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Basic Principles and Analytical Application of Derivative Spectrophotometry

Joanna Karpinska
Institute of Chemistry,
University of Bialystok, Bialystok
Poland

1. Introduction

Analytical methods based on measurements of UV or visible light absorption belong to the most popular and most often used in laboratory practice. Commercially available apparatuses are cheap and easy for operation. Spectrophotometric procedures usually are not time- and labour-consuming. The economical aspects of UV-Vis techniques is worth of emphasize too. It is one of the cheapest technique, so spectrophotometers are basic equipment of every laboratory. The main disadvantage and limitation of the spectrophotometry is its low selectivity. The measurement of absorbance is burden by interferences derived from others components of sample. A recorded UV-Vis spectrum is the sum of absorbances of analyte and matrix. Usually, recorded bands are well-defined but more or less distorted by a background. As the background is called absorbance exhibited by matrix (reagents or accompanied compounds). The problem with specific or nonspecific background can be omitted by measurements versus blank. Such procedure can be successfully applied only in the case of simple samples, which composition is stable and well known or when highly selective reagents are used. An isolation of an analyte from matrix is another solution for increasing the selectivity of assay. But every additional operation introduced into sample preparation procedure extents time and costs of single analysis and increases risk of loss or contamination of the analyte.

One of the simplest method for an increasing a selectivity is derivatisation of spectra. This operation allows to remove spectral interferences and as a consequence leads to increase selectivity of assay. Derivatisation of sets of digital data is well known method of separation useful signals from noised data [1]. Historically, the beginning of derivative spectrophotometry is dated on 1953 when the first analogue spectrophotometer was build by Singleton and Cooler [1]. But the fast development of this technique started in 70-s of twentieth century, when new generation of spectrophotometers controlled by computers were constructed. An apogee of its popularity occurred in 80-s of last century. Nowadays, it is only additional technique, rarely used, though it is fully available as a build-in function in software of modern spectrophotometers. I hope that this work gives some light on derivative spectrophotometry and restores it in some way.

2. Basic theory and properties of derivative spectrophotometry

Derivative spectrophotometry is a technique which is based on derivative spectra of a basic, zero-order spectrum. The results of derivatisation of function described a run of absorbance curve is called the derivative spectrum and can be expressed as:

$$^{n}D_{x,\lambda}=d^{n}A/d\lambda^{n}=f(\lambda) \quad \text{or} \quad ^{n}D_{x,\nu}=d^{n}A/d\nu^{n}=f(\nu)$$

where: n – derivative order, $^{n}D_{x,\lambda}$ or $^{n}D_{x,\nu}$ represents value of n-order derivative of an analyte (x) at analytical wavelength (λ) or at wavelength number (ν), A- absorbance.

Derivative spectrophotometry keeps all features of classical spectrophotometry: Lambert-Beer law and law of additivity.

Lambert-Beer low in its differential form is expressed as:

$$^{n}D=\frac{d^{n}A}{d\lambda^{n}}=\frac{d^{n}\varepsilon}{d\lambda^{n}}\cdot c\cdot l$$

Where ε-molar absorption coefficient ($cm^{-1}mol^{-1}l$) , c – concentration of analyte (mol l^{-1}), l-thickness of solution layer (cm).

Derivative spectrum of **n**-component mixture is a sum of derivative spectra of individual components:

$$^{n}D_{mix}=^{n}D_{1}+^{n}D_{2}+...+^{n}D_{n}$$

A new feature of derivative spectrophotometry is a dependence of derivatisation results on geometrical characteristic of starting, zero-order spectrum. A shape and an intensity of the resulted derivative spectrum depend on half- heights width of peak in basic spectrum:

$$^{n}D=P^{n}A_{max}L^{-1}$$

where P^{n}- polynomial described run of n-derivative curve, n- derivative order, L- width of half- heights of peak of zero-order spectrum.

Due to this property broad zero-order spectra are quenched with generation of higher orders of derivatives while narrow undergo amplification. If the zero-order spectrum possess two bands A and B which differ from their half- heights width ($L_B>L_A$), after a generation of n-order derivative a ratio of derivatives intensity can be expressed as:

$$^{n}D_{A}/^{n}D_{B}=(L_B/L_A)^{n}$$

This dependence leads to increase in selectivity and/or sensitivity of assay. It allows to use for analytical properties a narrow band, overlapped or completely hooded by a broad ones.

The shape of derivative spectrum is more complicated than its parent one (Fig. 1). New maxima and minima appeared as results of derivatisation. The generation of **n-th** order derivative spectrum produces (n+1) new signals: an intense main signal and weaker bands, so called satellite or wings signals. Position of maxima or minima depend on order of derivative. The main extreme of derivative spectra of even order is situated at the same wavelength as maximum in zero-order spectrum, but for 2, 6 and 10-th order it becomes minimum in

derivative spectrum and for 4, 8 and 12-th order it remains as a maximum (Fig. 1). The point of initial maximum converts into the point of inflection in derivative spectra of odd order. A narrowing of new signals is observed during generation of consecutive derivative spectra. This feature leads to narrowing bands and as a consequence to separation of overlapped peaks.

3. Generation of derivative spectra and their properties.

Modern software's controlled spectrophotometers allow not only acquisition and storage of registered spectra. They are equipped in modules enable mathematical operation like addition, subtraction, multiplication as well as derivatisation.

A registered UV-Vis absorption spectrum is a two-dimensional set of points with co-ordinates (λ, A), where λ – wavelength, A- absorbance. Derivative spectra can be obtained by direct calculation of ordinate increment or by fitting a function described a course of spectrum curve and next its derivatisation [1]. Another approach is to find a polynomial representing an absorption curve [1]. A proper form of the polynomial can be found if its all coefficients are known. If long set of n-data is disposed, determination of polynomial coefficients requires to solve **n** equations with **n**-unknowns. This is very hard, laborious job which could be impossible for long sets of data. There are many mathematical approaches simplifying this task [1]. The most popular is Savitzky-Golay algorithm [2] and its modifications [3,4]. Savitzky-Golay algorithm [2] does not analyze a whole set of points but only one exact point and its closest neighbourhood: **m** points from left and **m** points from right of the chosen neighbourhood of central point. A width of analysed set of points is equal **2m+1** and is called a derivatisation window. The coefficients of polynomial are calculated by the least square method for central point and next derivatisation window is moved right by one point and calculations for new central point are repeated. The result of this approach is a set of new points which creates a new – derivative spectrum. Usually the new set of points is shorter by **2m** points in comparison to the parent one. It isn't problem because the recorded spectrum usually is the long set of points and the clipped points are from beginning and end of zero order-spectrum which are useless from analytical point of view. Some improvements of Savitzky-Golay algorithm were done. Originally Savitzky-Golay algorithm was devoted for derivatisation of spectra with uniformly spaced sets of data. Nowadays it can be applied for nonuniformly spaced sequence [3]. There are modification which allow derivatisation without loss of extreme points [4].

The use of Savitzky-Golay algorithm requires optimalisation such parameters as derivative order, polynomial degree, width of derivatisation window and manner how derivative is generated. Analytical usefulness of resulted derivative spectrum depends on proper selection of mentioned parameters. Their selection should be done by taking into account a shape of initial zero-order spectrum and spectral properties of accompanied compounds.

- derivative order

Proper separation of overlapped signals can be achieved if appropriate derivative order is used. Optimal derivative order is a function of signals height, their width at half height and distance between maxima in basic spectrum [5,6]. It is recommended to use low orders if the basic spectrum is a sum of wide bands, while for the spectra consisted of narrow bands – higher orders. Generation of the high order derivative suppress very fast intensity of wide bands and magnify the narrow one[1, 5].

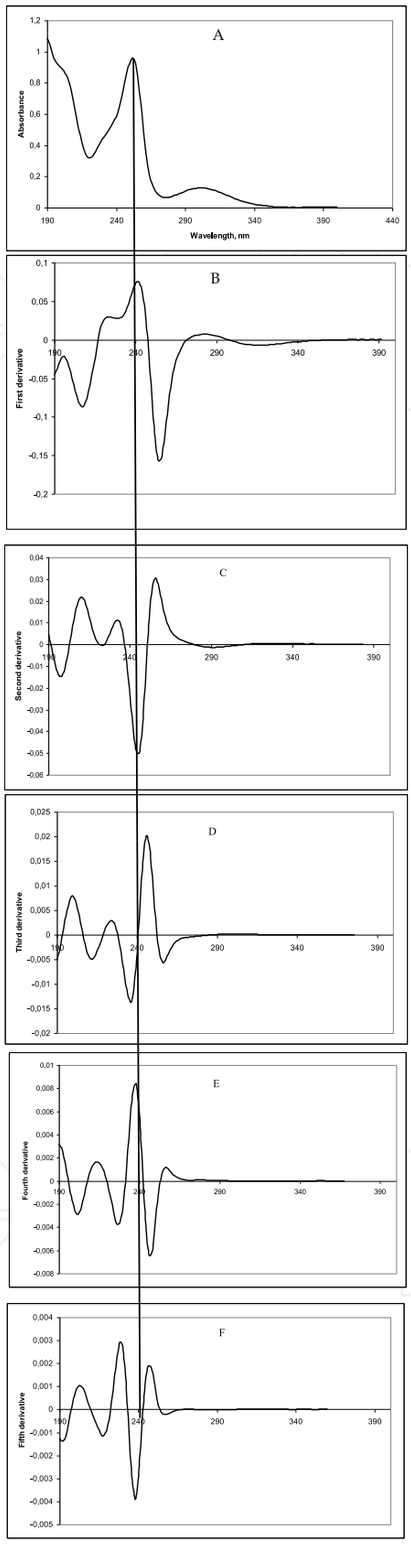


Fig. 1. Zero order (A) and consecutive derivative spectra (B→F) of aqueous solution of promazine hydrochloride (10 ppm); zero order spectrum has been recorded on Hewlett-

Packard HP-8452A diode array spectrophotometer with following working parameters: integration time 1 s, spectral bandwidth 2nm, spectrum scan 0.1 s. Derivative spectra were generated using Savitzky Golay algorithm by PC computer equipped with Excel for Microsoft Windows (Δλ=10 nm, second polynomial degree, derivatives of higher orders were generated by gradual derivatisation of derivative spectra of lower order).

- polynomial degree

The next optimized parameter is the polynomial degree. There is a similar dependence as in the case of derivative order. The high polynomial degrees should be used for spectral curves with sharp and narrow signals. Application of inappropriate polynomial degree gives a distorted derivative spectrum without useful analytical information [5]. In the case of multicomponent analysis, the use of polynomials of different degrees can allow to increase spectral differences of assayed compounds and their selective determination [5].

- width of derivatisation window

A proper selection of this parameter is crucial for quality and quantity of analytical information available in derivative spectrum. Application of the broad derivatisation window gives a smooth averaged derivative spectrum without spectral details. So, the broad derivatisation window is recommended for derivatisation of a zero-order spectra with broad irregular bands with a significant oscillatory constituent [5]. In the case of the basic spectrum with narrow absorption bands the narrow derivatisation window should be used. Otherwise the important analytical information could be lost and resulted maxima of derivative spectrum couldn't correspond to the real one[5].

- manner of generation of derivative spectra

Derivative spectra of higher orders can be obtained using Savitzky-Golay algorithm in two ways: by direct generation of desired derivative spectrum or by gradual generation of first order derivative on consecutive spectra: $^{0}A \xrightarrow{1} \frac{dA}{d\lambda} \xrightarrow{1} \frac{d(dA)}{d(d\lambda)} \xrightarrow{\dots} \dots \frac{d^n A}{d\lambda^n}$

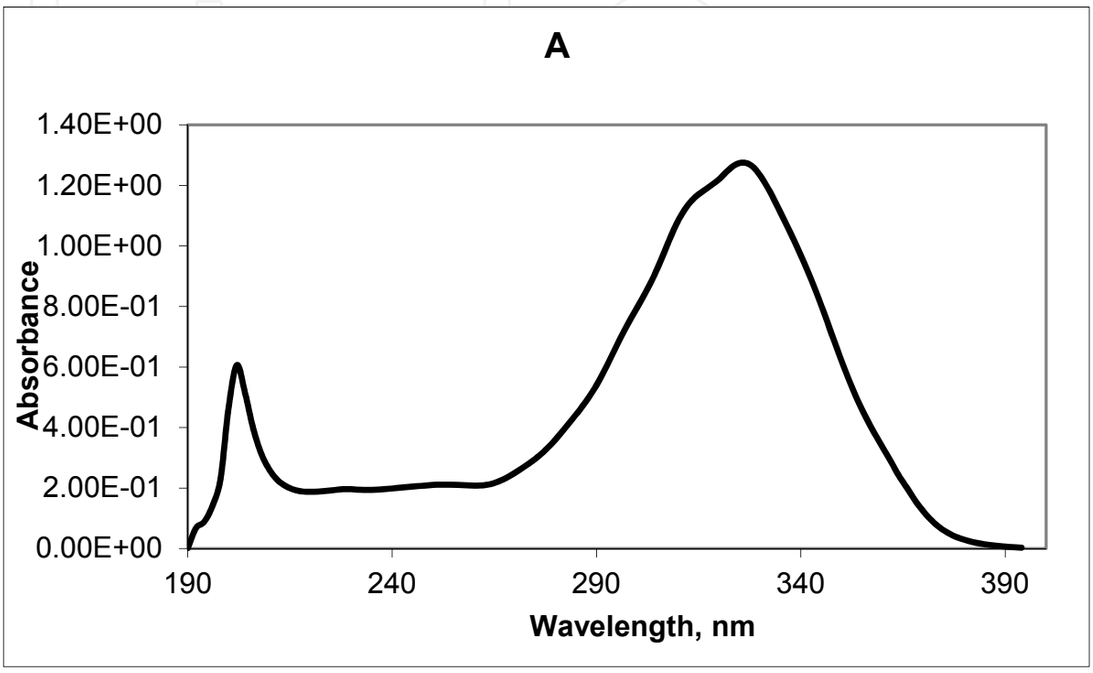
It is very often observed that direct generation of the high-order derivative gives distorted analytically useless spectra (Fig. 2). Selection of derivatisation manner depends on shape of basic spectrum. It is recommended to apply the gradual derivatisation in the case of complicated zero-order spectra. A progressive generation of derivative spectra gives smooth derivative spectrum with advantageous signal-to-noise ratio.

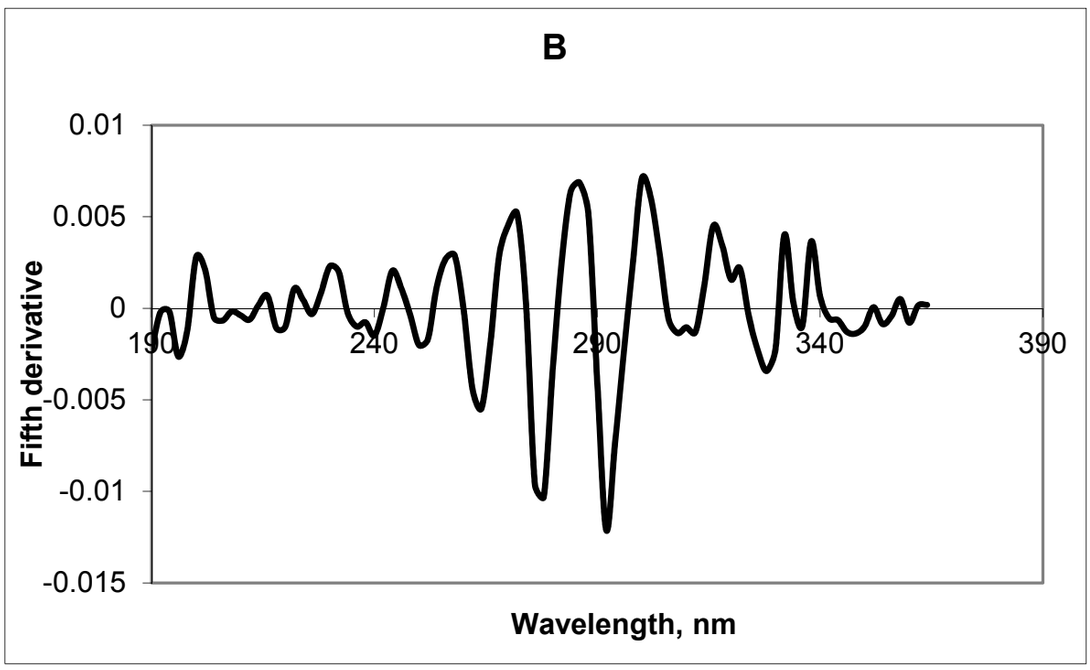
Derivative spectrophotometry can be very useful additional tool which helps to solve some complicated analytical problems. Mathematical processing of spectra is very easy to use as modern spectrophotometers are computer controlled and their software are equipped in derivatisation unit. A proper selection of mathematical parameters gives profits in improved selectivity, sometimes sensitivity and in simplification of analytical procedure.

4. Analytical application of derivative spectrophotometry

Derivative spectrophotometry (DS) has found a wide application in quantitative chemical analysis. As the latest applications have been gathered and described in reviews published previously [8,9], this part is focused on the recent use of DS. Based on scientific literature the following fields of application of derivative spectrophotometry can be distinguished:

a. Multicomponent analysis. This group is the most numerous. The goal of proposed methods is application of DS for determination of one analyte in presence of matrix or for simultaneous assaying of few analytes.
b. Calculation of some physico-chemical constants, e.g. reaction, complexation or binding constants [10].
c. Application for investigation of some processes kinetics[11, 12].





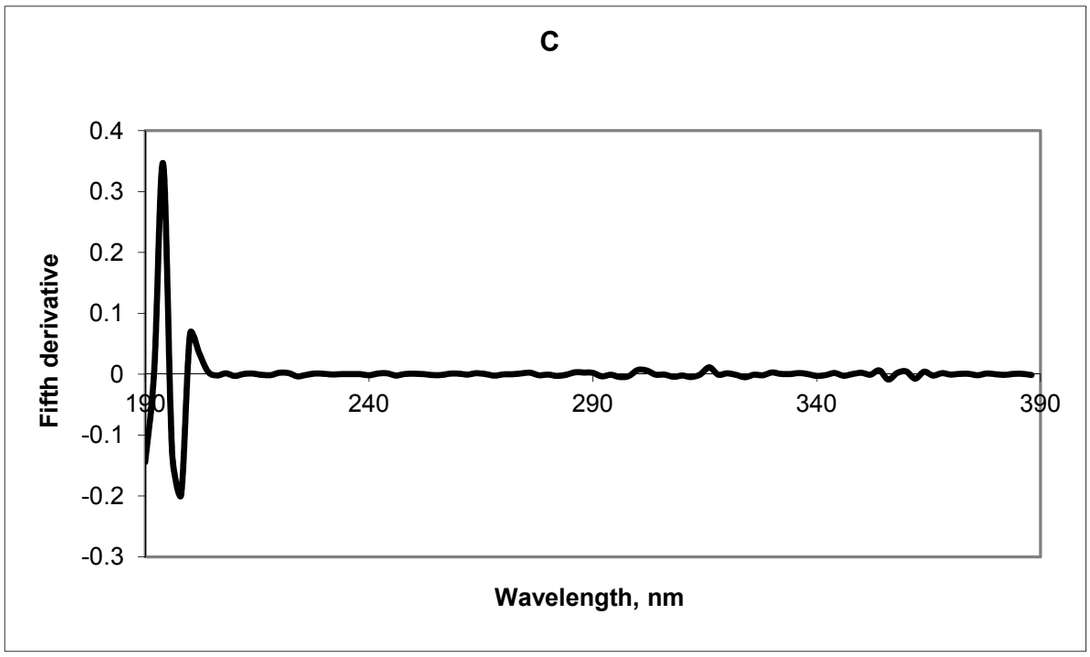


Fig. 2. Zero order (A) and fifth derivative order spectra of ethanolic solution of retinol acetate (10 ppm). Spectrum B has been obtained by gradual derivatisation, spectrum C by direct generation of fifth derivative from zero-order spectrum. Apparatus working conditions: Hewlett-Packard HP-8452A diode array spectrophotometer with following working parameters: integration time 1 s, spectral bandwidth 2nm, spectrum scan 0.1 s. Derivative spectra were generated using Savitzky Golay algorithm by PC computer equipped with Excel for Microsoft Windows ($\Delta\lambda$=14 nm, fourth polynomial degree).

a. Multicomponent analysis

Derivative spectrophotometry (DS) has been mainly used in pharmaceutical analysis for assaying of a main ingredient in a presence of others components or its degradation product. Pharmaceutical samples are characterised by high level of constituents and presence of a relatively simple and stable matrix. The spectral influences of disturbing compounds are easy to remove by derivatisation of spectra. The most numerous procedures based on derivative spectra have been devoted for determination of one components without sample purification. Another field of DS application is the use of it for simultaneous determination of two or more components. As a form of derivative spectrum is more complicated in comparison to its initial zero order, usually derivatives of low orders are employed for analytical purposes. Procedures used DS for pharmaceutical analysis are assembled in Tables 1 and 2.

b. Others applications

Derivative spectrophotometry was applied in different than pharmaceutical analysis areas of analysis. This method was utilised for the determination of amphothericin in various biological samples like plasma, serum, urine and brain tissue [40]. The combination of ratio spectra with their derivatisation allowed to remove spectral interferences caused by a presence of bilirubin in plasma [40].

Compound	Characteristic of the method	Reference
Sertraline	The proposed method is based on reaction of sertraline with chloranilic acid. First derivative spectrophotometry has been evaluated by measuring the derivative signal at 475.72 nm – 588.40 nm (peak to peak amplitude). Calibration graph was established for 5-100 µg mL^{-1} of sertraline	13
Estradiol valerate	The first-order derivative spectra were used for determination of estradiol in tablet. Measurements of derivative were made at 270 nm. The method showed specificity and linearity in the concentration range of 0.20 to 0.40 mg mL^{-1}.	14
Tropicamide	The measurements were carried out at wavelengths of 263.8 and 255.4 nm for third- and fourth-derivative, respectively. The method was found to be linear (r^2> 0.999) in the range of 10-100 µg mL^{-1} for tropicamide in the presence of excipients. The method was applied for analyte determination in eye drops.	15
Nebivolol hydrochloride	Derivative spectrophotometry used for determination of nebivolol in bulk and in preparates.	16
Gemifloxacin mesylate	The proposed methods were based on the reaction of gemifloxacin with chloranilic acid and parachloranil to give highly coloured complexes. The coloured products were quantified spectrophotometrically at 530 nm and 540 nm at zero order, 590 and 610 nm for the first derivative and 630 and 650 nm for second order derivative. Beer's law was obeyed in the concentrations range of 10 to 60 µg mL^{-1}, 5 to25 µg mL^{-1} at zero order, 5 to 25 µg mL^{-1}, 5 to 40 µg mL^{-1} at first order and 2 to 20 µg mL^{-1} and 2 to 14 µg mL^{-1} at second order.	17
Olanzapine	The first derivative values measured at 222 nm and the second derivative values measured at 230 nm (n=6) were used for the quantitative determination of the drug . Calibration graphs were linear in the concentration range of olanzapine using 2-10 µg mL^{-1} for first and second derivative spectrophotometric method.	18
Galanthamine	The 1st derivative zero crossing spectrophotometry was proposed for determination of galanthamine. Absorbance was measured at 277.4 nm. It obeyed Lambert-Beer's law in the range of 30-80 µg mL^{-1}.	19
Doripenon	The first derivative spectrophotometry was used for determination of doripenem in pharmaceuticals in the presence of its degradation products. The Beer low was obeyed in the range (0.42-11.30)x10^{-2} mg L^{-1}.	20
Tropisetron	The first derivative spectra were applied for determination of analyte in the presence of its degradates. The quantification was done by measurement of first-derivative amplitude at 271.9 nm. The obtained results were in a good	21

Compound	Characteristic of the method	Reference
	agreement with those obtained by HPLC and TLC methods.	
Fluphenazine Pernazine Haloperidol Promazine	Derivative spectrophotometry was used for quantification of fluphenazine, pernazine and haloperidol in their preparations. First and second derivative were applied for determination of active ingredients in pharmaceutical preparations.	22
Ezetimibe	First, second and third derivative spectrophotometric methods were proposed and utilised for determination of ezetimibe in pharmaceuticals.	23
Oxybutynin hydrochloride	First derivative of ratio spectra was used for determination of analyte in presence of its degradation product.	24
Ertapenem	First derivative and first derivative of ratio spectra methods were applied for determination of ertapenem in the presence of its degradation product. The analyte was assayed by the first method at 316 nm in the range 4-60 µg mL^{-1}. The second method allowed ertapenem determination at 298 nm and 316 nm in the same concentration range using spectrum of degradant at 28 µg mL^{-1}as a divisor.	25

Table 1. Determination of one component in sample

Compound	Characteristic of the method	Reference
Democlocycline and minocycline	First derivative spectra were used for simultaneous determination of drugs in synthetic mixtures. The linearity in the ranges 10-40 µg mL^{-1} and 10-50 µg mL^{-1} were obeyed for democlocycline and minocycline, respectively. The method was applied for the analysis of these drugs in clinical samples, urine and honey.	26
Rupatadine and montelukast	The quantification was achieved using first-order derivative method. Rupatadine was determined at 273.46 nm, while montelukast at 297.27 nm. The method was applied for determination of both compounds in their combined dosage form.	27
Ambroxol and doxycycline	First derivative of ratio spectra method was applied for simultaneous determination of both analytes in pharmaceutical formulations and in laboratory-made mixtures.	28
Tramadol and ibuprofen	The first-derivative method was proposed for simultaneous determination of both compounds. The measurements of amplitude was done at 230.5 and 280 nm for tramadol (Trama) and ibuprofen (Ibu), respectively. The linearity was obeyed in the rage 5-50 µg mL^{-1} for Trama and 5-100 µg mL^{-1} for Ibu.	29
Sodium rabeprazole and itopride	First derivative of ratio spectra method was applied for simultaneous determination of both analyte. The amplitudes at 231 nm and 260 nm were used for	30

Compound	Characteristic of the method	Reference
hydrochloride	quantification of rabeprazole and itopride, respectively.	
Alprazolam and fluoxetine hydrochloride	Second derivative spectrophotometry (D2) was applied for simultaneous estimation of alprazolam (ALP) and fluoxetine hydrochloride (FXT) in pure powder and formulation. Quantitative determination of the drugs was performed at 232.14 nm and at 225.25 nm for ALP and FXT, respectively. Quantification was achieved over the concentration range 4-14 µg mL^{-1} for both drugs with mean recovery of 99.36 ± 0.84 and 99.60 ± 0.93 % for ALP and FXT, respectively.	31
Drotaverine hydrochloride and mefenamic acid	The second-order derivative spectra were used for simultaneous determination of drotaverine (DRO) and mefenamic acid (MEF). Calibration graphs were constructed over the concentration range of 4-24 µg/mL^{-1} for DRO and MEF. Detection and quantitation limit were 0.4348 and 1.3176 µg/mL^{-1} for DRO and 0.6141and 1.8611 µg/mL^{-1} for MEF. The method was applied for determination of both ingredients in combined dosage forms.	32
Triprolidine hydrochloride and pseudoephedrine hydrochloride	Second derivative spectrophotometric method was proposed for simultaneous determination of pseudoephedrine hydrochloride (PSE) and triprolidine hydrochloride (TRI). The second derivative amplitudes of PSE and TRI were measured at 271 and 321 nm, respectively. The calibration curves were linear in the range of 200 to 1,000 µg mL^{-1} for PSE and 10 to 50 µg $mL^{-1}$for TRI.	33
Clopidogrel bisulphate and aspirin	The method was based on the second-derivative spectra of both ingredients. The amplitude at 254.0 nm was used for clopidogrel bisulphate, while at 216.0 nm for aspirin. The linearity was obeyed in the range 5.0- 30.0 µg mL^{-1} for both compounds.	34
Simvastatin and ezetimibe	The first-order derivative spectrophotometric method was proposed for simultaneous determination of analytes in their mixtures. The measurements were carried out at 219 and 265 nm for simvastatin and ezetimibe respectively. The validation of method was done. The range of application was estimated to be 2-40 µg mL^{-1} for simvastatin in the presence of 10 µg mL^{-1} ezetimibe and 1-20 µg mL^{-1} of ezetimibe in the presence of 20 µg mL^{-1} of simvastatin.	35
Fe(III) and Al(III) ions	The proposed method was based on the first derivative spectra of Al^{3+} and Fe^{3+}complexes with chrome azurol S. The proposed procedure was successfully applied for simultaneous determination of studied ions in standard mixtures, pharmaceuticals and in post-haemodialysis samples.	36

Compound	Characteristic of the method	Reference
Calcium and magnesium ions	The reaction of studied ions with pyrogallol red at presence of Tween 80 was applied. Next the first and second derivative spectra of complexes were applied for quantification of calcium and magnesium in multivitamin preparations, samples of human serum and in drinking water.	37
Copper and palladium	The proposed method utilise the reaction of studied ions with morpholinedithiocarbamate (MDTC). Derivative spectra of generated complexes allowed simultaneous determination of Cu and Pd in pharmaceutical samples, synthetic mixtures, alloys and biological samples.	38
Paracetamol, propiphenazone and caffeine	First to fourth derivative spectra of components were subjected to chemometric analysis (principal component regression, PCR; partial least squares with one dependent variable, PLS-1; three dependent variables, PLS2) and adopted for multicomponent analysis. The third derivative spectra of all ingredients became a basis of quantification method.	39

Table 2. Application of DS for multicomponent analysis

The fourth-derivative spectra of molybdenum complexes of tetramethyldithiocarbamate (tiram) fungicide were used for its quantification in commercial samples and in wheat grains [41]. Atrazine and cyanazine were assayed in food samples by first- derivative spectrophotometry [42]. In order to improve results of assay, the first-derivative spectra of the binary mixture were subjected to chemometric treatment (classical least squares, CLS; principal component regression, PCR and partial least squares, PLS). A combination of first-derivative with PCR and PLS models were applied for determination of both herbicides in biological samples [42]. A first-derivative spectrophotometry was used as a reference method for simultaneous determination Brillant Blue, Sunset Yellow and Tartrazine in food [43].

First derivative of ratio spectra was applied for determination of strontium, magnesium and calcium in Portland cement [44]. The proposed procedure was based on complexation of studied ions with Alizarin Complexone.

As it is mentioned above, derivative spectrophotometry seems to be a very useful tool for physico-chemical studies. It can be applied for investigation of reaction kinetics [11,12], or for determination of chemical reaction constants.

First derivative spectra of levomepromazine (LV) and its sulphoxide were employed for investigation of LV photodegradation [11]. The degradation process of biapenem was monitored by measurement of first-derivative amplitude at 312 nm [12]. The determined rate constants for studied process were in good agreement with those obtained by HPLC method [12]. The second-order derivative spectrophotometric method was used for investigation of solvolytic reaction 2-phenoxypropionate ester of fluocinolone acetonide [45]. The run of process was observed by measurement the second-order amplitude at 274.96 nm corresponded to fluocinolone acetonide. The solvolysis rate constant was calculated using derivative method and compare with those obtained by HPLC methods [45].

An interesting application of derivative spectrophotometry was described by Wu and Zivanovic [46]. They proposed the use of the first derivative spectra for determination of the degree of acetylation of chitin and chitosan. They employed the evaluated procedure for commercial samples.

5. New trends in derivative spectrophotometry

The provided short review shows good and bad sides of derivative spectrophotometry. It has mainly found application in pharmaceutical analysis for control of pharmaceuticals. It gives good results for samples with well defined composition. A main compound usually is present in its commercial forms at a relatively high level, convenient for spectrophotometric determination. An application of derivative spectrophotometry simplified procedure and allows to determine an active compound in presence of matrix (others ingredients, its degradation products) without primary sample preparation.

An analysis of scientific articles shows new trends in the use of derivative spectrophotometry. First direction of development is a combination of derivative spectra with chemometric methods [28, 36, 39, 42]. Procedures based on derivatisation of ratio spectra [24, 25,28, 30, 40, 44, 47] belong to the same group. An interesting modification of derivative spectrophotometric procedure described Eskandari [48]. A fusion of H-point standard addition method with the first derivative of mixture spectra was applied for simultaneous determination palladium and cobalt. The method was applied for their determination in synthetic mixtures and alloys.

The second observed trend is an association of derivatisation with others instrumental methods. Every set of digital data can be subjected derivatisation. So this mathematical approach was applied for data processing with synchronous fluorescence spectroscopy. The second derivative synchronous fluorimetry was used for simultaneous determination of sulpiride and its degradation product [49]. For quantification were used amplitudes of ^2D peaks at 295.5 nm and at 342 nm corresponded to main compound and its degradate, respectively. The method was applied for studies of the kinetics of alkaline degradation of drug.

Kang et al. [50] developed the first derivative synchronous fluorescence method for simultaneous assay of traces of some polycyclic aromatic hydrocarbons in human urine. Proposed method was fast, sensitive, selective and reliable. The results were comparable with those obtained by HPLC method.

Derivative spectrophotometry was applied for resolving and quantification of overlapped peaks in capillary electrophoresis [51]. Derivatisation of electropherogram improved separation of compounds. An elaborated procedure was used for determination of eleven derivatives of benzoic acid.

6. Disadvantageous of derivative spectrophotometry

Specific properties of derivative spectrophotometry can be a source of an additional errors. As it is mentioned previously a shape of derivative spectrum is closely connected with the shape of its parent zero-order spectrum. Small changes in a course of curve describing basic

spectrum are strongly magnified in derivative spectrum. Application of derivative spectrophotometry requires from analyst knowledge about its specific properties. The main disadvantage of derivative spectrophotometry is its poor reproducibility. It is result of strong dependence of derivative spectrum on recording parameters of used spectrophotometer like scan rate, spectral width of beam, integration time and interpoint distance[1, 5, 7]. Zero-order spectra of the same substance obtained on different spectrophotometers can be identical, but derivatisation of them gives different results. The generated derivative spectra can derived in intensity, shape and positions of maxima and minima. So restoration of given literature method requires to use the same type of apparatus with the same working parameters described in an article or reoptimisation parameters of method on an own spectrophotometer.

Optimisation of used working spectrophotometer parameters should be done when a new derivative-spectrophotometric method is elaborated. A construction of some spectrophotometers does not allow to check influence of whole factors, but if more advanced equipment is available it is worth to do.

As a result of derivatisation is closely connected with geometrical features of a zero-order spectrum, it is obvious that a method of spectrum registration is a key-point. The use of broad beams gives the averaged smoothed zero order spectra. Application of narrow beams results in intensification and narrowing of absorption bands. But from the other hands, the narrowing of monochromator' slit increases an effects connected with beams bending on edges of the slit. The edge phenomenon causes additional noises which are recorded with absorbance. So the absorption spectrum recorded with too narrow monochromator' slit can be distorted by high level of noise.

Interpoint distance of registered spectrum is very important parameter. Absorption spectrum obtained by spectrophotometer possess a digital structure which is the result of construction of a monochromator and a manner of registration. Spectra registered with large interpoint distance are averaged, flat without many spectral details.

A level of noise enclosed in zero order spectrum directly influences a quality of generated derivative spectrum. It was proved that spectra registered with low scan rates and long integration times are less biased by noise. This is advantageous if high order derivative are generated [7].

Taking into account above information, it is obvious that reproducibility of method based on derivative spectrophotometry depends on reproducibility of parameters of registration of zero-order spectra. So, adaptation of elaborated in another laboratory derivative spectrophotometric method, requires application the same working parameters as used by authors. But this problem is completely ignored by scientists. Based on analysis of articles concerned on application of derivative spectrophotometry it could be stated that working parameters of spectra registration are very rarely given [8]. There is noticeable lack of standardisation in description of procedures based on derivative spectra. Very often, authors of scientific articles give only information what model of apparatus they used without any details of its working parameters as well as algorithm for derivatisation of spectra. In this case the published procedure can be used only if our laboratory is equipped with the same model of spectrophotometer supplied with the same software. Otherwise verification of literature' method requires reoptimisation, adaptation to our conditions

A geometrical features of derivative spectra can be a source of analytical errors. A course of derivative curve is different than its initial spectrum. A main band gets narrowing but additional satellite bands appear. If basic spectrum of mixture is subjected to derivatisation a resulted derivative spectrum of mixture is a sum of derivative spectra of each individual components. New peaks in the final spectrum can be the result of addition or subtraction, so their intensity undergo amplification or reduction. Very often their positions are shifted in comparison to their position in derivative spectra of individual components. Some analytical information can be lost during derivatisation or new false peaks can be generated. A careful analysis of course of derivative spectra of components and their mixtures at different compositions should be done to avoid such errors. A selection of optimal derivatisation parameters should be make taking into account influence of others components on intensity of derivative peaks of determined analyte. This procedure seems to be time- and labour-consuming but gives good results. Properly done selection of mathematical parameters of derivatisation and instrumental parameters of spectral analysis allows to elaborate selective method of determination and leads to minimise errors connected with features of derivative spectra.

7. Conclusions

Nowadays, derivative spectrophotometry is fully available with software's controlling modern spectrophotometers. Analysts receive an elegant tool which allows extraction of analytically useful information from spectra. An understanding of specific features of this technique and its proper utilisation leads to simplification of procedure and to increase a selectivity of assay.

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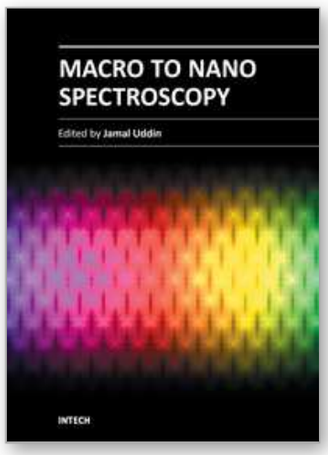

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In the last few decades, Spectroscopy and its application dramatically diverted science in the direction of brand new era. This book reports on recent progress in spectroscopic technologies, theory and applications of advanced spectroscopy. In this book, we (INTECH publisher, editor and authors) have invested a lot of effort to include 20 most advanced spectroscopy chapters. We would like to invite all spectroscopy scientists to read and share the knowledge and contents of this book. The textbook is written by international scientists with expertise in Chemistry, Biochemistry, Physics, Biology and Nanotechnology many of which are active in research. We hope that the textbook will enhance the knowledge of scientists in the complexities of some spectroscopic approaches; it will stimulate both professionals and students to dedicate part of their future research in understanding relevant mechanisms and applications of chemistry, physics and material sciences.

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