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Derivative spectrometry method for chemical analysis: A review

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Abstract

Various aspects of application of derivative spectrophotometry in chemical analysis and in investigations of equilibria and kinetics of reactions are scrutinized. The presented paper provides useful information about state-of-the-art and possibilities offered by derivative spectrophotometry in pharmaceutical, clinical or environmental fields of analysis.

Keywords: Derivative spectrophotometry; Multicomponent determinations; Chemical analysis; Internal standard method; Solid phase spectrophotometry; Reaction equilibria; Reaction kinetics

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INTRODUCTION

Derivative spectrophotometry (DS) is one of the advanced modern spectrophotometric techniques. It is based on so called derivative spectra [1] which are generated from parent zero-order ones. The derivatisation [2] of zero-order spectrum can lead to separation of overlapped signals, elimination of background caused by presence of other compounds in a sample. The mentioned properties can allow quantification of one or few analytes without initial separation or purification. Nowadays, this technique becomes very useful, additional tool which helps to resolve various analytical problems. It has found application in many fields of analysis, especially in pharmaceutical, clinical and biochemical as well as in inorganic or organic analysis. The aim of the presented paper is to review the recent applications and achievements of derivative spectrophotometry in chemical analysis. As the theoretical basic principles and the latest applications were described in monographs [3,4] and articles [5–7] published previously, this paper is focused on the newest achievements and applications described since 1995. Based on the scientific literature the following trends in applications of derivative spectrophotometry can be distinguished:

• Multicomponent analysis- This group is the most numerous among others applications of DS. It is consisted of methods of determination one or few analytes in complicated matrix. There are procedures which lead to increased selectivity, sensitivity and/or accuracy of assays.
• Determination of reaction equilibria and calculation of physico-chemical constants, e.g. complexation or binding constants.
• Investigations of reaction kinetics.

Obtaining Derivative Spectra:
Derivative spectra can be obtained by optical, electronic, or mathematical methods. The main optical technique is wavelength modulation, where the wavelength of incident light is rapidly modulated over a narrow wavelength range by an electromechanical device. The first and second derivatives may be generated using this technique. To use mathematical techniques the spectrum is first digitized with the sampling interval of $\Delta\lambda$. The size of $\Delta\lambda$ depends on the natural bandwidth of the bands being processed and of the bandwidth of the instrument used to generate the data. An advantage of this method is that it can be used to smooth the data.

Features and Applications
Derivative Spectra often yield a characteristic profile where subtle changes of gradient and curvature in the normal (zero order) spectrum are observed as distinctive bipolar functions. The first derivative of an absorption spectrum represent the gradient at all points of the spectrum and can be used to locate hidden peaks, since $dA/d\lambda = 0$ at peak maxima. However second order and higher even order derivative are potentially more useful in analysis.

The even order derivative are bipolar functions of altering sign at the centroid (i.e. negative for 2^{nd} , positive for 4^{th} , etc), whose position coincides with that of the original peak maximum. To this extent, even derivative spectra bear a similarity to the original spectrum, although the presence of satellite peaks flanking the centroid adds a degree of complexity to the derivative profile.

A key feature of the derivative spectroscopy is that the derivative centroid peak width of a Gaussian peak decreases to 53 %, 41% and 34% of the original peak width in the 2^{nd}, 4^{th} and 6^{th} order derivative respectively. These can increase the resolution of overlapping peaks.

A common, unwanted effect in the spectroscopy is baseline shift. This may arise either from instrument or sample handling effects. Because the first derivative of a constant absorbance offset is zero, using the first derivative spectra eliminates such baseline shifts and improves the accuracy of quantification.

2. Multicomponent analysis
Derivative spectrophotometry has found wide application in analysis of multicomponent samples. This technique is based on the use of derivative spectra resulted from derivatisation of zero-order spectra of UV-Vis absorption. The obtained derivative spectra yield a more characteristic profile in comparison to the parent one: new maxima and minima appeared and points where derivative spectra crosses the *X*-axis. Derivative spectrophotometry keeps all laws of classical spectrophotometry, e.g. dependence of derivative value on analyte concentration and additivity law. The Beer law, in derivative form, assumes the following form:

$$\frac{Dn}{d n\varepsilon} = \frac{dnA}{d\lambda n} \cdot cl$$

Where D is the value of derivative of n-order at wavelength λ, ε the molar absorption coefficient, l is the thickness of absorption layer.

As the additivity law is kept, the derivative spectrum of mixture is the sum of derivative spectra of each individual component:

$$D^{n}_{mix} = D^{n}_{1} + D^{n}_{2} + \cdots + D^{n}_{n}$$

where the value of n-order derivative of mixture at analytical wavelength, D^{n}_{1}, D^{n}_{2}, . .. D^{n}_{x} are the values of n-order derivative at analytical wavelength of 1st, 2nd, . . . , xth component of mixture.

The features mentioned above allow the determination of several components (*x*) in a mixture by measuring the amplitude of derivative spectrum of mixture at several (minimum *x*) wavelengths. If the measurements height of derivative peak of analyte is performed at those wavelengths at which spectra of other components undergo zeroing, the measured amplitude is proportional only to concentration of assayed compounds. This approach of quantitative determination is called "zero-crossing technique". It allows simultaneous determination of a few analytes in a sample.

The additional property of derivative spectrophotometry, as compared with the classical method, is the dependence of derivatisation result on the shape of zero-order spectra. Signals of analyte which are in basic spectrum narrow, undergo amplification, whereas broad even intense zero-order signals undergo flattening and in the end derivatisation leads to their zeroing. This property allows eliminating the influence of the background and increases selectivity of determination.

The discussed above properties of derivative spectrophotometry technique are valuable from analytical point of view. The derivative technique has found wide application in resolving these analytical problems where analyte is accompanied by constant matrix, mainly in analysis of pharmaceuticals, cosmetics or food additivities.

2.1. Determination of organic compounds

2.1.1. Applications in pharmaceutical analysis

Pharmaceutical samples are characterized by relatively high level of analyte, known and constant composition of accompanied matrix. These properties caused that derivative spectrophotometry are intensely exploited in pharmaceutical analysis. This technique is mainly used for determination of the main component of pharmaceuticals in the presence of drug additivities. It is also used for investigating the stability of pharmaceuticals or for determination of decomposition products. It is worth noticing that British Pharmacopoeia [8] recommends the use of second derivative spectra for determination of traces of benzene in 96% ethanol. The applications in pharmaceutical analysis are assembled in Tables 1 and 2.

It can be concluded, based on the analysis of procedures presented in Tables 1 and 2, that the most methods are devoted to the determination of one main compound in the presence of matrix or the simultaneous determination of two analytes in their binary mixtures. As derivatisation of zero-order spectrum, produces (*n*+1) new peaks (where *n*-derivative order), the resulted

derivative spectrum is more complex [1,2] then the parent-one. If the basic spectrum exhibits *m* maxima, the number of new extremes in the generated derivative spectrum is multiplied by *m*. The obtained derivative spectrum becomes to complicated. This property causes that the numbers of methods applied derivative spectrophotometry for resolving of ternary, quaternary or more complex mixtures are limited. Uzgur et al. [35] have used the second derivative method for determination of B6, B1 and B12 vitamins in their ternary mixtures. The method was applied to the simultaneous determination of mentioned vitamins in commercial preparations. The second derivative spectra were employed for simultaneous determination of some analgetics: acetaminophen, caffeine, propyphenazone and paracetamol [36]. The elaborated method was used for quantitative analysis of three-component tablets. The fourth derivative spectrophotometric method [37] was proposed for simultaneous determination of caffeine, acetaminophen and prophyphenazone in tablet formulations. The second derivative combined with PLS method was applied for assay of indomethacin, acemethacin, piroxicam and tenoxicam in their quaternary mixtures [38]. The ternary mixture of some phenothiazines (promethazine, chlorpromazine and perphenazine) [39] was resolved by conventional and derivative spectrophotometry in combination with PLS regression, singular values decomposition based PLS and artificial neutral network (ANN). The applicability of derivative spectrophotometry for simultaneous determination of retinol acetate, tocopherol acetate and coenzyme Q10 in pharmaceuticals was discussed [40] recently.

Table 1. Single component determinations of analyte in pharmaceuticals[9-22]

Analyte	Characteristic of method
Aceclofenac	Third derivative at 242 nm was used for determination of aceclofenac in presence of its main degradation product diclofenac
Acrivastine	Applied to the determination in capsules and in urine samples
Acyclovir, Diloxanide furoate	The second derivatives spectrophotometry was used for the determination of acyclovir in presence of its main impurity guanine and the third derivative for determination of diloxanide furoate in the presence of diloxanide (its degradation product)
Amlodipine	Third order of derivative was applied for direct determination of amlodipine in presence of its photodegradation product
Astemizole	Second derivative, applied to the determination in commercial formulations
Benazepril hydrochloride	Derivative spectrophotometry used to remove the interference due to formulation matrix; the method was applied to determination in its single and multicomponent dosage forms
Cephalexin	The method allows determination of cephalexin in the range 10^{-5} to 1.8 × 10^{-4}M as the intact cephalexin or as its acid degradation product
Cetrizine dihydrochloride	The applicability of first, second, third and fourth order of derivative were studied. The elaborated methods allowed determination of analyte in the concentration range 7.5–22.5 _gml^{-1}
Cinchocaine hydrochloride	Cinchocaine HCl was determined in the presence of its degradation product by measurement of its first derivative amplitude at 333.5 nm
Cinoxacin	The values of amplitude of the second-order derivative spectra between 268–284 nm were used. The calibration graph was linear in the

	concentration range 3.0–13.0 $\mu g ml^{-1}$
Cisapride	1D values at 264, 300 nm and 2D values at 276, 290 and amplitude 276–290 nm were used, the linearity was in the range 2–12 $\mu g ml^{-1}$. The methods were applied to the assay of commercial tablets and suspensions
Coenzyme Q10	First derivative, the Beer's law was obeyed in range 0.25–10 ppm; the method was applied for determination of main compound in pharmaceuticals
Cimetidine	Second derivative at 217.5 nm; the method allows to determine 2–10 $\mu g ml^{-1}$ of analyte in pharmaceuticals
Fluconazole	The value of the second derivative at 274 nm; the linearity in the range 4×10^{-4} to 1.5×10^{-3} M; the method was applied to determination in capsules

Table 2. Simultaneous determination of two compounds in a pharmaceutical sample[23-34]

Analyte	Characteristic of method
Acrivastine and pseudoephedrine hydrochloride	The measurements of the second derivative at 288 nm for acrivastine and at 270.2 nm for pseudoephedrine hydrochloride
Adrenaline and noradrenaline	The values of first derivative at 394 and 342 nm were used for simultaneous determination of adrenaline and noradrenaline, respectively. The method was applied in combination with flow system
Amiloride and furosemide	The amplitudes of the first derivative at 241.4 and 343.6 nm were used for amiloride and furosemide, respectively. The method allowed the simultaneous assay in the concentration range 6.9×10^{-8} to 1.6×10^{-4} M for amiloride and 6.9×10^{-8} to 0.8×10^{-4} M for furosemide
Amitryptyline and chlorpromazine hydrochlorides	The value of the first derivative at 254 nm was used for assay of amitryptyline in thepresence of chlorpromazine, while the third derivative at 260 nm was used for the determination of chlorpromazine in the presence of the first compound
Amoxicillin and bromohexine hydrochloride	The amplitudes of first derivative at 278.8 and 326.2 were used for detrmination of amoxicillin and bromohexine, respectively
Analgin and adamon	Analgin and adamon were determined in the form of ion-pair with thymol blue. For quantification were used the values of the first derivative at 600 and 310.5 nm
Analgin and hyoscine *N*-butyl bromide	Determination was performed using the measurements of the first derivative at 291.8 and 219.8 nm for analgin and hyoscine *N*-butyl bromide, respectively
Atenolol and nifedipine	The first derivative spectrophotometry at 276 nm for atenolol and at 340 nm for nifedipine
Azomicine and ornidazole	Azomicine and ornidazole were determined using the value of the first derivative spectra at 318.4 nm for azomicine and 324.4 nm for

	ornidazole
Cephalothin and cefoxitin	The both compounds were assayed in the range 4–32 μgml^{-1} by measurements the value of the first derivative at 235 nm for cephalothin and 236.75 nm for cefoxitin
Cefatoxime sodium and cefadroxil monohydrate	The values of second derivative amplitudes at 257 and 279 nm for cefatoxime and at 242 and 269 nm for cefadroxil were used for simultaneous determination of studied cephalosporins
Cilazapril and hydrochlorothiazide	Simultaneous determination was performed using measurements of first derivative at 242.8 and 282.8 nm for cilazapril and hydrochlorothiazide, respectively

2.1.2. Analysis of clinical and biological samples

Clinical samples are characterized by a very complicated matrix and low level of analyte. The sensitivity and selectivity of spectrophotometric measurements usually is to low for the direct use for clinical purposes. The assays of clinical interest with spectrophotometric determination require intensive pretreatment steps involving extraction, enrichment and cleaning operations, using solvent or solid phase extraction [41]. In spite of all these difficulties, there are some articles dealing with application of derivative spectrophotometric determination in clinical analysis.

Floctafenine and its main metabolite floctafenic acid were simultaneously determined by spectrofluorescence method. As their spectra were overlapped, for separation of the signals and for diminishing of the influence of the matrix, the first derivative of fluorescence spectra was applied. This approach allowed to determine 0.4–2.0 and 3.0 –10.0 gml^{-1} of floctafenine and floctafenic acid in plasma samples. The first derivative spectrophotometry was used for simultaneous determination of cefuroxime and cefadroxil in urine. The measurements of third-order derivative spectra at 402 nm were proposed for assay of amphoteracin-B [42] in serum and urine. The method allowed determination of amphoteracin down to 30 ng ml^{-1} in natural samples.

The second-order derivative method was proposed for the direct determination of pefloxacin in serum. The detection limit of determination was 15 ng of analyte in 1 ml of serum. The same group of authors has proposed derivative spectrophotometric method for determination of fleroxacin in human serum. Gazy has applied the first and the second derivative method for assay of guanoxan sulfate in pharmaceutical formulations as well as in spiked human urine and serum. The method elaborated for determination of some cephalosporin antibiotics based on the first derivative spectra was used for their determination in physiological serum and glucose physiological serum. The mentioned previously derivative method concerned on determination of acrivastine was applied for its assay in urine samples. The first derivative method was proposed for determination of triamterene and leucovorin in biological fluids: urine and serum samples [43]. The mentioned method is very efficient and characterized by high value of recovery (97%).

2.1.3. Analysis of food, cosmetics colorants and dyes

Derivative spectrophotometric methods have found applications in analysis of food or cosmetics. In these analysis, the mainly determined compounds are colorants or preservatives. The analysis of these substances in food or cosmetics samples as well as clinical analysis, usually required the isolation from accompanied matrix but is easier due to their relatively high concentration.

2.1.4. Applications in environmental analysis

The derivative spectrophotometry technique has found practical application in environmental analysis. This technique is quite intensively used for determination of various pesticides in groundwater, soil or plant samples [44–51]. The combination of derivative spectrophotometry with PLS-calibration method [47–49] and the use of solid phase extraction [46] for sample preparation has allowed the assay of trace levels of compounds. The simple, sensitive and highly selective method utilized the fourth derivative spectra [50] was proposed for determination of ferbam (iron(III) dimethyldithiocarbamate) fungicide in fortified samples of wheat grains and in commercial preparation. There is very interesting combination of derivative spectrophotometry with HPLC-DAD technique [49, 50 53]. These applications are based on analysis of spectra of assayed compounds recorded by DAD detector. Such approach was used for analysis of some insecticides [153], phenols [52] and some aromatic amines (*o*- and *m*-toluidyne, *m*and *p*-toluidyne and *o*- and *m*-phenylenediamine) [53].

2.1.5. Miscellaneous applications

Derivative spectrophotometry has found application in various, very often difficult to classify, fields of analysis. Among others procedures could be distinguished the applications for analysis of amino acids compositions [54,55] obtained by hydrolysis of proteins. The UV-spectra of post-reaction mixture were recorded and generated derivative spectra. The result of spectral analysis was used for identification of peptides composition. The derivative spectrophotometry [56] was applied for resolving of binary mixtures of some flavonolsand a flavon: quercetin–kaempferol, quercetin–myricetinand quercetin–luteolin. The developed UV-derivative method in case of mixture quercetin–luteolin, was employed as a complementary technique to a HPLC system, which did not separate these compounds. The trace of 5-*n*-alkyl-1,2,3,4-tetrahydronaphtalene sulfonate (DTHNS) in *n*-nonane [57] was assayed by derivative spectrophotometric technique. The proposed procedure was applicable for determination of impurity in the concentrations range 2–200 ppm. The derivative spectrophotometric technique was used for the dating of historical textiles [58]. The method was based on spectral analysis of dyes extracted from textile samples. Another interesting application of derivative spectrophotometry is its use for determination of antioxidants (2-mercaptobenz-imidazole [59] and phenyl-_ naphtylamine in rubber and polymeric materials.

2.2. Applications in inorganic analysis

The derivative spectrophotometry is intensely exploited in inorganic analysis. Usually the proposed spectrophotometric procedures for determination of cations or anions contents in environmental (soil, waters), food or clinical as well as in industrial samples are based on complexation reactions with chromogenic agents. Inorganic analytes, are usually accompanied by a complicated matrix—environmental or clinical. Probably, this is the reason for a very limited number of methods referring to simultaneous determination of ions in ternary, quaternary or in more complicated mixtures. Three rare earth elements: dysprosium, holmium and erbium

were determined by the second derivative spectrophotometry [60]. Bobrowska-Grzesiuk at al. have discussed the applicability of derivative spectrophotometry for quantitative analysis of binary, ternary and quaternary mixtures of divalent ions of cobalt, copper, lead, manganese, nickel, zinc and iron using PAR as chromogenic reagent. The authors stated that the use of the first derivative spectra allowed a simultaneous determination of analytes in the binary mixtures except of Cu(II) or Co(II) in presence of Fe(II), while the second and the third derivative spectra enabled to determine only one constituent in ternary and quaternary mixtures. The same reagent was proposed as chromogenic agent for simultaneous determination of zinc(II), manganese(II) and iron(II) in their ternary mixtures [61]. The spectrum of mixture of PAR complexes was recorded and spectral interferences were eliminated by generation of consecutive derivative spectra. Zinc was determined by measurement of the amplitude of the first derivative spectra at 499.0 nm, the determination of manganese required the third derivative at 539.5 nm and iron was assayed by reading the value at 537.0 nm of the second derivative. The proposed method was applied for assay of studied ions in multivitamins preparation.

3. Internal standard method

The use of internal standard for quantification of analyte allows to minimize the lost of studied compound during sample preparation process. This approach is commonly used with various chromatographic techniques for resolving complicated analytical problems. The application of this method led to an increase in the precision and accuracy of assays. The use of internal standard method in chromatographic estimations is quite easy, the combination of it with spectrophotometric analysis is complicated due to low selectivity of spectrophotometric measurements. The obtained results could be reliable only when the absorption spectrum of a compound used as internal standard displays negligible absorption in the wavelength range of intensive absorption of analyte and high absorption in the wavelength range where absorption of analyte is equal to zero. This condition prevents the widespread application of internal standard technique into spectrophotometric assays. The combination of the derivative spectrophotometry with internal standard method allows the separation of analyte and internal standard signals and uses them for quantification. The main advantage of such procedure is its simplicity and lower cost than the chromatographic method.

4. Application of derivative spectrophotometry for kinetic studies

Investigations of reaction kinetics are usually performed by monitoring of the changes in amounts of reagent or products in reaction solution. For this purpose there are required selective methods which enable the determination of one compound in the presence of others (parent reagents or products). Derivative UV-Vis spectrophotometry is one of technique which allows for the observation of reaction kinetics without separation of each compound and spectra can be recorded in the fixed periods of time without disturbing the run of reaction. The recent applications of derivative spectrophotometry in kinetic studies are presented in Table 3.

Table 3: The applications of derivative spectrophotometry for kinetic studies [62-67]

Investigated reaction	Characteristic of the method
Stability of (dimethylamino)-ethylo-chloro, *p*-dimethyl amino (sulphamoxylphenoxy)-acetate hydrochloride in aqueous solution	The amplitude of the third derivative spectra at 246.2 nm
Degradation of indomethacin in alkaline solution	The monitoring of the degradation product using its four derivative spectra at 360 nm
Acidic hydrolysis of lorazepam	The kinetics of hydrolysis was observed by monitoring of the main degradation product. It was assayed using the first derivative values at 231.6 nm
Photochemical degradation of nisoldipine	The first and the second derivative spectrophotometric methods at 285 and 291 nm were proposed for investigation of photodegradation reaction
Acidic hydrolysis of nordazepam	The amplitude between 244–251 nm of the fourth-order derivative spectra of nordazepam were used
Decomposition of omeprazole in aqueous solution	The values at 313 nm of the first derivative spectra of omeprazole were used
The photo degradation of thioridazine	The second derivative spectra at 280 nm were used for examination of kinetics of degradation of thioridazine

5. Disadvantages of derivative spectrophotometry

As the final comments, the limitations of derivative spectrophotometric technique are discussed. The main disadvantage of this technique is its low reproducibility. This is caused by the following reasons:

• Dependence on instrumental parameters,
• Non-robust properties of the derivatisation parameters,
• lack of homogeneous protocol of optimization the parameters of the method and presentation of results.

The main disadvantage of this technique is its dependence on instrumental parameters like speed of scan and the slit width [5]. The instrumental conditions of recording parent zero-order spectrum have strong influence on the shape and intensity of its derivative generations. The acquired spectrum is more or less distorted by instrumental noises and as the consequence the derivative spectrum is distorted too. The derivatisation can amplify the noise signals in the resulted curves.

Another disadvantage of derivative spectrophotometry is non-robust character of the selected parameters of elaborated methods. They can be used only for the system for which they were chosen. As the analytical use of derivative spectrophotometry is based on the analysis of the

derivative spectra, the introduction of additional compound into the studied object changes the shape of derivatisation results. The selected parameters of derivative spectrophotometric method are applicable only for the studied system and every change in its composition require the re-optimization and selection of new parameters of derivatisation.

CONCLUSION

Derivative spectrophotometry is the well established analytical technique with a number of possible applications in organic as well as in inorganic field of analysis. In the presented paper there are gathered and shown in the concise and easy-to-read form recent achievements and new trends of this instrumental technique of analysis. The observed intense use of this spectrophotometric method is a consequence of the widespread combination of acquired apparatus with computer control. As derivatisation function is a part of built-in acquisition program, the selection of optimal parameters can be done automatically. An easy access to modern generation of spectrophotometers resulted in the extensive number of applications of derivative technique in chemical analysis. Based on the presented review, it is worth to emphasize the innovatory combination of this technique with fluorimetry, liquid chromatography flow analysis or IR-spectrometry. As derivatisation separates signals hidden, n zero-order spectrum, this property allows to join this technique with internal standard (IS) method. Until now, this approach was usually used with chromatographic techniques of quantification. The derivatisation of zero-order spectra of sample containing analyte and internal standard gives the opportunity to improve the precision of spectrophotometric determination and minimize the influence of sample preparation operations.

Derivative spectrophotometry as a technique which allows to non-invasive extraction of information included in basic spectrum appears to be a very valuable tool in physico-chemical studies. It permits to investigate the reaction equilibria or kinetics without disturbing their run.

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