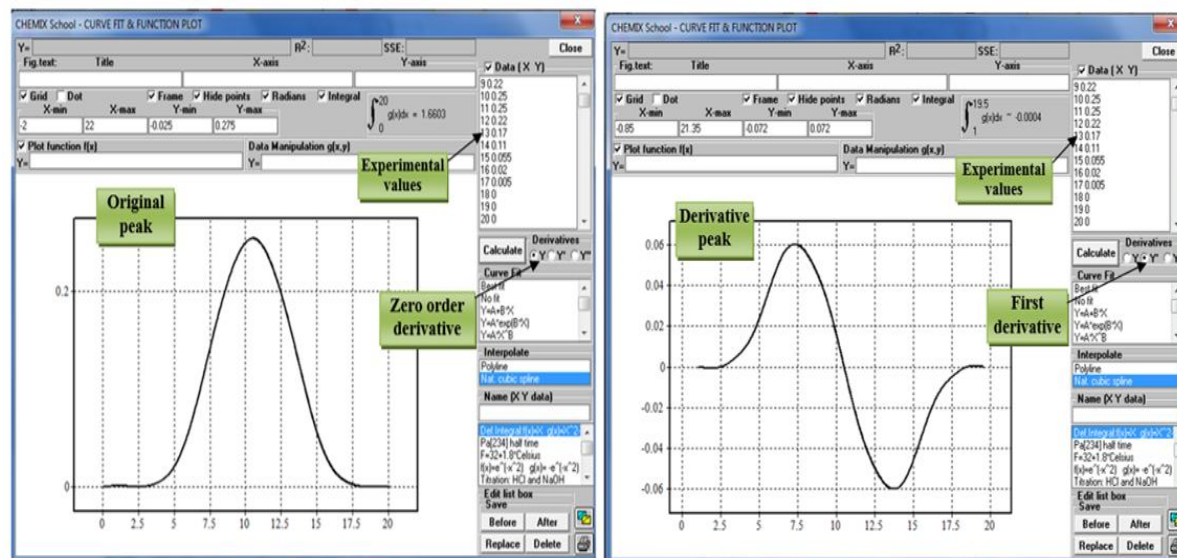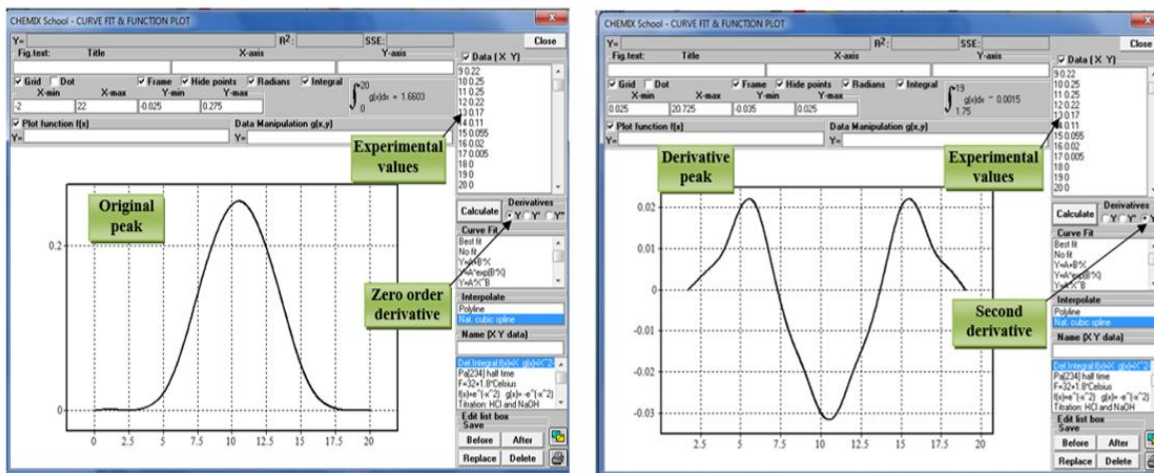
Figure 8-Zero and second order derivative for real values by using CHEMIX-School software

When taking real values obtained from reaction of sulfate (50 mmol) with barium (400 mmol) the plot is asymmetry. Second derivative was applied on real value and the output plot is asymmetry as shown in figure 9.


	A	B	C	D	E	F	G
1	x	y	dx=x2-x1	dy	(dy/dx)/dx	reverse d2	y
2	0	0	0	0	0	0	0
3	0	0	0	-0.000139	0	0	0
4	0	0	2	0.0001235	-0.00014	-0.00055488	0
5	2	-0.0001387	1	-4.82E-05	3.09E-05	3.088E-05	-0.0001
6	3	-0.0001539	1	0.0013501	-4.8E-05	-4.816E-05	-0.0002
7	4	-0.0002173	1	0.0014786	0.00135	0.00135008	-0.0002
8	5	0.0010694	1	0.0027344	0.001479	0.00147856	0.00107
9	6	0.0038347	1	-0.000834	0.002734	0.0027344	0.00383
10	7	0.0093344	1	-0.003726	-0.00083	-0.00083392	0.00933
11	8	0.0140002	1	-0.001494	-0.00373	-0.00372592	0.014
12	9	0.01494	1	-0.024678	-0.00149	-0.00149376	0.01494
13	10	0.0143861	1	-0.082554	-0.02468	-0.0246776	0.01439
14	11	-0.0108454	1	0.0687686	-0.08255	-0.08255408	-0.0108
15	12	-0.118631	1	0.0293184	0.068769	0.06876864	-0.1186
16	13	-0.157648	1	-0.006191	0.029318	0.0293184	-0.1576
17	14	-0.1673466	1	0.0199315	-0.00619	-0.00619088	-0.1673
18	15	-0.183236	1	0.0107398	0.019932	0.01993152	-0.1832
19	16	-0.1791939	1	0.0075512	0.01074	0.01073984	-0.1792
20	17	-0.164412	1	0.0033706	0.007551	0.0075512	-0.1644
21	18	-0.1420789	1	0.0063978	0.003371	0.00337056	-0.1421
22	19	-0.1163752	1	0.0035738	0.006398	0.00639776	-0.1164

Figure 9-Derivative2 sheet contain data, plot of original peak and second derivative for real values for barium sulphate

The same real values obtained from reaction of sulphate (50 mmol) with barium (400 mmol) that used in the established of a new program. The second derivative was applied on real value by using CHEMIX-School software as shown in figure 10.
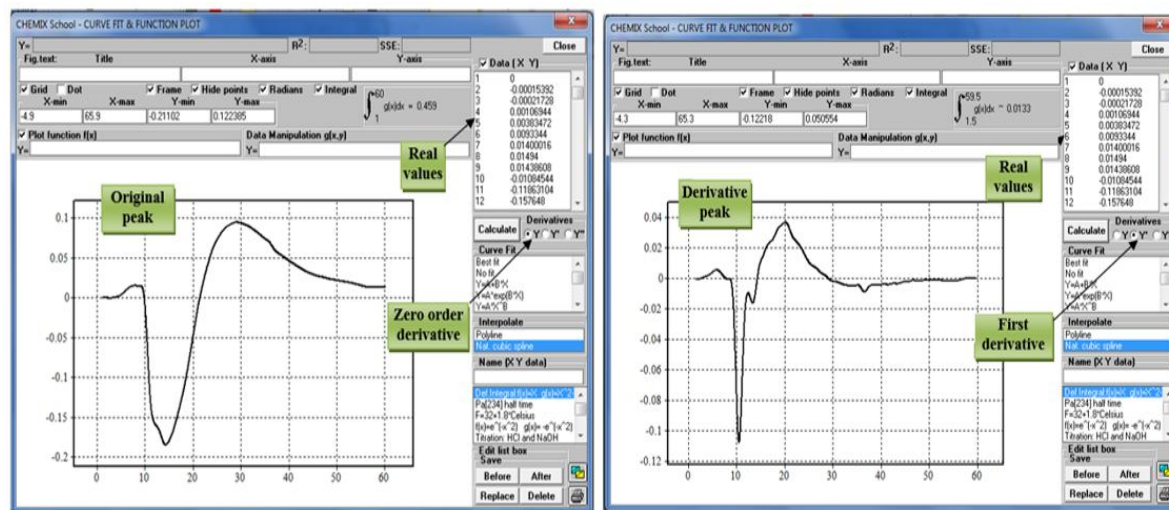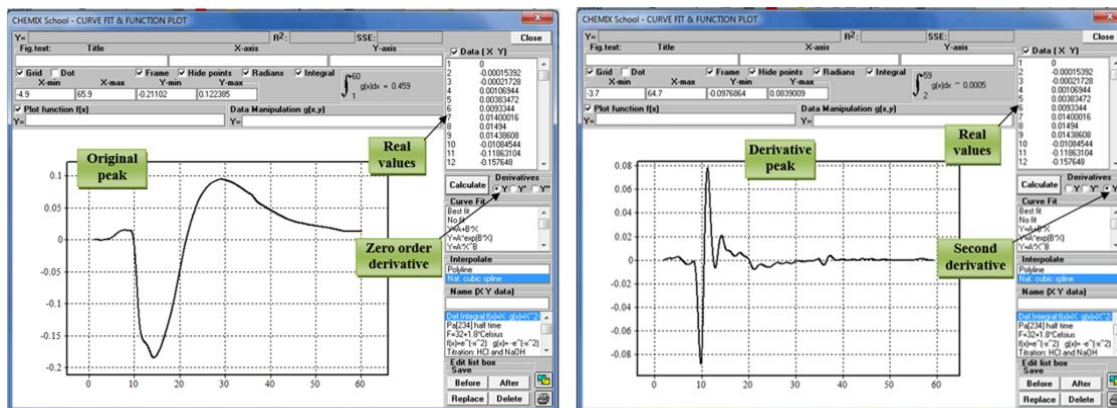
**Figure 10-**Zero and second order derivative for real values by using CHEMIX-School software

Third Derivative

Assuming that there is a set of values (x, y). The attenuation of the incident light that is on the y-axis and time values on the x-axis. Third Derivate of data is done by drawing the values of $[((dy^{\backslash\backslash}/dx)/dx)/dx]$ versus (x) values. This process done through the following steps:

First: find the values of (dx), where it represents time difference between the two readings one after the other by the following equation:

$dx_n=(x_{n+1})-(x_n)$……..(1)

Second: find the values of $(dy^{\backslash\backslash})$, which represents the second difference of attenuation of incident light expressed mV between the two readings within the same response but with a time difference represented by dx to give the y values. These processes done by the following equation:

$dy^{\backslash\backslash}_n=(dy^{\backslash}_{n+1})-(dy^{\backslash}_n)$…………..(2)
when n=1, then $\rightarrow dy^{\backslash\backslash}_1 = (dy^{\backslash}_2)-(dy^{\backslash}_1)$

Third: find the third derivative by dividing the $dy^{\backslash\backslash}$ values on dx values three times as shown below:

Derivative-3 = $[((dy^{\backslash\backslash}_n/dx_n)/dx_n)/dx_n]$ …………..(3)

Then draw the $[((dy^{\backslash\backslash}/dx)/dx)]/dx]$ values versus the (x) values. These operations are carried out through using of the commands in appendix A.

For example, assume experimental (trial) values (x,y)to plot high symmetry response as shown in figure 11. Third derivative function was applied on experimental values.
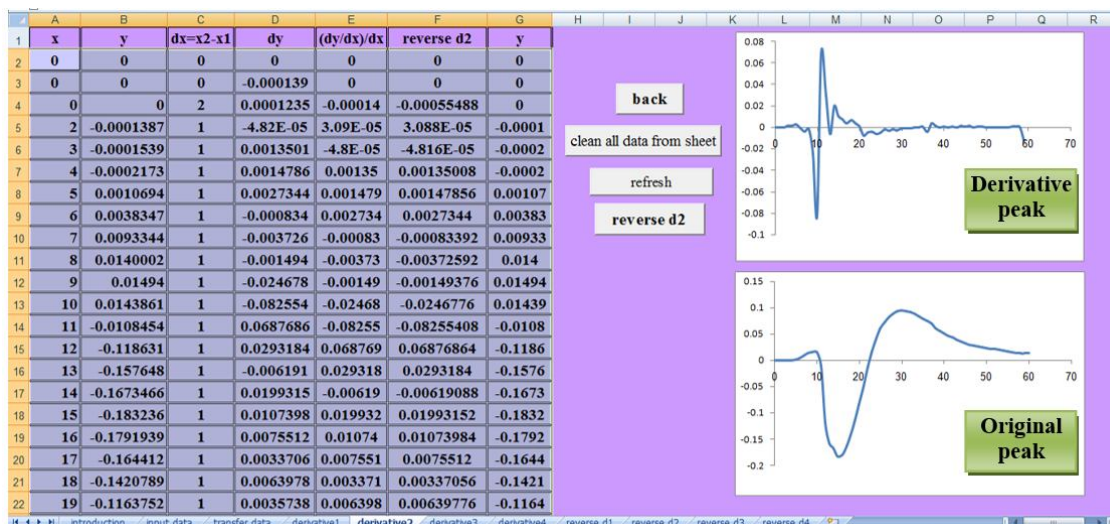
	A	B	C	D	E	F	G
1	x	y	dx=x2-x1	dy	((dy/dx)/dx)/dx	reverse d3	y
2	0	0	0	0	0	0	0
3	0	0	0	0	0	0	0
4	0	0	2	0.005	0.000625	0.005	0
5	2	0	1	0.005	0.005	0.005	0
6	3	0	1	0.01	0.01	0.01	0
7	4	0.01	1	1E-17	1.38778E-17	1.388E-17	0
8	5	0.02	1	-0.015	-0.015	-0.015	0
9	6	0.06	1	-0.015	-0.015	-0.015	0.1
10	7	0.11	1	-0.01	-0.01	-0.01	0.1
11	8	0.17	1	-0.01	-0.01	-0.01	0.2
12	9	0.22	1	0	0	0	0.2
13	10	0.25	1	0.01	0.01	0.01	0.3
14	11	0.25	1	0.01	0.01	0.01	0.2
15	12	0.22	1	0.015	0.015	0.015	0.2
16	13	0.17	1	0.015	0.015	0.015	0.2
17	14	0.11	1	-1E-17	-1.38778E-17	-1.39E-17	0.1
18	15	0.06	1	-0.01	-0.01	-0.01	0.1
19	16	0.02	1	-0.005	-0.005	-0.005	0
20	17	0.01	1	-0.005	-0.005	-0.005	0

Figure 11-Derivative3 sheet contain data, plot of original peak and third derivative for experimental values

When taking real values obtained from reaction of sulfate (50 mmol) with barium (400 mmol) the plot is asymmetry. Third derivative was applied on the real values and the output plot is asymmetry as shown in figure 12.

	A	B	C	D	E	F	G
1	x	y	dx=x2-x1	dy	((dy/dx)/dx)/dx	reverse d3	y
2	0	0	0	-1E-04	0	0	0
3	0	0	0	0.0003	-0.00013872	-0.0001387	0
4	0	0	2	-2E-04	0.00026224	0.00209792	0
5	2	-1E-04	1	0.0014	-2.146E-05	-2.146E-05	-0.0001387
6	3	-2E-04	1	0.0001	0.00139824	0.00139824	-0.0001539
7	4	-2E-04	1	0.0013	0.00012848	0.00012848	-0.0002173
8	5	0.0011	1	-0.004	0.00125584	0.00125584	0.0010694
9	6	0.0038	1	-0.003	-0.00356832	-0.0035683	0.0038347
10	7	0.0093	1	0.0022	-0.002892	-0.002892	0.0093344
11	8	0.014	1	-0.023	0.00223216	0.00223216	0.0140002
12	9	0.0149	1	-0.058	-0.02318384	-0.0231838	0.01494
13	10	0.0144	1	0.1513	-0.05787648	-0.0578765	0.0143861
14	11	-0.011	1	-0.039	0.15132272	0.15132272	-0.0108454
15	12	-0.119	1	-0.036	-0.03945024	-0.0394502	-0.118631
16	13	-0.158	1	0.0261	-0.03550928	-0.0355093	-0.157648
17	14	-0.167	1	-0.009	0.0261224	0.0261224	-0.1673466
18	15	-0.183	1	-0.003	-0.00919168	-0.0091917	-0.183236
19	16	-0.179	1	-0.004	-0.00318864	-0.0031886	-0.1791939
20	17	-0.164	1	0.003	-0.00418064	-0.0041806	-0.164412
21	18	-0.142	1	-0.003	0.0030272	0.0030272	-0.1420789
22	19	-0.116	1	-0.003	-0.002824	-0.002824	-0.1163752

Figure 12-Derivative3 sheet contain data, plot of original peak and third derivative for real values for barium sulphate
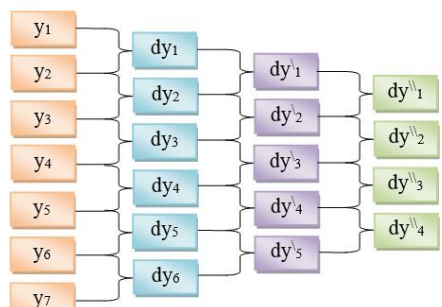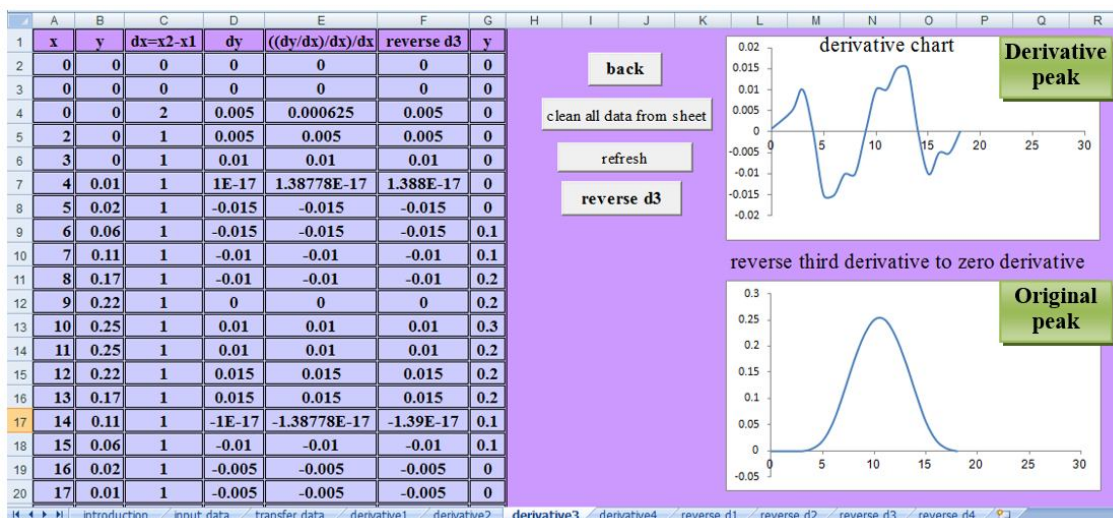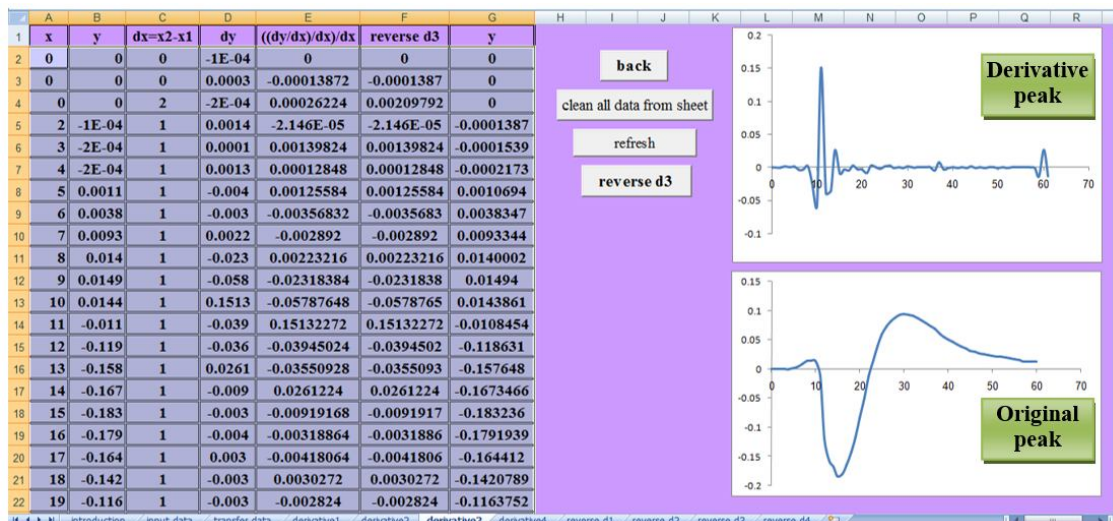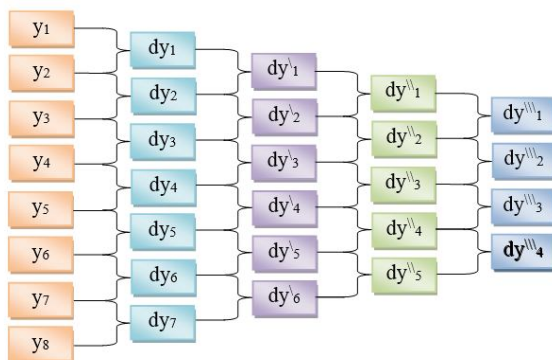
Fourth Derivative

Assuming that there is a set of values (x, y). The attenuation of the incident light that is on the y-axis and time values on the x-axis. Forth Derivate of data is done by drawing the values of $[(((dy^{\prime\prime\prime}/dx)/dx)/dx)/dx]$ versus (x) values. This process is done through the following steps:

First: find the values of (dx), where it represents time difference between the two readings one after the other by the following equation:

$$dx_n=(x_{n+1})-(x_n)\ldots\ldots..(1)$$

Second: find the values of $(dy^{\prime\prime\prime})$, which represents the second difference of attenuation of incident light expressed mV between the two readings within the same response but with a time difference represented by dx to give the y values. This process is done by the following equation:

$$dy^{||||}{}_n = (dy^{|||}{}_{n+1}) - (dy^{|||}{}_n)\ldots\ldots..(2)$$

when n=1, then $\rightarrow dy^{||||}{}_1 = (dy^{|||}{}_2) - (dy^{|||}{}_1)$

Third: find the fourth derivative by dividing the $dy^{||||}$ values on dx values four times as shown below:

Derivative-4 = [(((dy$^{||||}{}_n$/dx$_n$)/dx$_n$)/dx$_n$)/dx$_n$] ……………..(3)

Then draw the [[[((dy$^{||||}$/dx)/dx)]/dx]/dx] values with the (x) values. These operations are carried out through using of the commands in appendix A.

For example, assume experimental (trial) values (x,y) to plot high symmetry response as shown in figure 13. Fourth derivative function was applied on experimental values.
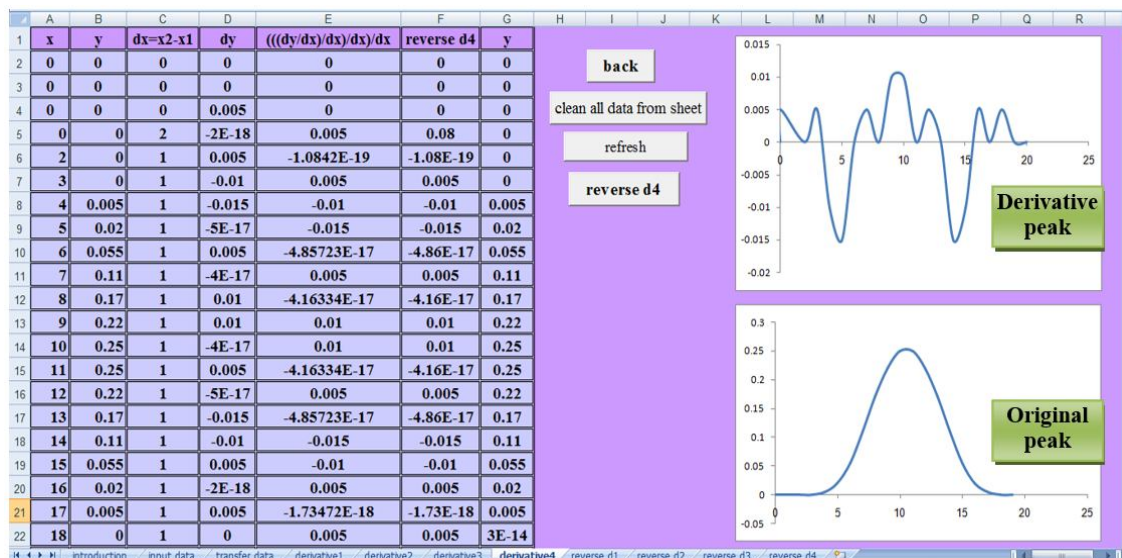

x	y	dx=x2-x1	dy	(((dy/dx)/dx)/dx	reverse d4	y
0	0	0	0	0	0	0
0	0	0	0	0	0	0
0	0	0	0.005	0	0	0
0	0	2	-2E-18	0.005	0.08	0
2	0	1	0.005	-1.0842E-19	-1.08E-19	0
3	0	1	-0.01	0.005	0.005	0
4	0.005	1	-0.015	-0.01	-0.01	0.005
5	0.02	1	-5E-17	-0.015	-0.015	0.02
6	0.055	1	0.005	-4.85723E-17	-4.86E-17	0.055
7	0.11	1	-4E-17	0.005	0.005	0.11
8	0.17	1	0.01	-4.16334E-17	-4.16E-17	0.17
9	0.22	1	0.01	0.01	0.01	0.22
10	0.25	1	-4E-17	0.01	0.01	0.25
11	0.25	1	0.005	-4.16334E-17	-4.16E-17	0.25
12	0.22	1	-5E-17	0.005	0.005	0.22
13	0.17	1	-0.015	-4.85723E-17	-4.86E-17	0.17
14	0.11	1	-0.01	-0.015	-0.015	0.11
15	0.055	1	0.005	-0.01	-0.01	0.055
16	0.02	1	-2E-18	0.005	0.005	0.02
17	0.005	1	0.005	-1.73472E-18	-1.73E-18	0.005
18	0	1	0	0.005	0.005	3E-14

(buttons: back | clean all data from sheet | refresh | reverse d4)

(charts labeled: **Derivative peak**, **Original peak**)

(sheet tabs: introduction, input data, transfer data, derivative1, derivative2, derivative3, **derivative4**, reverse d1, reverse d2, reverse d3, reverse d4)

Figure 13-Derivative4 sheet that contain data, plot of original peak and fourth derivative for experimental values

When taking the real values obtained from reaction of sulfate (50 mmol) with barium (400 mmol), the plot is asymmetry. Fourth derivative was applied on real value and the output plot is asymmetry as shown in figure 14.
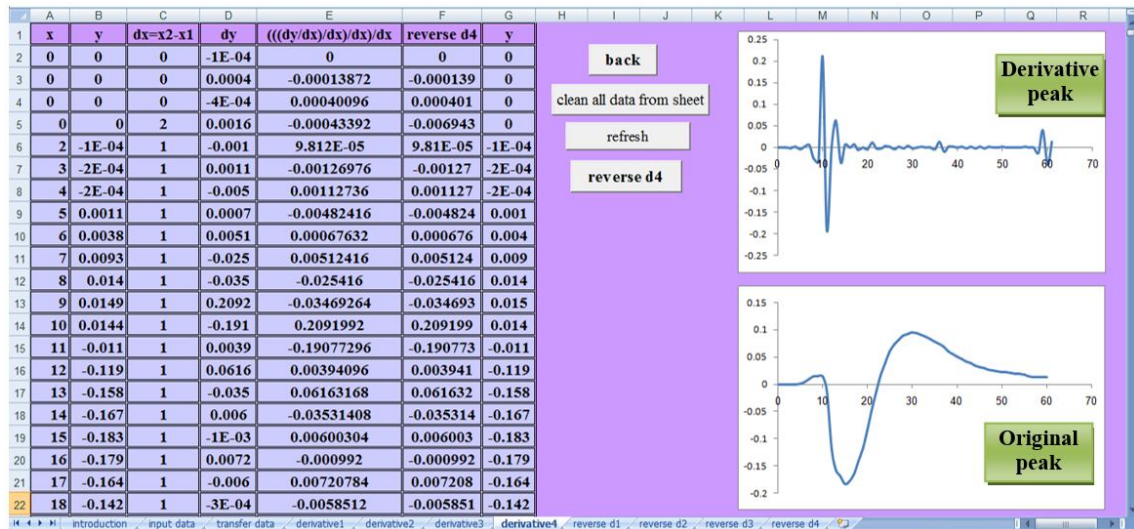
x	y	dx=x2-x1	dy	(((dy/dx)/dx)/dx)/dx	reverse d4	y
0	0	0	-1E-04	0	0	0
0	0	0	0.0004	-0.00013872	-0.000139	0
0	0	0	-4E-04	0.00040096	0.000401	0
0	0	2	0.0016	-0.00043392	-0.006943	0
2	-1E-04	1	-0.001	9.812E-05	9.81E-05	-1E-04
3	-2E-04	1	0.0011	-0.00126976	-0.00127	-2E-04
4	-2E-04	1	-0.005	0.00112736	0.001127	-2E-04
5	0.0011	1	0.0007	-0.00482416	-0.004824	0.001
6	0.0038	1	0.0051	0.00067632	0.000676	0.004
7	0.0093	1	-0.025	0.00512416	0.005124	0.009
8	0.014	1	-0.035	-0.025416	-0.025416	0.014
9	0.0149	1	0.2092	-0.03469264	-0.034693	0.015
10	0.0144	1	-0.191	0.2091992	0.209199	0.014
11	-0.011	1	0.0039	-0.19077296	-0.190773	-0.011
12	-0.119	1	0.0616	0.00394096	0.003941	-0.119
13	-0.158	1	-0.035	0.06163168	0.061632	-0.158
14	-0.167	1	0.006	-0.03531408	-0.035314	-0.167
15	-0.183	1	-1E-03	0.00600304	0.006003	-0.183
16	-0.179	1	0.0072	-0.000992	-0.000992	-0.179
17	-0.164	1	-0.006	0.00720784	0.007208	-0.164
18	-0.142	1	-3E-04	-0.0058512	-0.005851	-0.142

back

clean all data from sheet

refresh

reverse d4

Derivative peak

Original peak

introduction / input data / transfer data / derivative1 / derivative2 / derivative3 / **derivative4** / reverse d1 / reverse d2 / reverse d3 / reverse d4

Figure 14-Derivative4 sheet contain data, plot of original peak and fourth derivative for real values for barium sulphate

Second Part: Back Return

The recoded signal from detector of our system Linear Array Ayah-5SX1-T-1D-CFI analyser is appeared like derivative spectrum and measuring peak height is difficult, therefore the new program was built to measure peak height by using Visual Basic within Microsoft Excel. The new program is treatment of derivative spectrum by converting it into zero or first derivative spectrum.

Back Return for First Derivative

Data processing has been mathematically convert the first derivative order to zero derivative order, assuming that the values on the y-axis for obtaining response from the system under study represents the values of (dy/dx) against the x values of x-axis.

First: The dx values are calculated from the equation:

$$dx_n = (x_{n+1}) - (x_n) \ldots\ldots\ldots\ldots (1)$$

Second: For dy values are multiplied by the values on the y-axis, which represents the values of (dy/dx) by dx values as calculated from following equation.
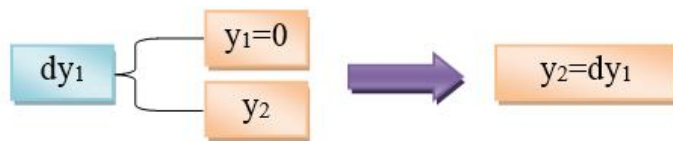
$$dy = (dy/dx) * dx \ldots\ldots\ldots\ldots (2)$$

Third: In order to get the y-values, the following steps are done:

A- Apply the general equation for calculating dy values.

$$dy_n = (y_{n+1}) - (y_n) \ldots\ldots\ldots\ldots (3)$$

B- When the value of n= 1, and assuming that the first value of y1=0; the y2 value is get.
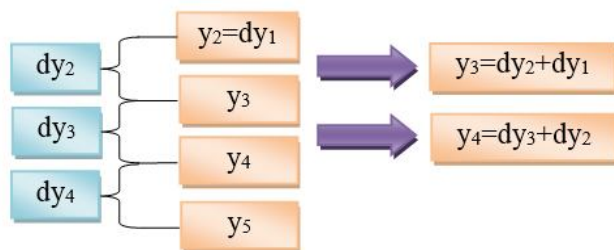
dy_1 → $y_1 = 0$ / y_2 ⟹ $y_2 = dy_1$

when n=1, $y_1 = 0$
$dy_1 = y_2 - y_1$
$dy_1 = y_2 - 0$
$dy_1 = y_2$

C - When the value of n = 2 get the values of y3

$dy_2 = y_3-y_2$

$dy_2 = y_3-dy_1$

$y_3 = dy_2+dy_1$

Thus, the applications of the above equations are obtained y values. These operations are carried out through using of the commands in Appendix B:

For example, when taking the experimental (trial) values which represent (x, dy/dx) to draw a curve as shown in figure 15. Back Return for First Derivative function was applied on experimental values.
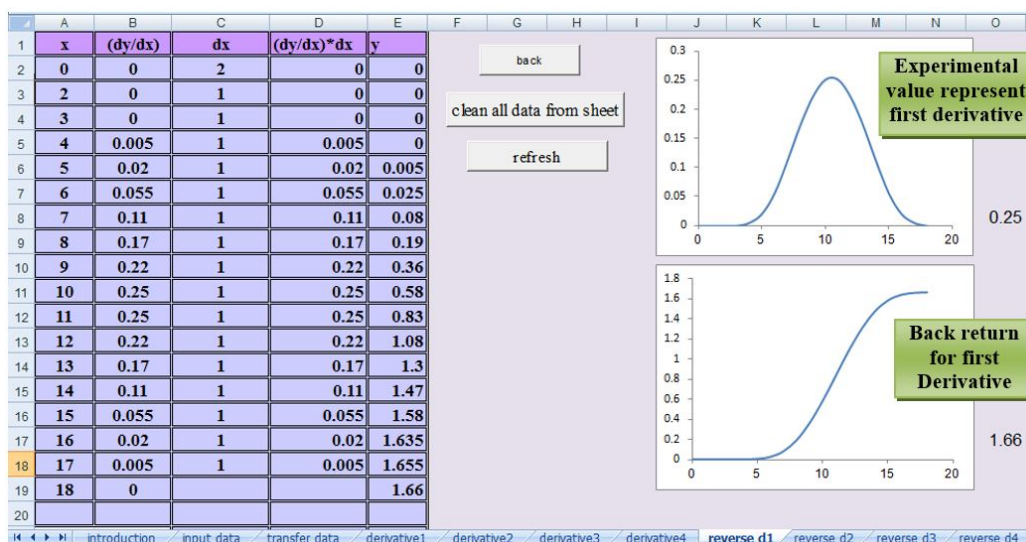

Figure 15-Revers d1 sheet contain data, plot of original peak and back return for first derivative of experimental values

When taking the real values obtained from reaction of sulfate (200 mmol) with barium (500 mmol). Back Return for First derivative was applied on real value as shown in figure 16.
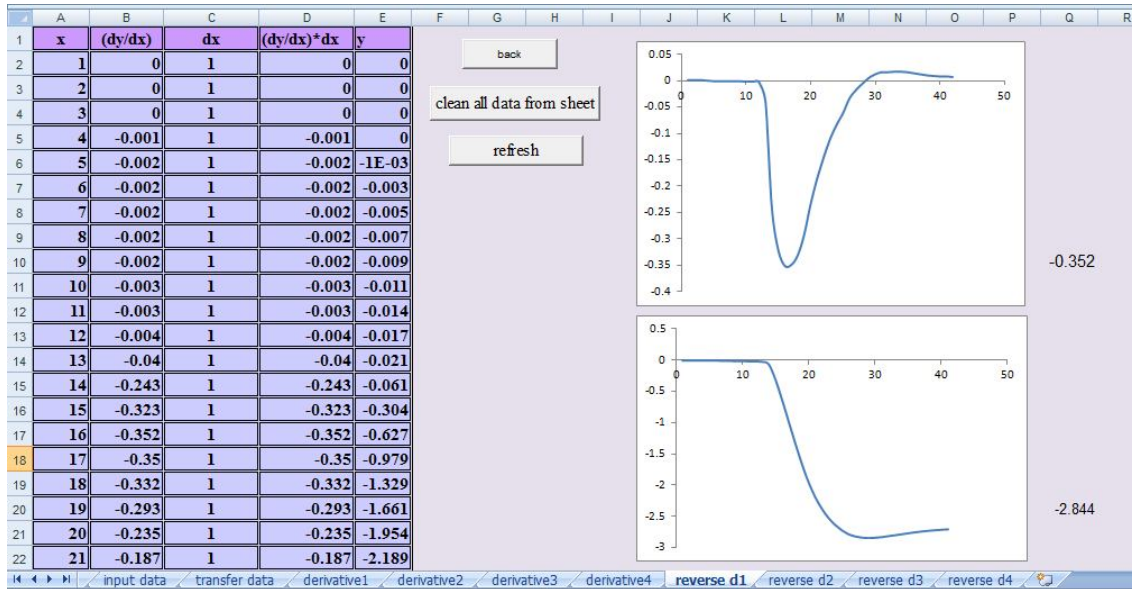
Figure 16-Revers d1 sheet contain data, plot of original peak and back return for first derivative of real values

Back Return for Second Derivative

Data processing has been mathematically convert the second derivative order to zero derivative order, assuming the values on the y-axis for obtain response from the system under study represents the values of $[(dy^\backslash/dx)/dx]$ against the x values of x-axis.

First: The dx values are calculated from the equation:

$dx_n=(x_{n+1})-(x_n)$ ....(1)

Second: For $dy^\backslash$ values are multiplied by the values on the y-axis, which represents the values of $((dy^\backslash/dx)/dx)$ by dx values as calculated from following equation.

$dy^\backslash = [(dy^\backslash/dx)/dx]*dx*dx$ ....(2)

Third, in order to get the y-values are through the following steps:

A- Apply the general equation for calculating $dy^\backslash$ values.

$dy^\backslash_n=(dy_{n+1})-(dy_n)$ ....(3)
$dy_{n+1} = (y_{n+2})-(y_{n+1})$ ....(4)
$dy_n=(y_{n+1})-(y_n)$.....................(5)

Compensation (2) and (3) in (1)

$dy^\backslash_n=[(y_{n+2})-(y_{n+1})]-[(y_{n+1})-(y_n)]$
$dy^\backslash_n = (y_{n+2})-(y_{n+1})-(y_{n+1})+(y_n)$
$dy^\backslash_n = (y_{n+2})-2(y_{n+1})+(y_n)$ ....(6)

B- When the value of n= 1, and assuming that the first value of y1, y2 =0; the y3 value is get.
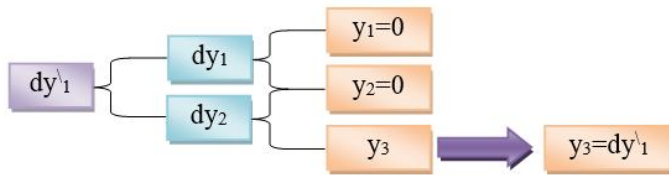
when n=1, y$_1$=0, y$_2$=0
$dy^\backslash_1 = (y_3)-2(y_2)+(y_1)$
$dy^\backslash_1 =(y_3)-2(0)+(0)$
$dy^\backslash_1 = (y_3)$

C- When the value of n = 2, get the values of y4
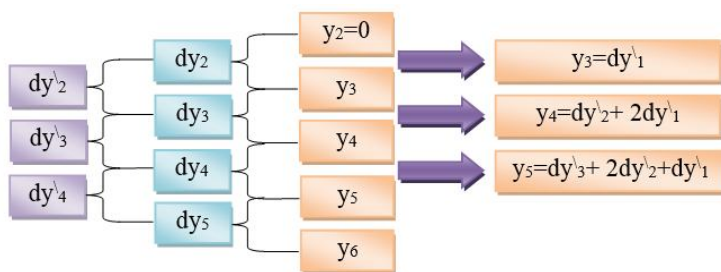
$$dy^\backslash_2 = (y_4)-2(y_3)+(y_2)$$
$$dy^\backslash_2 = (y_4)-(2dy^\backslash_1)+(0)$$
$$y_4 = dy^\backslash_2+2dy^\backslash_1$$

Thus, the applications of the above equations are obtained y values. These operations are carried out through use of the commands in Appendix B:

For example when taking the experimental (trial) values represent $(x, (dy^\backslash/dx)/dx)$ to draw a curve as shown in figure 17. Back Return for Second Derivative function was applied on experimental values.
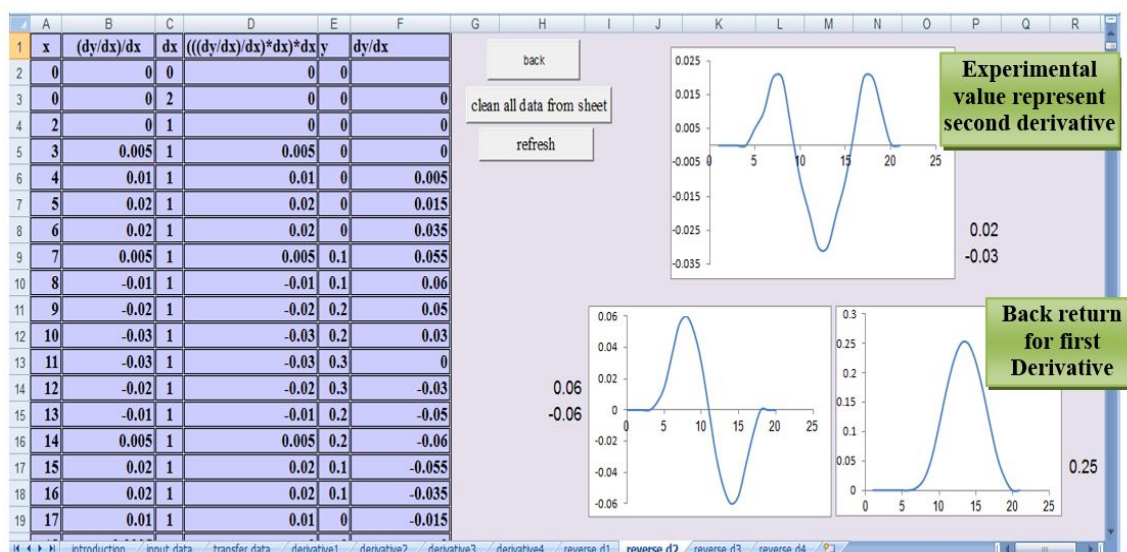
Figure 17-Revers d2 sheet contain data, plot of original peak and back return for second derivative of experimental values

When taking real values obtained from reaction of sulfate (200 mmol) with barium (500 mmol). Back Return for Second derivative was applied on real value as shown in figure 18.
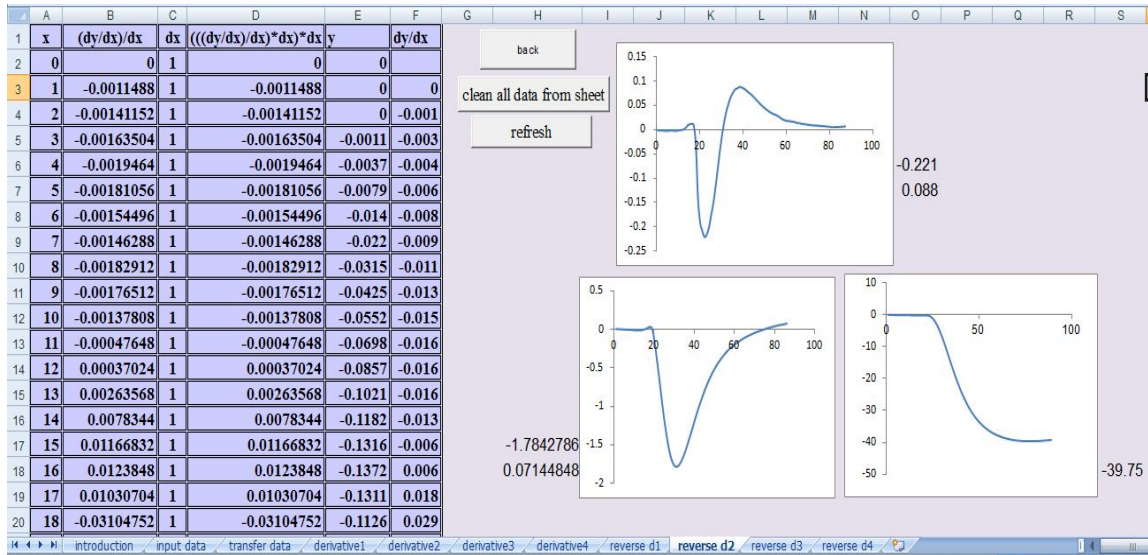
x	(dy/dx)/dx	dx	(((dy/dx)/dx)*dx)*dx	y	dy/dx
0	0	1	0	0	
1	-0.0011488	1	-0.0011488	0	0
2	-0.00141152	1	-0.00141152	0	-0.001
3	-0.00163504	1	-0.00163504	-0.0011	-0.003
4	-0.0019464	1	-0.0019464	-0.0037	-0.004
5	-0.00181056	1	-0.00181056	-0.0079	-0.006
6	-0.00154496	1	-0.00154496	-0.014	-0.008
7	-0.00146288	1	-0.00146288	-0.022	-0.009
8	-0.00182912	1	-0.00182912	-0.0315	-0.011
9	-0.00176512	1	-0.00176512	-0.0425	-0.013
10	-0.00137808	1	-0.00137808	-0.0552	-0.015
11	-0.00047648	1	-0.00047648	-0.0698	-0.016
12	0.00037024	1	0.00037024	-0.0857	-0.016
13	0.00263568	1	0.00263568	-0.1021	-0.016
14	0.0078344	1	0.0078344	-0.1182	-0.013
15	0.01166832	1	0.01166832	-0.1316	-0.006
16	0.0123848	1	0.0123848	-0.1372	0.006
17	0.01030704	1	0.01030704	-0.1311	0.018
18	-0.03104752	1	-0.03104752	-0.1126	0.029

Figure 18: Revers d2 sheet contain data, plot of original peak and back return for second derivative of real values of barium sulphate

Back Return for Third Derivative

Data processing has been mathematically convert the third derivative order to zero derivative order, assuming the values on the y-axis for obtain response from the system under study represents the values of $[((dy^{\backslash\backslash}/dx)/dx)/dx)]$ against the x values of x-axis.

First: The dx values are calculated from the equation:

$dx_n=(x_{n+1})-(x_n)$ ………………(1)

Second: For $dy^{\backslash\backslash}$ values are multiplied by the values on the y-axis, which represents the values of $[(((dy^{\backslash\backslash}/dx)/dx)]$ by dx values three times as calculated from following equation.

$dy^{\backslash\backslash} = [((dy^{\backslash\backslash}/dx)/dx)\backslash dx]*dx*dx*dx$ …………………(2)

Third, in order to get the y-values are through the following steps:

A- Apply the general equation for calculating $dy^{\backslash\backslash}$ values.

$dy^{\backslash\backslash}{}_n=(dy^{\backslash}{}_{n+1})-(dy^{\backslash}{}_n)$ ………………(3)

Use equation number 3 in the Back Return for Second Derivative to detect $(dy^{\backslash}{}_n)$ and $(dy^{\backslash}{}_{n+1})$

$dy^{\backslash}{}_n = (y_{n+2})-2(y_{n+1})+(y_n)$ …………………..(4)

$dy^{\backslash}{}_{n+1} = (y_{n+3})-2(y_{n+2})+(y_{n+1})$ ……………….(5)
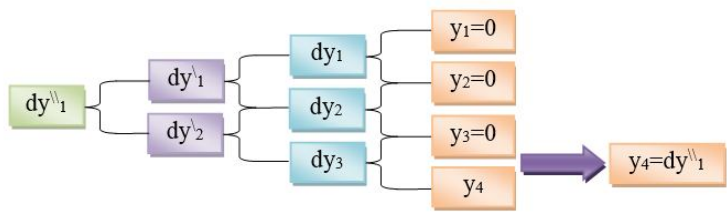
The compensation equation (4) and (5) in equation (3) produces:

$dy^{\backslash\backslash}{}_n=[(y_{n+3})-2(y_{n+2})+(y_{n+1})]-[(y_{n+2})-2(y_{n+1})+(y_n)]$

$dy^{\backslash\backslash}{}_n=(y_{n+3})-2(y_{n+2})+(y_{n+1})-(y_{n+2})+2(y_{n+1})-(y_n)$

$dy^{\backslash\backslash}{}_n=(y_{n+3})-3(y_{n+2})+3(y_{n+1})-(y_n)$…………..(6)

B- When the value of n = 1, and assuming that the first three values of y (y1, y2, y3) is equal to zero and the compensation equation (7) get the value of y4.
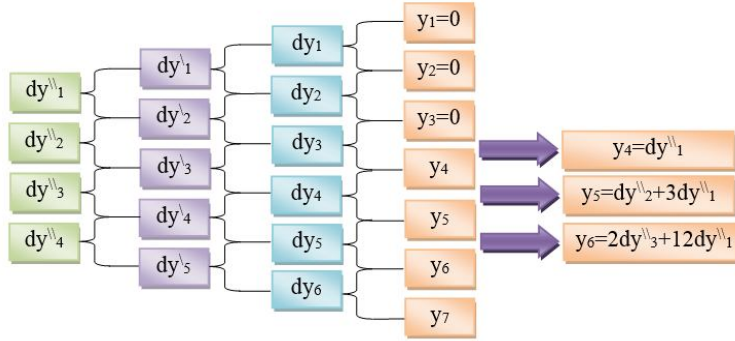
when n=1, $y_1=0$, $y_2=0$, $y3=0$

$dy^{\backslash\backslash}{}_1=(y_4)-3(y_3)+3(y_2)-(y_1)$

$dy^{\backslash\backslash}{}_1 =(y_4)-3(0)+3(0)-(0)$

$dy^{\backslash\backslash}{}_1 = y_4$

C- When the value of n = 2 get the values of y5

$dy^{\prime\prime\prime}_2=(y_5)-3(y_4)+3(y_3)-(y_2)$
$dy^{\prime\prime\prime}_2=(y_5)-3(dy^{\prime\prime\prime}_1)+3(0)-(0)$
$dy^{\prime\prime\prime}_2 = (y_5)-3(dy^{\prime\prime\prime}_1)$
$y_5=dy^{\prime\prime\prime}_2+3dy^{\prime\prime\prime}_1$

Thus, the applications of the above equations are obtained y values. These operations are carried out through using of the commands in Appendix B.

For example, when taking the experimental values represent (x, (((dy$^{\prime\prime\prime}$/dx)/dx)/dx) to draw a curve as shown in figure 19. Back Return for Third Derivative function was applied on experimental values.
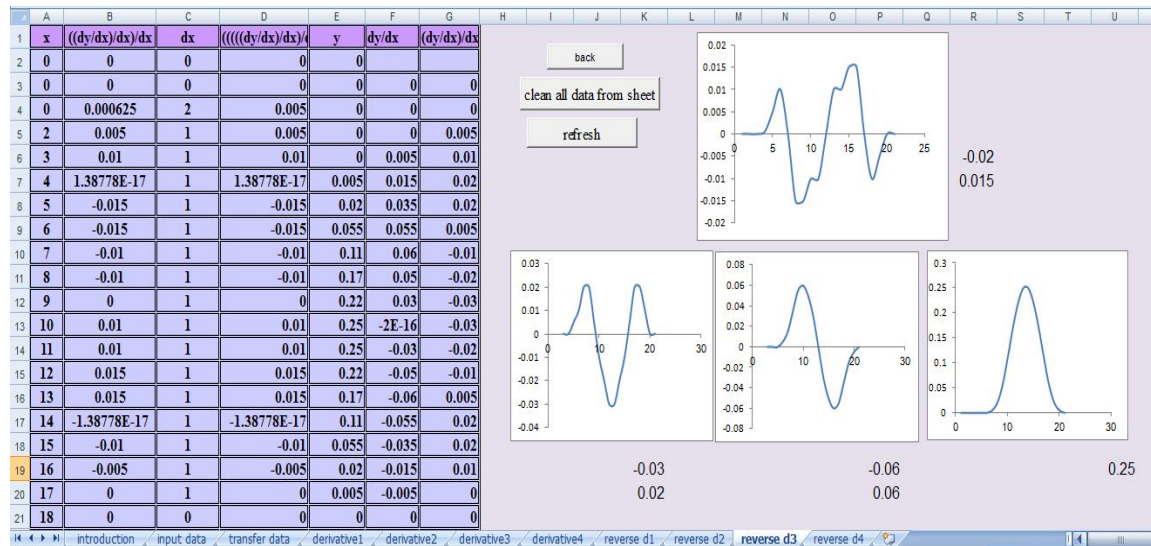
Figure 19-Revers d3 sheet that contain data, plot of original peak and back return for third derivative of experimental values

Back Return for Fourth Derivative

Data processing has been mathematically convert the fourth derivative order to zero derivative order, assuming the values on the y-axis for obtain response from the system under study represents the values of $[(((dy^{\prime\prime\prime}/dx)/dx)/dx)/dx]$ against the x values of x-axis.

First: The dx values are calculated from the equation:

$dx_n=(x_{n+1})-(x_n)$ ....(1)

Second: For $dy^{\prime\prime\prime}$ values are multiplied by the values on the y-axis, which represents the values of $[(((dy^{\prime\prime\prime}/dx)/dx)/dx)/dx]$by dx values four times as calculated from following equation.

$dy^{\prime\prime\prime} = [(((dy^{\prime\prime\prime}/dx)/dx)\backslash dx]*dx*dx*dx*dx$ ....(2)

Third: in order to get the y-values are through the following steps:

A- Apply the general equation for calculating $dy^{\prime\prime\prime}$ values.

$dy^{\prime\prime\prime}_n=(dy^{\prime\prime}_{n+1})-(dy^{\prime\prime}_n)$ ....(3)

Use equation number 6 in the Back Return for third Derivative to find (dy'''_n) and (dy'''_{n+1})

$$dy'''_n = (y_{n+3}) - 3(y_{n+2}) + 3(y_{n+1}) - (y_n) \dots\dots\dots\dots..(4)$$

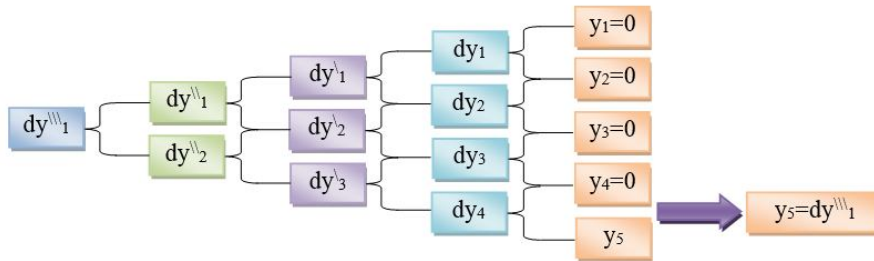$$dy'''_{n+1} = (y_{n+4}) - 3(y_{n+3}) + 3(y_{n+2}) - (y_{n+1}) \dots\dots\dots..(5)$$

The compensation equation (4) and (5) in equation (3) produces:

$$dy''''_n = [(y_{n+4}) - 3(y_{n+3}) + 3(y_{n+2}) - (y_{n+1})] - [(y_{n+3}) - 3(y_{n+2}) + 3(y_{n+1}) - (y_n)]$$

$$dy''''_n = (y_{n+4}) - 3(y_{n+3}) + 3(y_{n+2}) - (y_{n+1}) - (y_{n+3}) + 3(y_{n+2}) - 3(y_{n+1}) + (y_n)$$

$$dy''''_n = (y_{n+4}) - 4(y_{n+3}) + 6(y_{n+2}) - 4(y_{n+1}) + (y_n) \dots\dots\dots(6)$$

B- When the value of n = 1, and assuming that the first four values of y (y1, y2, y3, y4) is equal to zero and the compensation equation (6) get the value of y5.

when n=1, $y_1=0$, $y_2=0$, $y_3=0$, $y_4=0$
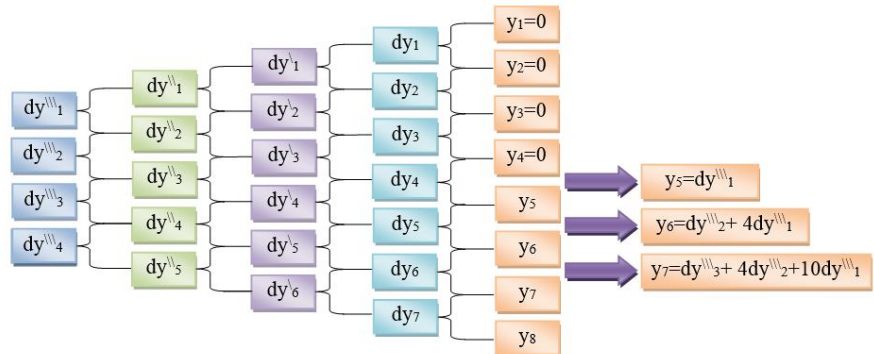
$$dy''''_1 = (y_5) - 4(y_4) + 6(y_3) - 4(y_2) + (y_1)$$

$$dy''''_1 = (y_5) - 4(0) + 6(0) - 4(0) + (0)$$

$$dy''''_1 = y_5$$

C- When the n = 2 get the values of y6.

$$dy''''_2 = (y_6) - 4(y_5) + 6(y_4) - 4(y_3) + (y_2)$$

$$dy''''_2 = (y_6) - 4(dy''''_1) + 6(0) - 4(0) + (0)$$

$$dy''''_2 = y_6 - 4(dy''''_1)$$

$$y_6 = dy''''_2 + 4\ dy''''_1$$

Thus, the application of the above equations are obtained y values. These operations are carried out through using of the commands in Appendix B.

For example, when taking the experimental values represent $(x, (((dy''/dx)/dx)/dx)/dx)$ to draw a curve as shown in figure 20. Back Return for Fourth Derivative function was applied on experimental values.
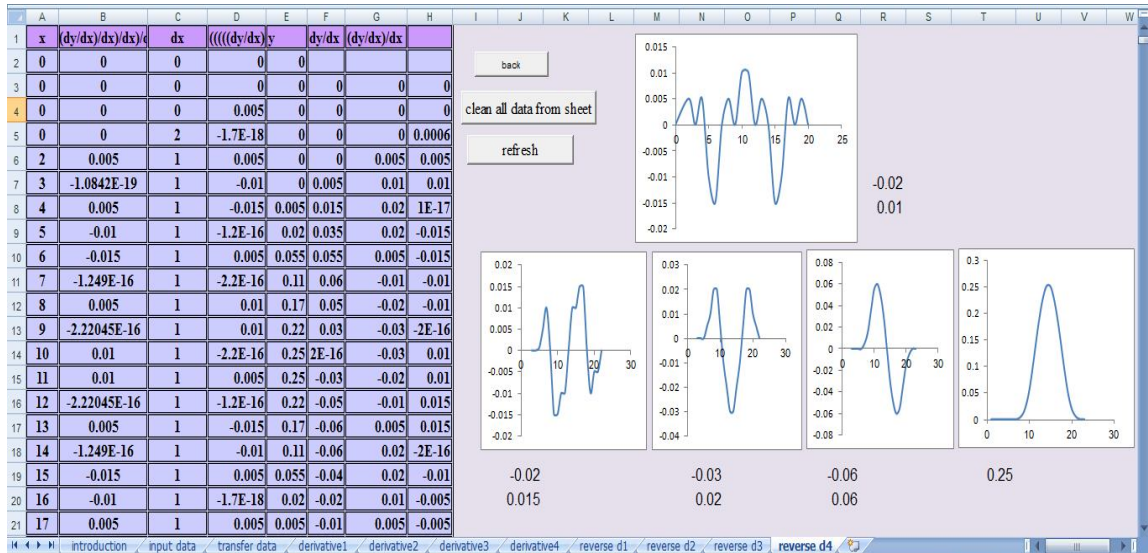
x	(dy/dx)/dx)/dx)/d	dx	(((((dy/dx)	y	dy/dx	(dy/dx)/dx	
0	0	0	0	0			
0	0	0	0	0	0	0	
0	0	0	0.005	0	0	0	0
0	0	2	-1.7E-18	0	0	0	0.0006
2	0.005	1	0.005	0	0	0.005	0.005
3	-1.0842E-19	1	-0.01	0	0.005	0.01	0.01
4	0.005	1	-0.015	0.005	0.015	0.02	1E-17
5	-0.01	1	-1.2E-16	0.02	0.035	0.02	-0.015
6	-0.015	1	0.005	0.055	0.055	0.005	-0.015
7	-1.249E-16	1	-2.2E-16	0.11	0.06	-0.01	-0.01
8	0.005	1	0.01	0.17	0.05	-0.02	-0.01
9	-2.22045E-16	1	0.01	0.22	0.03	-0.03	-2E-16
10	0.01	1	-2.2E-16	0.25	2E-16	-0.03	0.01
11	0.01	1	0.005	0.25	-0.03	-0.02	0.01
12	-2.22045E-16	1	-1.2E-16	0.22	-0.05	-0.01	0.015
13	0.005	1	-0.015	0.17	-0.06	0.005	0.015
14	-1.249E-16	1	-0.01	0.11	-0.06	0.02	-2E-16
15	-0.015	1	0.005	0.055	-0.04	0.02	-0.01
16	-0.01	1	-1.7E-18	0.02	-0.02	0.01	-0.005
17	0.005	1	0.005	0.005	-0.01	0.005	-0.005

Figure 20-Revers d4 sheet that contain data, plot of original peak and back return for forth derivative of experimental values

Conclusion

The proposed program of first, second, third, fourth derivative data and back return of first, second, third, fourth spectrum to zero order. The new program is characterized by a simple and rapid for use. The derivative of data and back return are based on mathematical method. Generally, the new program can be used to derivative and back return for any recorded data.

Acknowledgment

Appendix A

Code of First Order Derivative

First order derivative codes are carried out through use of the following commands:

```
Cells(1, 1) = "x": Cells(1, 2) = "y": Cells(1, 3) = "dx=x2-x1": Cells(1, 4) = "dy=y2-y1":Cells(1, 5) =
"dy/dx"  Cells(1, 6) = "reverse d1": Cells(1, 7) = "y":    i = 2
Do While Not (Cells (i + 1, 1) = Empty) or (Cells (i, 1) = "0")
Cells (i, 3) = Cells (1 + i, 1) - Cells (i, 1):  Cells (i, 4) = Cells (1 + i, 2) - Cells (i, 2): i = i + 1
Loop
For x = 2 To i - 1
If Cells(x, 3) = 0 Then: Cells(x, 5) = Cells(x, 4)
Else Cells(x, 5) = (Cells(x, 4) / Cells(x, 3))
End If
Next x
```

The code used to back return of first derivative to zero order via click on Reverse button to execute the following commands.

```
i = 2
Do While Not (Cells (i, 3) = Empty) or (Cells (i, 3) = "0")
If Cells (i, 3) = 0 Then: Cells (i, 6) = Cells (i, 5)
Else Cells (i, 6) = Cells (i, 3) * Cells (i, 5)
End If
i = i + 1
Loop
Cells (2, 7) = 0
For x = 3 To i - 1
Cells(x, 7) = Cells(x - 1, 6) + Cells(x - 1, 7)
Next x
```

Code of Second Order Derivative
   Second order derivative codes are carried out through use of the following commands:
Cells (1, 5) = "(dy/dx)/dx": Cells(1, 1) = "x": Cells(1, 2) = "y": Cells(1, 3) = "dx=x2-x1"
Cells (1, 4) = "dy": Cells (1, 6) = "reverse d2": Cells (1, 7) = "y": Cells (2, 1) = 0: Cells (2, 2) = 0
Cells (3, 1) = 0: Cells (3, 2) = 0: i = 2
Do While Not (Cells (i + 1, 1) = Empty) Or ((Cells(i + 1, 1) = "0"))
Cells (i, 3) = Cells (1 + i, 1) - Cells (i, 1): Cells (i, 4) = Cells (1 + i, 2) - Cells (i, 2): i = i + 1
Loop
For x = 2 To i - 1
Cells(x, 8) = Cells (1 + x, 4) - Cells(x, 4)
Next x
For x = 2 To i - 1
Cells(x, 4) = Cells(x, 8): Cells(x, 8) = ""
Next x
For x = 2 To i - 1
If Cells(x, 3) = 0 Then Cells(x, 5) = Cells(x, 4)
Else Cells(x, 5) = (Cells(x, 4) / Cells(x, 3)) / Cells(x, 3)
End If
Next x
   The code used to back return of second derivative to zero order via click on Reverse button to execute the following commands.

Cells (1, 6) = "reverse d2": i = 2
Do While Not (Cells (i, 3) = Empty) or ((Cells (i, 3) = "0"))
If (Cells (i, 3) = "0") Then Cells (i, 6) = Cells (i, 5)
Else Cells (i, 6) = Cells(i, 3) * Cells(i, 5) * Cells(i, 3)
End If
i = i + 1
Loop
Cells (2, 7) = "0": Cells (3, 7) = "0": Cells (1, 7) = "y"
For x = 3 to i - 2
Cells(x + 1, 7) = Cells(x - 1, 4) + (2 * Cells(x, 7)) - Cells(x - 1, 7)
Next x
Code of Third Order Derivative
   Third order derivative codes are carried out through use of the following commands:
Cells (1, 1) = "x": Cells (1, 2) = "y": Cells (1, 3) = "dx=x2-x1": Cells (1, 4) = "dy"
Cells (1, 5) = "((dy/dx)/dx)/dx": Cells (1, 7) = "y": Cells(1, 6) = "reverse d3":Cells(2, 1) = "0"
Cells (2, 2) = "0": Cells (3, 1) = "0": Cells (3, 2) = "0": i = 2
Do While Not (Cells (i + 1, 1) = Empty) or ((Cells (i + 1, 1) = "0"))
Cells (i, 3) = Cells (1 + i, 1) - Cells (i, 1): Cells (i, 4) = Cells (1 + i, 2) - Cells (i, 2): i = i + 1
Loop
For x = 2 to i - 1
Cells(x, 8) = Cells (1 + x, 4) - Cells(x, 4)
Next x
For x = 2 to i - 1
Cells(x, 4) = Cells (1 + x, 8) - Cells(x, 8): Cells(x, 8) = ""
Next x
For x = 2 to i - 1
If Cells(x, 3) = 0 Then Cells(x, 5) = Cells(x, 4)
Else Cells(x, 5) = ((Cells(x, 4) / Cells(x, 3)) / Cells(x, 3)) / Cells(x, 3)
End If
Next x
   The code used to back return of third derivative to zero order via click on Reverse button to execute the following commands.
i = 2

```
Do While Not (Cells (i, 3) = Empty) or ((Cells (i, 3) = "0"))
If (Cells (i, 3) = "0") Then Cells (i, 6) = Cells (i, 5)
Else Cells (i, 6) = Cells (i, 5) * Cells (i, 3) * Cells (i, 3) * Cells (i, 3)
End If
i = i + 1
Loop
Cells (2, 7) = "0": Cells (3, 7) = "0": Cells (4, 7) = "0"
For x = 2 to i - 4
Cells(x + 3, 7) = Cells(x, 4) + (3 * Cells(x + 2, 7)) - (3 * Cells(x + 1, 7)) + Cells(x, 7)
Next x
```

Code of Fourth Order Derivative

Fourth order derivative codes are carried out through use of the following commands:

```
Cells (1, 1) = "x": Cells (1, 2) = "y": Cells (1, 3) = "dx=x2-x1": Cells (1, 4) = "dy"
Cells(1, 5) = "((((dy/dx)/dx)/dx)/dx)":Cells(1, 6) = "reverse d4": Cells(1, 7) = "y": Cells(2, 1) = "0"
Cells(2, 2) = "0": Cells(3, 1) = "0": Cells(3, 2) = "0":Cells(4, 1) = "0": Cells(4, 2) = "0": i = 2
Do While Not (Cells (i + 1, 1) = Empty) or ((Cells (i + 1, 1) = "0"))
Cells (i, 3) = Cells (1 + i, 1) - Cells (i, 1): Cells (i, 4) = Cells (1 + i, 2) - Cells (i, 2): i = i + 1
Loop
For x = 2 To i - 1
Cells(x, 8) = Cells (1 + x, 4) - Cells(x, 4)
Next x
For x = 2 To i - 1
Cells(x, 4) = Cells (1 + x, 8) - Cells(x, 8)
Next x
For x = 2 To i - 1
Cells(x, 8) = Cells (1 + x, 4) - Cells(x, 4)
Next x
For x = 2 To i - 1
Cells(x, 4) = Cells(x, 8): Cells(x, 8) = ""
Next x
For x = 2 To i - 1
If Cells(x, 3) = 0 Then Cells(x, 5) = Cells(x, 4)
Else Cells(x, 5) = (((Cells(x, 4) / Cells(x, 3)) / Cells(x, 3)) / Cells(x, 3)) / Cells(x, 3)
 End If Next x
```

The code used to back return of fourth derivative to zero order via click on Reverse button to execute the following commands.

```
i = 2
Do While Not (Cells (i, 3) = Empty) or ((Cells (i, 3) = "0"))
If (Cells (i, 3) = "0") Then Cells (i, 6) = Cells (i, 5)
Else Cells (i, 6) = Cells (i, 5) * Cells (i, 3) * Cells (i, 3) * Cells (i, 3) * Cells (i, 3)
End If
i = i + 1
Loop
Cells (2, 7) = "0": Cells (3, 7) = "0": Cells (4, 7) = "0": Cells (5, 7) = "0"
For x = 2 To i - 5
Cells(x + 4, 7) = Cells(x, 4) + (4 * Cells(x + 3, 7)) - (6 * Cells(x + 2, 7)) + (4 * Cells(x + 1, 7)) -
Cells(x, 7)
Next x
```

Appendix B

Back Return of First Derivative

The code used to back return of first derivative to zero order is carried out through of the following commands:

```
Cells (1, 2) = "(dy/dx)": Cells (1, 3) = "dx": Cells (1, 4) = "(dy/dx)*dx": Cells (1, 5) = "y": i = 2
Do While Not (Cells (i + 1, 1) = Empty)
```

Cells (i, 3) = Cells (1 + i, 1) - Cells (i, 1): i = i + 1
 Loop
i = 2
Do While Not (Cells (i + 1, 1) = Empty)
Cells (i, 4) = Cells (i, 3) * Cells (i, 2): i = i + 1
Loop
Cells (2, 5) = 0
For x = 3 to i
Cells(x, 5) = Cells(x - 1, 4) + Cells(x - 1, 5)
Next x

Back Return of Second Derivative
   The code used to back return of second derivative to zero order is carried out through of the following commands:
Cells (1, 1) = "x": Cells(1, 2) = "(dy/dx)/dx": Cells(1, 3) = "dx": Cells(1, 4) = "(((dy/dx)/dx)*dx)*dx"
Cells (2, 1) = 0: i = 2
Do While Not (Cells (i + 1, 1) = Empty) Or (Cells (i, 1) = "0")
Cells (i, 3) = Cells (1 + i, 1) - Cells(i, 1): i = i + 1
 Loop
Cells (2, 4) = Cells (2, 2): i = 3
Do While Not (Cells (i + 1, 1) = Empty) or (Cells (i, 1) = "0")
Cells (i, 4) = Cells (i, 3) * Cells (i, 2) * Cells (i, 3): i = i + 1
Loop
Cells (2, 5) = "0": Cells (1, 5) = "y": Cells (3, 5) = 0
For x = 3 to i - 1
Cells(x + 1, 5) = Cells(x - 1, 4) + (2 * Cells(x, 5)) - Cells(x - 1, 5)
Next x
For x = 3 to i - 1
Cells(x, 6) = Cells (1 + x, 5) - Cells(x, 5)
Next x
For x = 3 to i
If Cells(x, 3) = 0 Then Cells(x, 6) = Cells(x, 6)
Else Cells(x, 6) = Cells(x, 6) / Cells(x, 3)
End If
Next x

Back Return of Third Derivative
   The code used to back return of third derivative to zero order is carried out through of the following commands:
Cells (1, 1) = "x": Cells (1, 2) = "((dy/dx)/dx)/dx": Cells (1, 3) = "dx"
Cells (2, 1) = "0": Cells (3, 1) = "0": Cells (1, 4) = "(((((dy/dx)/dx)/dx)*dx)*dx)*dx)": i = 2
Do While Not (Cells (i + 1, 1) = Empty) or (Cells (i + 1, 1) = "0")
Cells (i, 3) = Cells (1 + i, 1) - Cells (i, 1): i = i + 1
Loop
Cells (2, 4) = Cells (2, 2): Cells (3, 4) = Cells (3, 2): i = 4
Do While Not (Cells (i + 1, 1) = Empty) or (Cells (i, 1) = "0")
Cells (i, 4) = Cells (i, 3) * Cells (i, 2) * Cells (i, 3) * Cells (i, 3): i = i + 1
Loop
Cells (2, 5) = "0": Cells (3, 5) = "0": Cells (4, 5) = "0": Cells (1, 5) = "y"
For x = 2 to i - 3
Cells(x + 3, 5) = Cells(x, 4) + (3 * Cells(x + 2, 5)) - (3 * Cells(x + 1, 5)) + Cells(x, 5)
Next x
For x = 3 to i - 1
Cells(x, 6) = Cells (1 + x, 5) - Cells(x, 5)
Next x
For x = 3 to i - 2
Cells(x, 7) = Cells (1 + x, 6) - Cells(x, 6)

Next x
For x = 3 to i - 1
If Cells(x, 3) = 0 Then Cells(x, 6) = Cells(x, 6)
Else Cells(x, 6) = Cells(x, 6) / Cells(x, 3)
End If
Next x
For x = 3 to i - 2
If Cells(x, 3) = 0 Then Cells(x, 7) = Cells(x, 7)
Else Cells(x, 7) = (Cells(x, 7) / Cells(x, 3)) / Cells(x, 3)
End If
Next x

Back Return of Fourth Derivative
  The code used to back return of fourth derivative to zero order is carried out through of the following commands:
Cells (1, 1) = "x": Cells (1, 2) = "(((dy/dx)/dx)/dx)/dx": Cells (1, 3) = "dx": Cells (1, 5) = "y"
Cells (2, 1) = "0": Cells (2, 4) = Cells (2, 2): Cells (3, 1) = "0": Cells (3, 4) = Cells (3, 2)
Cells (4, 1) = "0": Cells (4, 4) = Cells (4, 2): i = 2
Do While Not (Cells (i + 1, 1) = Empty) or (Cells (i, 1) = "0")
Cells (i, 3) = Cells (1 + i, 1) - Cells (i, 1): i = i + 1
Loop
Cells (1, 4) = "(((((dy/dx)/dx)/dx)*dx)*dx)*dx*dx": i = 5
Do While Not (Cells (i + 1, 1) = Empty) or (Cells (i, 1) = "0")
Cells (i, 4) = Cells (i, 3) * Cells (i, 2) * Cells (i, 3) * Cells (i, 3) * Cells (i, 3): i = i + 1
Loop
Cells (2, 5) = "0": Cells (3, 5) = "0": Cells (4, 5) = "0": Cells (5, 5) = "0"
For x = 2 to i - 4
Cells(x + 4, 5) = Cells(x, 4) + (4 * Cells(x + 3, 5)) - (6 * Cells(x + 2, 5)) + (4 * Cells(x + 1, 5)) - Cells(x, 5)
Next x
For x = 5 to i - 1
Cells(x, 6) = Cells (1 + x, 5) - Cells(x, 5)
Next x
For x = 3 to i - 2
Cells(x, 7) = Cells (1 + x, 6) - Cells(x, 6)
Next x
For x = 3 to i - 2
Cells(x, 8) = Cells (1 + x, 7) - Cells(x, 7)
Next x
For x = 3 to i
If Cells(x, 3) = 0 Then Cells(x, 6) = Cells(x, 6)
Else Cells(x, 6) = Cells(x, 6) / Cells(x, 3)
End If
Next x
For x = 3 to i - 2
If Cells(x, 3) = 0 Then Cells(x, 7) = Cells(x, 7)
Else Cells(x, 7) = (Cells(x, 7) / Cells(x, 3)) / Cells(x, 3)
End If
Next x
For x = 3 to i - 2
If Cells(x, 3) = 0 Then Cells(x, 8) = Cells(x, 8)
Else Cells(x, 8) = ((Cells(x, 8) / Cells(x, 3)) / Cells(x, 3)) / Cells(x, 3)
End If
Next x

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