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Review

Derivative spectrophotometry—recent applications and directions of developments

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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 scrutinised. 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

1. 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.

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,

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in derivative form, assumes the following form:

$$D^n = \frac{\mathrm{d}^n A}{\mathrm{d}\lambda^n} = \frac{\mathrm{d}^n \varepsilon}{\mathrm{d}\lambda^n} cl$$

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:

$$D^n_{\mathrm{mix}} = D^n_1 + D^n_2 + \cdots + D^n_n$$

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 to eliminate 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 characterised 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. [112] 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 [113]. The elaborated method was used for quantitative analysis of three-component tablets. The fourth derivative spectrophotometric method [114] 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 [115]. The ternary mixture of some phenothiazines (promethazine, chlorpromazine and perphenazine) [116] 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 [117] recently. The spectral properties of Vitamin A, caused that only this compound can be assayed in presence of others studied compounds. It was proved that others examined vitamins can be quantified only in binary (Q + A, Q + E, E + A) mixtures.

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 [118]. 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 [108] were simultaneously determined by spectrofluorescence

Table 1
Single component determinations of analyte in pharmaceuticals

Analyte	Characteristic of method	Reference
Aceclofenac	Third derivative at 242 nm was used for determination of aceclofenac in presence of its main degradation product diclofenac	[9]
	The amplitude of third derivative spectra at 283 nm	[10]
Acrivastine	Applied to the determination in capsules and in urine samples	[11]
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)	[12]
Amlodipine	Third order of derivative was applied for direct determination of amlodipine in presence of its photodegradation product	[13]
Astemizole	Second derivative, applied to the determination in commercial formulations	[14]
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	[15]
Ceftazidime (I), cefuroxime sodium (II), cefotaxime sodium (III)	First derivative at 268.6, 306, and 228.6 nm for I, II and III, respectively were used for determination of these cephalosporines in the presence of their degradation products; the methods were applied for determination of these compounds in their commercial products	[16]
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	[17]
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 $\mu g\,ml^{-1}$	[18]
Cinchocaine hydrochloride	Cinchocaine HCl was determined in the presence of its degradation product by measurement of its first derivative amplitude at 333.5 nm	[19]
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 $\mu g\,ml^{-1}$	[20]
Ciprofloxacin, norfloxacin, ofloxacin	Three of fluorinated quinolone antibiotics were determined individually in their pharmaceuticals. The amplitude of the fourth derivative at 320 nm was used for assay of ciprofloxacin. The best results for norfloxacin were obtained when the value of fourth derivative at 250 nm were used. For assay of ofloxacin the measurement of second derivative high at 338.8 nm were selected. The methods were applied for the assay of active compounds in their pharmaceuticals	[21]
Cisapride	^{1}D values at 264, 300 nm and ^{2}D 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	[22]
Coenzyme Q_{10}	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	[23]
Cimetidine	Second derivative at 217.5 nm; the method allows to determine 2–10 $\mu g\,ml^{-1}$ of analyte in pharmaceuticals	[24]
Hydrochlorothiazide	First and second derivative at 278.8 and 254.4 nm, respectively, applied for determination of hydrochlorothiazide in presence of its degradation products methoxyhydrothiazine, hydroxyhydrothiazine and 5-chloro-2,4disulfonamidoaniline; the method was used for testing its stability in bulk and in pharmaceutical preparations	[25]
Fleroxacin	The method was applied for determination in dosage form	[26]
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	[27]
	The amplitude of the first derivative at 271.6 nm allowed determination in the concentration range 126.0–462.0 $\mu g\,ml^{-1}$. The method was applied for assay in syrup	[28]
Guanoxan sulfate	The method based on the measurement of the first and second derivative values at 250–274 and 260–276 nm, respectively was applied to the determination of analyte in tablets	[29]
Ipratropium bromide	The value of second derivative at 232 nm; the linearity in the concentration range 5–30 $\mu g\,ml^{-1}$; the method was applied to determination of analyte in a liquid for nebulization	[30]

Table 1 (*Continued*)

Analyte	Characteristic of method	Reference
	Amplitude at 254–268 of the first derivative in the range 10–35 $\mu g\,ml^{-1}$; preparation Atrovent®	[31]
Linezolid	The value of first derivative at 251.4 nm was used for analyte determination in presence of its alkaline-induced degradation product	[32]
Metronidazole	Zero-crossing first derivative method; the Beer's law is obeyed in the range of 2.5–10 $\mu g\,ml^{-1}$ in absence or in presence of ciprofloxacin	[33]
Micronazole	The value of the second derivative at 276 nm applied for determination of analyte in cream formulations containing benzoic acid; the linearity in the range 100–500 $\mu g\,ml^{-1}$	[34]
3-Chloro-*N*-chloro-*N*-(3,4-dimethyl-5-isoxazolyl)-4-amine-1,2-naphthoquinone	Second derivative method applied to determination of analyte in presence of its degradation product	[35]
Meloxicam	Meloxicam was determined in the presence of its degradation products by first derivative spectrophotometry at 338 nm	[36]
Olanzapine	The signals of first derivative at 290.7 nm were used for construction of calibration graph in the concentration range 2.56×10^{-5} to 1.24×10^{-3} M	[37]
Omeprazole	Omeprazole was estimated in the presence of its degradation products sulphenamid and benzimidazole sulphide using the first, second, and third derivative spectrophotometry at 290.4, 320.6 and 311.6 nm, respectively	[38]
Oxindol	The amplitude at 260 and 265 nm of the second derivative was applied to determination of oxindol (the degradation product of sodium diclofenac in gel-ointment)	[39]
Oxolinic acid	The amplitude at 272 nm of second derivative spectra allowed determination of oxolinic acid in the concentration range 1.0–10.0 $\mu g\,ml^{-1}$	[18]
Pefloxatin	The analyte was determined in tablets and ampoules using the second-order derivative spectra in the 337–347 nm wavelength range; the linearity was obtained in the concentration range 2–30 $\mu g\,ml^{-1}$	[40]
Pyridoxine hydrochloride	The derivative spectrophotometry method was used for determination of analyte in multivitamin preparations	[42]
Secnidazole	Secnidazole was determined using the first derivative spectrophotometry at 296 nm in the presence of its degradation products	[42]
Terazosin	The assay is based on the measurements of the first and second derivative. The method is applied for the determination of analyte in commercial tablets	[43]
Timolol maleate	The analyte was assayed in ophthalmic solutions by the first-order spectrophotometry without previous treatment	[44]
Triamcinolone acetonide	The first derivative at 274 nm was used for the determination of triamcinolone acetonide in ointment formulations	[45]
Trimethoprim	The method is based on reaction of diaminopyrimidine derivatives with *p*-benzoquinone. The use of 4th derivative allowed determination of trimethoprim in presence of sulfamethoxazole	[46]
Trifluoperazine hydrochloride	The first and second derivative amplitudes at 268.4 and 262.5 nm were used for quantification of trifluoperazine in the presence of its sulphoxide	[47]

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 $g\,ml^{-1}$ of floctafenine and floctafenic acid in plasma samples. The first derivative spectrophotometry was used for simultaneous determination of cefuroxime and cefadroxil [67] in urine. The measurements of third-order derivative spectra at 402 nm were proposed for assay of amphoteracin-B [119] 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 [38] in serum. The detection limit of determination was 15 ng of analyte in 1 ml of serum. The same group of authors [25] has proposed derivative spectrophotometric method for determination of fleroxacin in human serum. Gazy [28] 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 cephalosporine antibiotics [65] based on the first derivative spectra was used for their determination in physiological

Table 2
Simultaneous determination of two compounds in a pharmaceutical sample

Analytes	Characteristic of method	Reference
Acrivastine and pseudoephedrine hydrochloride	The measurements of the second derivative at 288 nm for acrivastine and at 270.2 nm for pseudoephedrine hydrochloride	[48]
	The measurements of the fourth derivative at 315 nm for acrivastine and 269 nm for pseudoephedrine hydrochloride were used for their simultaneous assay in capsules	[49]
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	[50]
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	[51]
Amitryptyline and chlorpromazine hydrochlorides	The value of the first derivative at 254 nm was used for assay of amitryptyline in the presence of chlorpromazine, while the third derivative at 260 nm was used for the determination of chlorpromazine in the presence of the first compound	[52]
Amitryptyline and perphenazine	The amplitude of the first derivative at 255 nm was used for assay of amitryptyline while the second derivative at 256 and 254 nm was used for perphenazine. The elaborated method in combination with FIA manifold was used to obtain the dissolution profile of both drugs in pils	[53]
Amoxicillin and bromohexine hydrochloride	The amplitudes of first derivative at 278.8 and 326.2 were used for detrmination of amoxicillin and bromohexine, respectively	[54]
Ascorbic acid and acetylsalicylic acid	The values of the first derivative at 245 and 256 nm for ascorbic acid (I) and acetylsalicylic acid (II), allowed determination of (I) in the concentration range 6.6×10^{-6} to 1.5×10^{-4} M and the (II) in the range 3.4×10^{-6} to 2.0×10^{-4} M	[55]
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	[56]
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	[57]
Atenolol and nifedipine	The first derivative spectrophotometry at 276 nm for atenolol and at 340 nm for nifedipine	[58]
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	[59]
Benazepril hydrochloride and hydrochlorothiazine	The second-order derivative spectra were used for simultaneous determination of benazepril hydrochloride by the measurements of amplitude between 253.6 and 282.6 nm, and hydrochlorothiazine at 282.6 nm. The Beer's law is obeyed in the ranges 14.80–33.80 and 18.50–42.20 $\mu g\,ml^{-1}$ for benazepril and hydrochlorothiazine, respectively	[60]
	The values of the first derivative at 260.7 and 239.8 nm were used for determination of benazepril hydrochloride and hydrochlorothiazine, respectively	[61]
	The amplitudes of the second derivative peaks were used for assay of benazepril hydrochloride at 214.8 nm and hydrochlorothiazine at 227.4 nm	[62]
Butamirate citrate and sodium benzoate	The method was applied to assay in pharmaceutical dosage forms	[63]
Benzocaine and cetylpiridinium chloride	The first derivative values measured at 231.4 and 310.0 for benzocaine and at 220.7 for cetylpiridinium chloride. The calibration graphs were linear in the ranges from 10–25 $mg\,l^{-1}$ of benzocaine and from 4–20 $mg\,ml^{-1}$ of cetylpiridinium chloride	[64]
Cephalothin and cefoxitin	The both compounds were assayed in the range 4–32 $\mu g\,ml^{-1}$ by measurements the value of the first derivative at 235 nm for cephalothin and 236.75 nm for cefoxitin	[65]
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	[66]
Cefuroxime and cefadroxil	Amplitudes of the first derivative at 292.5 and 267.3 nm for cefuroxime and cefadroxil, respectively allowed determinations of both drugs in the range 2–10 $\mu g\,ml^{-1}$. The method was applied for determination in pharmaceuticals	[67]
Chlordiazepoxide and clidinum bromide	The values of the first derivative at 220.8 nm for clidinum bromide (I) and 283.6 nm for chlordiazepoxide (II). The calibration graphs were liner in the ranges from 0.983 to 21.62 $mg\,l^{-1}$ for clidinum bromide and from 0.740 to 12.0 $mg\,l^{-1}$ for chlordiazepoxide	[68]
Cilazapril and hydrochlorothiazide	Simultaneous determination was performed using measurements of first derivative at 242.8 and 282.8 nm for cilazapril and hydrochlorothiazide, respectively	[69]

Table 2 (*Continued*)

Analytes	Characteristic of method	Reference
Chlorpheniramine maleate and phenylephrine hydrochloride	The first derivative zero-crossing technique based on measurement of derivative value at 246.5 and 238.6 nm for chlorpheniramine maleate and phenylephrine hydrochloride, respectively was used	[70]
Chlorpheniramine maleate and noscapine hydrochloride	Values of the first derivative at 268.0 and 261.0 nm were used for determination of chlorpheniramine and noscapine, respectively	[71]
Chlorpheniramine maleate and guaiphenesin	The amplitudes of first derivative at 273.2 and 261.0 were applied for simultaneous assay of chlorpheniramine and guaiphenesin, respectively	[71]
Dapsone and pyrimethamine	The determination of both compounds was performed by first derivative at 249.4 nm for dapsone and at 231.4 nm for pyrimethamine	[72]
Dexamethasone and polymyxin B	The first derivative method	[73]
Domperidone and cinnarizine	The peak amplitude of the first derivative spectra at 302 nm for domperidone and at 257 nm for cinnarizine were used for construction of calibration graphs. The linearity were obeyed in the concentration range of 2.5–30.0 $\mu g\,ml^{-1}$ for domperidone and 5–25 $\mu g\,ml^{-1}$ for cinnarizine	[74]
Dorzolamide hydrochloride and timolol maleate	The amplitude of first derivative at 250.3 nm and at 315.8 nm was used for construction of calibration graphs for dorzolamide and timolol, respectively	[75]
Dextromethorphan hydrobromide and triprolidine hydrochloride	The zero-crossing first derivative technique was used for the simultaneous determination of both compounds in dosage forms	[76]
Ethinylestradiol and levonorgestrel	The simultaneous determination of both compounds using the first derivative spectra. The calibration graphs were linear up to 26 and 33 $\mu g\,ml^{-1}$ of ethinylestradiol and levonorgestrel, respectively	[77]
Estradiol and medroxyprogesterone acetate	The method is based on measurements of second derivative amplitudes at 297.4 nm for estradiol and 273.4 nm for medroxyprogesterone	[78]
Ethinylestradiol and gestodene	The linearity was achieved up to 38 and 22 $\mu g\,ml^{-1}$ of ethinylestradiol and gestodene, respectively, applying the first derivative spectra	[79]
Fosinopril and hydrochlorthiazine	The fourth derivative at 217.7 and 227.9 nm used for simultaneous determination of fosinopril and hydrochlorthiazine, respectively	[80]
Hydrochlorthiazide and amiloride	The first derivative spectrophotometry was used for resolution of overlapped spectra. The determination has been done using CLS, ILS, PCR and PLSR chemometric techniques based on measurements of amplitudes of derivative spectra at selected wavelengths	[81]
Hydrochlorthiazide and candesartan cilexetil	The first derivative at 270.1 and 255.5 nm were used for simultaneous determination of hydrochlorthiazide and candesartan cilexetil, respectively	[82]
Hydrochlorthiazide and irbesartan	The amplitudes of second derivative at 230.1 and 232.7 nm were used for simultaneous assay of irbesartan and hydrochlorthiazide, respectively	[83]
	The zero-crossing first derivative spectrophotometric method was proposed. The calibration graph for irbesartan at 263 nm was linear in the concentration range 1.0–12.0 $\mu g\,ml^{-1}$. Hydrochlorthiazide was determined in the concentration range 2.0–50.0 $\mu g\,ml^{-1}$ by direct measurement of absorbance at 317 nm of zero-order spectra	[84]
Hydrochlorthiazide and losatran	Hydrochlorthiazide was determined by measurement of fourth derivative amplitude at 330–340 nm. For assay of losartan the amplitude of fourth derivative spectra at 280–290 nm was applied	[85]
Hydrochlorthiazide and moexipril hydrochloride	The first derivative spectrophotometric method utilised the measurement of amplitudes at 215 and 234 nm for moexipril and hydrochlorthiazide, respectively	[86]
Hydrocortizone and Zn-bacitracin	The derivative method was used for simultaneous determination of both analytes in synthetic mixtures without separation	[87]
Lamivudine and zidovudine	The amplitudes of the first derivative at 265.6 and 271.6 nm were selected for the assay of lamivudine and zidovudine, respectively. The linearity were obeyed for both compounds in the concentration ranges 1–50 $\mu g\,ml^{-1}$	[88]
Lisinopril and hydrochlorthiazine	The first derivative at 289.6 and 279.8 nm for lisinopril and hydrochlorthiazine, respectively. The Beer's law were obeyed in the range 25.56–129.50 $\mu g\,ml^{-1}$ for lisinopril and 10.60–139.50 $\mu g\,ml^{-1}$ for hydrochlorthiazine	[89]
Neopterin and pterin	The simultaneous determination of neopterin and pterin; the detection limits were 0.3 and 0.12 $\mu g\,ml^{-1}$ for neopterin and pterin, respectively	[90]
Naphazoline hydrochloride and chlorpheniramine maleate	The value of the first derivative at 295.5 nm was used for the assay of naphazoline in the presence of chlorpheniramine and the second derivative at 261.7 nm for determination of chlorpheniramine in the presence of naphazoline	[91]

Table 2 (*Continued*)

Analytes	Characteristic of method	Reference
Naphazoline nitrate and tetramethylthionine base	Both drugs were assayed by measurement of amplitudes of first derivative at 257.2 nm for naphazoline nitrate and at 247.5 nm for tetramethylthionine base	[92]
Lidocaine and cetrimonium bromide	The height of the second derivative peaks at 250 and 215 nm were used for lidocaine and cetrimonium bromide, respectively	[93]
Omeprazole and omeprazole sulphone	The first-order derivative method using amplitudes at 304 and 307 nm was applied for determination of omeprazole and its sulphone, respectively	[94]
Pantoprazole and *N*-methylpantoprazole	The amplitudes of first derivative spectra at 291.5 nm for pantoprazole and at 296.5 for its *N*-methyl derivative were used for their simultaneous determination	
Paracetamol and mefenamic acid	The first derivative; the linearity was obeyed in the ranges from 1.8×10^{-6} to 1.6×10^{-4} M of mefenamic acid and from 4.1×10^{-6} to 1.4×10^{-4} M of paracetamol	[95]
Paracetamol and propacetamol	The first derivative at 242.0 nm for propacetamol and 239 nm for paracetamol. The calibration graphs were linear up to 20.0 and 15.0 of propacetamol and paracetamol, respectively	[96]
Paracetamol and codeine	The zero-crossing first derivative method; calibration graphs were linear in the ranges 4.3×10^{-5} to 1.0×10^{-3} M for codeine and 6.1×10^{-5} to 1.6×10^{-3} M for paracetamol	[97]
Paracetamol and analgine	The heights of the first derivative peaks at 249.2 and 264.8 nm for analgine and paracetamol, respectively	[98]
Pitophenone (I) and dipyrone (II)	The zero-crossing second and third derivative spectra were used. The linearity by second derivative method was obeyed at 266.5 and 302.5 nm for (II) and at 257 and 286 nm for (I). The third derivative spectra allowed determination of (I) at 228.5 and 300 nm and (II) at 242 and 278.3 nm	[99]
Promazine hydrochloride (I) and promazine sulphoxide (II)	(I) and its main metabolite (II) were simultaneous assayed using first-order derivative spectra (at $\lambda = 268$ nm) for (I) and amplitude at 342–344 nm of third derivative spectra for (II)	[100]
Pseudoephedrine hydrochloride (I) and triprolidine hydrochloride (II)	The measuring of the first derivative at 266.3 nm for (I) and at 275.4 nm for (II). The linearity were in the ranges 200–1200 and 10–50 $\mu g\,ml^{-1}$ for (I) and (II), respectively	[101]
Perindopril and indapamide	The method of simultaneous determination of both drugs in their binary mixture using the values of first derivative at 225.7 and 255.4 nm for peridopril and indapamide, respectively	[102]
Trifluoperazine HCl and isopropamide iodide	The assay was performed using the second derivative peaks at 270.4 and 320.2 nm for trifluoperazine and isopropamide, respectively	[103]
Salicydamide and acetylsalicylic acid	Zero-crossing derivative spectrophotometry was used for simultaneous determination of salicylamide and acetylsalicylic acid in ranges 1.0–30.0 and 2.0–25.0 $\mu g\,ml^{-1}$, respectively	[104]
Sulfadiazine and trimethoprim	First derivative at 288 and 248.5 nm was selected for simultaneous determination of sulfadiazine and trimethoprin, respectively. Derivative spectrophotometry was used for assay of drugs dissolution profile in FI-mode	[53]
Pseudoephedrine sulfate (I) and dexbrompheniramine maleate (II)	The values of amplitude of first derivative spectra at 245.6 and 281.6 nm were used for quantification of (I) and (II) in synthetic mixtures and pharmaceutical preparations	[105]
Pseudoephedrine (I)–ibuprofen (II) and pseudoephedrine (I)–loratadine (III)	The second derivative method was proposed for determination of (I) in combination with (II) and (I) with (III) [106].The method utilised the first derivative spectra [107] was proposed for determination of (III) and (I) in Clarinase® tablets	[106,107]
Oxfendazole (I) and oxyclozanide (II)	The amplitudes of first derivative spectra at 308.8 nm were used for determination of (I) and at 326.0 nm for assay of (II). The linearity were achieved in the ranges 4–32 and 2–16 $\mu g\,ml^{-1}$ for (I) and (II), respectively	[108]
Floctafenine and floctafenic acid	The generation of the first derivative was used for the isolation of partially overlapped their fluorescence spectra. The method was applied for the determination of both compounds in synthetic binary mixtures and in plasma samples	[109]
Gentamycin sulfate (IV)—dexamethasone and gentamycin sulphate,methyl or propyl 4-hydroxy-benzoate esters	For simultaneous determination of gentamycin in presence of dexamethazone or 4-hydroxybenzoates aliphatic esters the first derivative spectra were used. The assay of gentamycine and dexamethazone was performed at 253 and 257 nm, respectively. The same wavelength was used for quantification of gentamycine in the presence of methyl or propyl 4-hydroxy-benzoate ester, while the esters were determined by Vierordot method	[110]
Medazepam (I) and hyoscine (II) butylbromide	Two methods of the measurements of amplitude of the second derivative spectra were used. The peak-to-peak method utilised amplitude at 252.6 and 264.8 nm was applied for assay of (I) and the zero-crossing method at 212.5 nm was used for the determination of (II)	[111]

serum and glucosed physiological serum. The mentioned previously derivative method concerned on determination of acrivastine [11] 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 [120]. The mentioned method is very efficient and characterised by high value of recovery (97%). Piroxicam and its main metabolite—5′-hydroxypiroxicam were determined spectrophotometrically in human plasma using the first derivative spectra of sample [121]. The assay was followed by liquid–liquid extraction step of these two drugs from plasma sample. The method allows to determine up to 10 and 8 ppm of piroxicam and its metabolite, respectively. The method [23] elaborated for determination of coenzyme Q10 in pharmaceuticals was applied for its assay in plasma too. The first derivative method was developed for simultaneous determination of leucovorin and methotrexate [122] in the ranges 2–30 and 1–12 ppm, respectively. The method was used for assay of both drugs in serum and urine samples. The achieved main recovery values were 91 and 97% for methotrexate and leucovorin, respectively. The second and third UV derivative spectrophotometric method was elaborated for determination of roxatidine [118]. The assay required the isolation of drug from the biological matrix by solid phase or liquid phase extraction. The fourth UV derivative spectrophotometry was used for determination of protein and casein contents in cow milk samples [123]. The assay was based on the measurements of UV absorption of aromatic amino acids of denatured proteins. The results were compared with those obtained by Kjedahl methods and confirmed the usefulness of the derivative method.

Derivative spectrophotometry appeared to be efficient and easy for maintenance tool for determination of the level and deposition of vitamin E in animal muscles and its protective action against an oxidative stress [124,125]. The stability of subcellural fractions of lipids in pigs [124] and chicken [125] muscles after supplementation by α-tocopherol was examined using the first derivative spectrophotometry. The oxidative stability of beef muscle during refrigerated storage was studied by conventional and derivative spectrophotometry [126]. Both methods appeared to be equally effective confirming the usefulness of derivative method for such kind of analysis. Second and fourth derivative UV spectrophotometry appeared to be a useful tool for studying the influence of various aromatic residues of proteins on their polarity and spectral characteristic [127].

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. The recent applications of derivative spectrophotometry in food or cosmetics analysis are gathered in Table 3.

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 [148–155]. The combination of derivative spectrophotometry with PLS-calibration method [151–153] and the use of solid phase extraction [150] for sample preparation has allowed the assay of trace levels of compounds. The simple, sensitive and highly selective method utilised the fourth derivative spectra [154] was proposed for determination of ferbam (iron(III) dimethyldithiocarbamate) fungicide in fortified samples of wheat grains and in commercial preparation. There are very interesting combination of derivative spectrophotometry with HPLC-DAD technique [153,156,157]. 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 [156] and some aromatic amines (*o*- and *m*-toluidyne, *m*- and *p*-toluidyne and *o*- and *m*-phenylenediamine) [157]. The employed procedures do not require the complete chromatographic separation of studied compounds. The overlapped spectra of co-eluting substances were resolved by the derivative spectrophotometry, without modification of chromatographic conditions. The fast and precise spectrophotometric method was proposed for determination of diquat and paraquat [155] in blood, tissue and urine samples. The assay of both compounds was based on the spectral differences of their second derivative spectra. The proposed procedures required only 2-ml sample volume. The first derivative spectra were used for determination of o-nitrophenol and *p*-nitrophenol [158]. The analytes were separated from matrix by liquid–liquid extraction as tetrabutylammonium ion pairs into 1,2-dichloroethane and spectra of organic phase were recorded and used for further analysis. The described procedure was applied for quantification of both compounds in fruit juices. The UV-derivative spectrophotometry was used for monitoring of aromatic hydrocarbons [159] in water. The mentioned method employed the transmission spectra for quantitative analysis.

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 [127,160,161] obtained by hydrolysis of proteins. The UV-spectra of post-reaction mixture were recorded and generated derivative spectra. The results of spectral analysis was used for identification of peptides composition. The derivative spectrophotometry [162] was applied for resolving of binary mixtures of some flavonols

Table 3
The applications of derivative spectrophotometry in food or cosmetics analysis

Main determined compound	Accompanied with	Remarks	Reference
Tartrazine	Brillant blue	The first derivative method was applied for determination of Tartrazine and Brillant blue in colognes	[128]
	Sunset yellow	The first derivative method was applied for determination Tartrazine and Sunset yellow in cosmetics. The linearity was achieved in the range 0.5–10 $\mu g\,ml^{-1}$ of Tartrazine and 0.5–12 $\mu g\,ml^{-1}$ of sunset yellow	[129]
	Sunset yellow	The method is based on the formation and the extraction of ion pairs formed between dyes and trioctylmethylammonium chloride into toluene. The quantification was done by the first derivative spectrophotometry and bivariate methods	[130]
	Erythrosine, amaranth	Three food colorants: Tartrazine, Erythrosine and Amaranth were simultaneously determined in their synthetic mixtures and in commercial products	[131]
	Patent blue V and Indigo carmine	The first derivative method was applied for resolving the synthetic and commercial mixtures of these colorants	[132]
	Ponceau 4R and Sunset yellow	The studied colorants were determined using the first derivative spectrophotometry in their binary (ponceau 4R–Sunset yellow and Tartrazine–Sunset yellow) mixtures	[133]
	Allura red and Sunset yellow	The first derivative spectrophotometry combined with PLS-1 and PLS-2 methods was used for resolving of colorants ternary mixtures. The elaborated method was applied for determination of these colorants in soft drinks and beverage samples	[134]
	Amaranth and Curcumin	The amplitudes of the first derivative spectra at 414, 468 and 600 nm were used for the determination of Curcumin, Tartrazine and amaranth, respectively, in their synthetic ternary mixtures and in a commercial food product	[135]
Sunset yellow	Allura red	The elaborated method was based on ion-pair formation between colorants and tricaprylymethylammonium chloride and their extraction into isobutyl methyl ketone	[136]
	Erytrosine	Using the first derivative spectrophotometry both dyes were determined in pharmaceutical syrup sample	[137]
		The values of first derivative at 526.3 and 482.7 nm were used for Erythrosine and Sunset yellow, respectively	[138]
	Ponceau 4R	Sunset yellow and Ponceau 4R were simultaneously determined in gelatin powder samples by the first derivative spectrophotometry and PLS-methods	[139]
Ponceau 4R	Anthocyanin	Both colorants were assayed in drink powder samples by the second derivative spectrophotometry and PLS multivariate methods	[140]
Patent—blue V	Carmosine	Patent blue V and Carmosine were determined by the first derivative spectrophotometry in different gelatine desserts samples. The methods involved the SPE purification step in order to eliminate turbidity of the samples	[141]
Ascorbic acid	-	The third-order UV derivative spectrophotometry was used for direct determination of vitamin C in fruits. The proposed method does not required any separation or background correction techniques and reagents	[142]
2-Hydroxy-4-methoxy-benzo-phenone-5-sul-phonic acid (UVA) and 2-phenylbenzy-midazole-5-sul-phonic acid (UVB) sunscreens		The second derivative spectrophotometry was used for quantification of both UVA and UVB sunscreens in their binary mixtures. The method was applied for assay of their contents in sunscreen gel samples	[143]
Flavonoid chrystin	Quercetin	The first and second derivative spectrophotometric methods were used for determination of flavonoids and quercetin in propolis samples	[144]

Table 3 (*Continued*)

Main determined compound	Accompanied with	Remarks	Reference
Oxytetracycline	Others tetracyclines	The second derivative synchronous spectrofluorimetry was applied for determination of oxytetracycline alone and in presence of others drugs in medical premixes and medicated food samples	[145]
γ-Oryzanol		The quantitative analysis of γ-oryzanol was performed by measurements of 310–360 nm amplitude of the second derivative spectra. The method was applied for determination of its content in rice bran oil	[146]
Parathion and *p*-nitrophenol		The method is based on measurement of first derivative amplitudes at 253.0 nm for parathion and at 273.1 nm for *p*-nitrophenol. The method was applied for determination of both analytes in samples of spiked leafs of corn	[147]

and a flavon: quercetin–kaempferol, quercetin–myricetin and 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 [163] 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 [164]. 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 [165] and phenyl-β-naphtylamine [166]) in rubber and polymeric materials. The proposed methods allow the assay of analytes without separation from other polymer aditivites.

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. The presentation of described methods is organized in the same way as chapter 2.1. First, described single-component assays, next methods devoted to two-component determinations and in the end the analysis of more complex systems are presented (Tables 4 and 5).

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 [260]. The proposed method based on measurements of values of the second derivative at 338.346, 628.644 and 393.400 for dysprosium, holmium and erbium, respectively, allowed the determination of 0.001 to 0.2% of each element in several rare earth oxides. Bobrowska-Grzesiuk at al. [261] 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 [262]. 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.

It could be concluded at the end of this chapter, that the derivative spectrophotometry is intensely employed in analysis of inorganic cations in various kinds of samples. On the other side, the limited number of derivative spectrophotometric procedures proposed for quantitative assays of inorganic anions is very surprising. There are only a few articles concerned with this problem. Bobrowska-Grzesiuk et al. [263] have proposed the second-order derivative spectrophotometric method for simultaneous determination of nitrate and nitrite ions in bath solutions. The content of fluoride ions in technical samples was determined by the third derivative spectrophotometry based on the generation of ternary complexes La(III)-F-alizarin [264]. The first derivative method for simultaneous determination of phosphate and silicate ions was described by El-Sayed et al. [265,266]. The elaborated procedures were based on the reaction of formation of phospho- and silicomolybdenum blue complexes in the presence of metol and ascorbic acid. The methods were applied for determination of the studied ions in detergents and waters samples.

Table 4
Single-component inorganic analysis

Analyte	Description of the method	Reference
Aluminium	The method based on complexation reaction between aluminium and quinizarin. The influence of iron was eliminated by the use the first derivative spectrophotometry. The method was applied for determination of analyte in Portland cement samples	[167]
Beryllium	The colour reaction between beryllium and 1,4-dihydroxy-9,10-anthracenedione in aqueous medium in presence of Triton X-100 is used. The method was applied for determination of analyte in alloys and spiked samples of distilled water	[168]
Bismuth	Bismuth was determined as 2-(5-bromo-2-pyridyltizo)-5diethylaminophenol–ammonium tetraphenylborate complex using the third derivative spectrophotometry	[169]
Cobalt	The method is based on generation of ion-pair between cobalt ion and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol tetraphenylborate. The value of the first derivative at 611.5 nm was used for determination of cobalt in standard alloys and biological samples	[170]
	Cobalt was determined in the complex form with nitroso-R salt and tetradecyldimethylbenzylammonium chloride. Third derivative spectrophotometry was used for its determination	[171]
Copper	The microamounts of copper in various samples of water were determined using solvent extraction coupled with the first derivative spectrophotometry. The method was based on reaction with 3-4-phenyl-2-pyridinyl-5-phenyl-1,2,4-triazine and picrate	[172]
	The element was determined in biological samples in the form naphtalene-Cu-(nitroso-R)-(tetradecyldimethylbenzylammonium) complex using the third derivative spectra	[173]
	Copper was determined in the form of 2-nitroso-1-naphtol-4-sulphonic acid and tetradecyldimethyl-benzylammonium chloride complex. The second derivative spectra were used for quantification of the element in standard alloys and biological samples	[174]
Germanium	Phenylfluorone-cetylpyridynium chloride was used as reagent. The second derivative spectra of complex were applied for the determination of element in herbs	[175]
Iridium	Iridium was determined in the form Ir-PAN complex using the first derivative spectrophotometry	[176]
Iron	2-(2-Pyridylmethyleneamino)phenol was used as chromogenic reagent for iron determination by the first derivative method. The elaborated procedure was used for quantification of iron in several industrial samples (caustic soda, cotton yarn and fabric, woollen fabric and industrial water)	[177]
	The assay was based on reaction of iron with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP). After preconcentration of (5-Br-PADAP)-Fe complex onto ammonium tetraphenylborate retained on naphtalene and dissolving in DMF, iron was determined by measuring the amplitude of the third derivative between 773 and 737 nm	[178]
	Iron was determined in the form of complex with 1,10-phenantroline. The element was determined using values of third derivative spectrophotometry	[179]
Lead	The complexation reaction between lead and meso-tetra-(3,5-dibromo-4-hydroxylphenyl)porphyrin was used. The second derivative spectrophotometry was applied for quantification of the element and its determination in clinical samples	[180]
Magnesium	Magnesium(II) was determined using purpurin as chromogenic reagent. The application of the first derivative increased sensitivity and allows the determination of 0.2 μg Mg ml^{-1}	[181]
Manganese	The element was preconcentrated on 2-nitroso-1-naphtol-4-sulphonic acid–tetradecyldimethylbenzylammonium naphtalene, next adsorbent with retained Mn complex was dissolved in DMF and manganese contents determined by the second derivative	[182]
	The assay was based on complexation reaction Mn(II)-purpurin. The quantification of the element was done by the first derivative spectrophotometry	[183]
	5-Br-PADAP was used as complexation reagent. The assay was performed by measurement of amplitude of third derivative	[184]
Nickel	The formation of complex Ni–1-nitroso-2-naphtol-3,6-disulfonate acid–tetradecyldimethylbenzylammonium and its preconcetration on naphtalene was used. The assay was done by mesasuring the amplitude between 537 and 507 nm of the third derivative spectrum of dimethylformamide solution of complex	[185]
	The first derivative spectrophotometry based on complexation of nickel by 2-nitroso-1-naphtol-4-sulphonic acid–tetradecyldimethylbenzylammonium was applied for the element determination in standard alloys and biological samples	[186]

Table 4 (*Continued*)

Analyte	Description of the method	Reference
	The first derivative spectrophotometric method based on reaction of nickel with hydroxynaphtol blue was used for its determination in standard brasses	[187]
	The elaborated method proposed the combination of the use colour reaction of Ni–2-(5-bromo-2-pyridylaxo)-5-diethyl-aminophenol with the first derivative spectrophotometry for determination of nickel and elimination of cobalt interferences	[188]
Palladium	Pyridopyridazine dithione was applied as chromogenic reagent for palladium determination by the fourth derivative spectrophotometry. The derivative method allowed determination of palladium in the range 0.013–0.23 μg Pd ml^{-1} with detection limit 3.7 ng Pd ml^{-1}	[189]
	The metal was determined by the third derivative spectrophotometry in the form of 2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol–ammonium tetraphenylborate complex in dimethylformamide medium	[190]
	The reaction Pd-2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol was the base of the first derivative method of palladium determination	[191]
	PAN was used for development of colour reaction. The contents of element was assayed by measuring the amplitude between 650 and 680 nm of the first derivative spectra of complex in DMF medium	[192]
	The formation of complex between Pd and disodium 1-nitroso-2-naphtol-3,6-disulfonate and tetradecyldimethylbenzylammonium chloride was used. The value of amplitude between 566 and 602 nm of the third derivative spectra was used for the determination of element	[193]
Platinum	Platinum was determined as Pt-SCN-Rhodamine 6G complex using the first derivative spectrophotometric technique	[194]
Titanium	The first-order derivative spectrophotometry was applied for determinatioum of titanium in the form of complex with 2,4-dihydroxybenzaldehyde isonicotinoyl hydrazone in alloys and steel samples	[195]
Tungsten	Tungsten was estimated as thiocyanate complex using the second derivative spectrophotometry. The presence of Nb, Mo, V did not interfere	[196]
Rare-earth elements		
1. Americium	The second derivative spectrophotometry was proposed for determination Am(III) using arsenazo-III as chromogenic reagent. The presence of plutonium and uranium does not interfere. The method was successfully applied for the determination of Am (III) in uranium–plutonium mixed ore	[197]
2. Holmium	2-Isobutylformyl-1,3-dione-indan and TX-100 were used as reagents for complexation of holmium. The second derivative spectrophotometric technique was used for determination of element contents and elimination of interferences of others lanthanides	[198]
	The second derivative spectra of the holmium complex with benzoyl-indan-1,3-dione and cetylpyridinum chloride were used for estimation of this element. The method was applied for holmium determination in rare earth mixtures	[199]
	2-(Diphenylacetyl)indan-1,3-dione and octyphenyl poly(ethyleneglycol) ether were used for complexation of holmium. The third derivative spectrophotometry was applied for increasing of selectivity and sensitivity of determination	[200]
3. Neodymium, holmium, erbium	The complexes of 1-ethyl-6,8-difluoro-7-(3-methyl-1-piperazinyl)-4-oxo-1,4-dihydro-3-quinoline carboxylic acid with neodymium, holmium and erbium were used for spectrophotometric determination of these elements. The generation of second derivative spectra eliminated the interference of others elements and increased the sensitivity of determination	[201]
4. Neodymium and erbium	Benzoyl-indan-1,3-dione and cetyltrimethyl-ammonium bromide were used as complexation agents for determination of neodymium and erbium. The third derivative spectrophotometry was used for direct assay of these elements in mixed rare earths	[202]
	The spectra of Nd and Er complexes with 2-isobutylformyl-1,3-dione-indan in presence of TX-100 were studied using the second derivative spectrophotometric method	[203]
5. Praseodymium	Ciprofloxacin was used as complexation agent for determination of praseodimium. The normal and the third derivative spectrophotometric methods were used for studying the run and equilibria of reaction	[204]
	The contents of element was studied using 1-cyclopropyl-6-fluoro-1,4-dihydro-7-(4-ethyl-1-piperazinyl)-4-oxo-3-quinoline carbocyclic acid hydrochloride as complexation agent. The use of the third derivative spectra allowed to eliminate the interference of the presence of neodymium, erbium and holmium	[205]
	The complex of prasedimium with lomefloxacin was used for its quantitative determination. The application of the second derivative spectrophotometry increased the selectivity of the assay	[206]

Table 4 (*Continued*)

Analyte	Description of the method	Reference
Scandium	Scandium was assayed as chelate with 1-(2-thiazolylazo)-2-naphtol using the second derivative spectrophotometric method	[207]
Rhodium	The traces of rhodium were determined using the third derivative spectra of rhodium complexes with 1-(2-thiazolyl-azo)-5-dimethylaminobenzoic acid	[208]
	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol was used as chromogenic agent for rhodium determination. The application of third derivative spectrophotometric method increased the selectivity of the assay	[209]
	The complexation reaction with 1-(2-pyridylazo)-2-naphtol combined with analysis of the complexes by the first derivative spectra was used for quantification of rhodium	[210]
Osmium	Osmium in the form of thiourea complexes was quantitatively assayed in the presence of ruthenium by the measurement of second derivative peak at 605 nm	[211]
Uranium	Uranium was determined by the measurements of the amplitude between 582–592 nm of the fourth derivative spectra of uranium complex with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol	[212]
Vanadium	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol was used as complexation agent for determination of vanadium by the second derivative spectrophotometry	[213]
	The values of amplitude between 510–575 nm of second derivative spectra of vanadium complexes with 2-nitroso-1-naphtol-4-sulfonic acid were used for the assay of this element in alloys and synthetic samples	[214]
	The complexation reaction between V and PAN was the basis of the third derivative spectrophotometric method of vanadium quantification	[215]
	The third derivative spectrophotometry was used for determination of vanadium in the form of complexes with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol–ammonium tetraphenyl-borate	[216]
Zirconium	2,4-Dihydroxy benzaldehyde isonicotinyl hydrazone was applied as chromogenic reagent. The analysis of the first derivative spectra was used for quantification	[217]
Zinc	Trace zinc was determined using the fourth derivative spectrophotometry and 1-2-(thiazolylazo)-2-naphtol	[218]

3. Internal standard method

The use of internal standard for quantification of analyte allows to minimise 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 use them for quantification. The main advantage of such procedure is its simplicity and lower cost than the chromatographic method. The application of internal standard (IS) technique was proposed for determination of azinphos-methyl [267]. As internal standard were used acethophenone alone and mixture of acetophenone and Erioglaucine. The same authors [268] proposed the derivative method combined with internal standard technique for quantification of traces of chromium(VI). The method employed the colour reaction of Cr(VI) with benzyltributylammonium bromide. Diphenylcarbazide was used as IS. The separation of signals of analyte and IS was achieved by generating the first derivative spectra of reagents mixture. The methylene blue [269] was used as internal standard for the second derivative spectrophotometric method of determination of micronazole. The procedure was applied for drug quantification in commercial products. The combination of internal standard technique with derivative spectrophotometry was proposed for determination of chlorpromazine hydrochloride [270] and coenzyme Q10 [271]. The assay of chlorpromazine [270] utilised 1,10-phenantroline as IS and the second derivative spectrophotometry for separation of analytical signals. The second procedure [271] used α-tocopherol acetate as IS for the first derivative spectrophotometric estimation of coenzyme Q10 in pharmaceuticals and clinical samples.

4. Solid phase derivative spectrophotometry (SPS-DS)

The solid phase spectrophotometry (SPS) is a technique which enables simultaneous preconcentration and spectrophotometric determination of analyte. The SPS

Table 5
Simultaneous determination of two inorganic analytes in sample

Analyte	Accompanied compound	Characteristic of the method	Reference
Aluminium	Iron	The hematoxylin in the presence of cetyltrimethyl-ammonium bromide was applied as complexation agent. The first and the second derivative spectrophotometry was used for simultaneous assay of both analytes	[219]
Antimonium(III)	Bismuth(III)	First derivative method based on reaction of assayed elements with iodide in acidic media	[220]
Cadmium	Mercury	The direct and first derivative spectrophotometric methods were proposed for simultaneous determination of both elements. The procedures were based on colour reaction with PAR	[221]
Cobalt	Bismuth(III)	The reaction of methylethylenediaminetetraacetic acid with assayed elements was basis of their determination by zero-crossing derivative spectrophotometric method	[222]
	Iron	The assay was based on the colour reaction of ions with ferrozine was performed in stopped flow injection system using the first derivative spectrophotometry as detection method	[223]
		The method was based on complexation reaction with 4-(2-pyridylazo)resorcinol. The determination of cobalt and iron was performed using the second derivative spectra with extrema at 515 nm (cobalt) and 485 (total)	[224]
	Copper	Measurements of the second derivative spectra at 530 nm	
	Nickel	The first derivative at 510 nm was used for cobalt and second derivative at 515 nm	
	Nickel(II)	*N*-(2-Thienylmethylene) phenyl hydrazine was used as chromogenic reagent	[225]
		The first derivative spectrophotometric method was proposed for determination of nickel and cobalt in the form as dithizone complexes	[226]
Copper(II)	Chromium(III)	Derivative spectrophotometry was proposed for simultaneous determination of chromium and copper with MEDTA	[227]
	Iron	Iron and copper were determined by the second derivative method. The assay is based on property of iron and copper picrates to form ion pairs with 5-phenyl-3-(4-phenyl-2-pyridynyl)-1,2,4-triazine and bathocuproine, respectively	[228]
		The assay was based on colour reaction of copper and iron with 2-hydroxy-1-naphtalene benzoylhydrazone. The assay applied reading of the first derivative value at 443 nm for copper and the value of amplitude of the first derivative peaks between 450 and 540 nm for iron	[229]
	Mercury	Both elements were determined by derivative spectrophotometry with methylenediaminetetraacetic acid (MEDTA)	[230]
Gallium(III)	Indium(III)	The method was based on reaction with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol in cationic micellar medum	[231]
Iron(III)	Molybdenum (VI)	The first derivative spectrophotometric method based on the analysis of the first derivative spectra of elements complexes with morin in the presence of cationic surfactant was used	[232]
Manganese	Zinc	The first and the second derivative spectrophotometric method based on colour reaction with 5,8-dihydroxy-1,4-naphtoquinone was proposed for the simultaneous determination of Mn^{2+} and Zn^{2+}	[233]
Neodymium	Erbium, praseodymium, holmium	The method utilises reaction with fleroxacin. The application of second derivative spectra improved the sensitivity and allowed simultaneous determination of these elements in rare earth mixtures	[234]
	Erbium	The method was based on reaction with benzoyl-indan-1,3-dione as complexation agent at the presence of cetylpyridinum chloride. The quantification was done by measurements of the amplitudes of the second derivative spectra	[235]
		The second derivative spectra of complexes with 8-hydroxyquinoline at the presence of TX-100 were used for the determination of both elements	[236]
Nickel	Bismuth	Diethylentriaminepentaacetic acid (DTPA) was proposed for the determination of nickel and bismuth by the derivative spectrophotometry	[237]
	Iron(III)	The method is based on complexation reaction with 4-(2′-benzothiazolyazo) salicylic acid. The use of first derivative allowed simultaneous determination of both cations in the concentrations range 0.59–7.08 μg Ni ml^{-1} and 2.1–8.4 μg Fe ml^{-1}	[238]

Table 5 (*Continued*)

Analyte	Accompanied compound	Characteristic of the method	Reference
	Lead	The method was based on complexation reaction with methylethylenediaminetetraacetic acid (MEDTA)	[239]
	Mercury	Diethylenetriaminepentaacetic acid (DTPA) was used as the complexation reagent	[240]
Palladium	Cobalt	PAN was used as chromogenic reagent in presence of aqueous SDS micellar media. The assay was based on the measurement of amplitudes of second derivative spectra at 268 or 578 nm for palladium and at 614 nm for cobalt	[241]
	Gold	3-Hydroxy-2-methyl-1-phenyl-4-pyridone was used as reagent. The use of third derivative enables simultaneous determination of both elements without previous separation	[242]
	Iron	The first derivative spectrophotometric method based on the complexation reaction with nitroso R salt was proposed	[243]
	Nickel	2-(2-Thiazolylazo)-5-dimethylaminobenzoic acid was used as reagent for the determination of both elements by the first derivative spectrophotometry	[244]
	Platinum	The formation of Pt and Pd complexes with 3-(2-thiazolylazo)-2,6-diaminopiridyne was used for their simultaneous determination by the second derivative spectrophotometry	[245]
		Platinum and palladium were determined in the forms of iodide complexes (PtI_4^{2-} and Pd I_4^{2-}) using values of the first (387.4 nm) for Pd and of the second derivatives (331.2 nm) for Pt	[246]
		The method was based on the formation of ion associates Rh(Pt, Pd)-$SnCl_3$-diantipirydilmethane and the measurements of complexes derivative spectra	[247]
	Mercury	The first derivative spectrophotometric method based on complexation reaction with 5-(3,4-methoxyhydroxyphenylmethylene)-2-thioxo-1,3-thiazolidyne and cetyltrimethylammonium bromide	[248]
	Copper(II)	The elaborated method was based on reaction with 5-imino-3-(*p*-methoxyphenyl)-2-methyloxazolidin-4-thione. For quantification the values of the first derivative at 412 and 376 nm were used for copper and palladium, respectively	[249]
	Rhodium(III)	The values at 558 nm for Pd(II) and 460 nm for Rh(III) of the first derivative spectra of their complexes with 5-(2,4-dihydroxybenzylidene) rhodanine were applied for simultaneous determination of both elements	[250]
Rhodium	Iridium	Derivative spectrophotometry based on the reaction with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol was proposed	[251]
Rhutenium	Osmium	The second derivative spectrophotometric based on the measurements of the values of amplitudes of tetraoxide complexes of ruthenium and osmium at 310 and 250 nm, respectively	[252]
	Iron	The second derivative spectra of ternary complexes of studied elements with 4,7-diphenyl-1,10-phenantroline at the presence of ethyleneglycol were applied for the simultaneous assay of both analytes	[253]
	Platinum	The assay was based on the generation of complexes of studied ions with $SnCl_3$ ligand. For determination of platinum was used the amplitude at 377 nm of the first derivative spectra, while the value of the second derivative at 495 nm was applied for determination of ruthenium	[254]
		The complexes of studied metals with $SnCl_3$ were extracted using trioctylamine or diantipyridilmethane and next determined by the second derivative method (the amplitude between 395 and 437 nm for Pt and amplitude 497–463 for Ru, 2-nd degree polynomal and 75 points derivatisation winows)	[255]
	Osmium	The chloride complexes: $OsCl_6^{2-}$ and $RuCl_6^{2-}$ were generated and their third derivative spectra were used for the determination of Os at the presence of Ru	[256]
Uranium	Plutonium	The measurements of values at 632 nm for uranium and at 606.5 nm for plutonium of the first derivative spectra of their complexes with Arsenazo III	[257]
Uranium(VI)	Uranium(IV)	The different oxide states of uranium were determined using Arsenate I as reagent. The quantification was done by the first derivative spectrophotometric method	[258]
Zirconium	Molybdenium	The method was based on reaction with Alizarin red. The simultaneous determination was performed by measurements of amplitude of first derivative at 490.5 nm for zirconium and at 446. 0 nm for molybdenium	[259]

Table 6
The solid phase derivative spectrophotometric methods

Analyte	Adsorbent used	Characteristic of the method	Reference
Aluminium and beryllium	Dextran type anion exchanger	The method is based on complexation of metal ions with eriochrome cyanine R. The first derivative spectra of adsorbent with retained complexes were used for determination of each analyte	[274]
Cadmium and zinc	Sephadex QAE A-25	The amplitudes of the second derivative spectra of Cd–PAR and Zn–PAR complexes adsorbed on the anion exchanger were used. The measurements were performed at 540.5 nm for zinc and 537.2 nm for cadmium	[275]
Iron	SP Sephadex C-25	2,4,6-Tripyridyl-1,3,5-triazine was used as chromogenic reagent. The amplitude at 660 nm of the second derivative spectrum was used for determination of iron	[276]
Iron and copper	SP Sephadex C-25	2,4,6-tripyridyl-1,3,5-triazine and neocuproine were used as chromogenic reagents. The signals of third derivative spectra at 622 and 477 nm were used for quantification of iron and copper, respectively	[277]
Iron and ruthenium	SP Sephadex C-25	The assay is based on the complexation reaction with 2,4,6-tri-(2-pyridil)-1,3,5-triazine. Next the retained on solid support complexes were evaluated by the second derivative spectrophotometry. Ruthenium and iron were determined at 539.7 and 553.3, respectively	[278]
Molybdenum	Sephadex QAE-A-25	The values at 716 nm of the first derivative spectra of Mo-pyrocatechol violet complexes adsorbed on Sephadex	[279]
Quinoline yellow and Brilliant blue FCF	Sephadex DEAE A-25	The determination of Brilliant blue is based on the measurements of the value of the zero-order absorbance at 632 nm. The assay of Quinoline yellow required the generation of the first derivative spectra and measurement the amplitude at 453 nm	[280]
Calcium oxalate monohydrate and dihydrate	Their solid form	The first derivative infrared spectra of calcium oxalates were used to distinguished them and perform the quantification of each species	[281]

procedures are based on the measurement of light absorption of species absorbed on solid support. As the detailed discussion of theoretical base of SPS technique is out of scope of this work, the appropriate references [272,273] are given. The combination of solid phase spectrophotometry with derivative spectrophotometry allowed the selective determination of micro amounts of analytes without separating them. This method is mainly applied for resolving the analytical problems, which required the analyte preconcentration or isolation from accompanied matrix. The application of SPS-DS allows reduction the risk connected with sample preparation such as contamination of sample or loss of analyte, due to lower number of steps necessary for conversion of analyte into determined form. The recently proposed solid phase derivative spectrophotometric procedures are gathered in Table 6.

5. The study of reaction equilibria by derivative spectrophotometry

The knowledge of chemical–biochemical equilibria is very important for understanding the reaction mechanism or processes occurring in the environment or living organisms. The study of equilibrating processes is a difficult analytical task. For this purpose should be used such analytical tools and procedures which do not disturb the subtle equilibrium state of the investigated system. The rigid compliance to this condition is very important in case of biological or living systems, e.g. the use of centrifugal separation or membrane filtration may disturb the equilibrium state of the sample solutions. As the derivative spectrophotometry enables the direct determination of analyte in presence of background or turbidity, it seems to be an appropriate technique for characterisation of equilibrium state and determination of its physico-chemical quantities like partition coefficients or equilibrium constants. The derivative spectrophotometric technique was used for determination of dissociation constants, for investigation of acid–base equilibrium or stability constants of complexes. The dissociation constants of sparingly soluble in water free organic bases were determined by the derivative spectrophotometric method [282]. The used technique allowed to eliminate the turbidity caused by the precipitation of free bases and the direct study of water–precipitate system. The second-order spectra were used for the determination of acidity constants of some pharmaceuticals [283,284] and indicators [285]. The knowledge of partition processes of drugs, or natural substances, e.g. lecithin occurred in biological systems between natural membranes and their environment or two phases is very important for understanding of drug acivity, toxicity, distribution and metabolism. The second derivative spectra of indomethacin and acemetacin [286] were used for determination of partition coefficients of these drugs

between aqueous and a micellar pseudo-phases. The same method was used by Kitamura et al. [287] for examination of equilibria in the system chlorpromazine-β-cyclodextrin and estimation of the binding constant between these compounds. The second derivative spectrophotometry appeared to be a very effective tool for investigating the partition coefficients of some phenothiazine derivatives between humane erythrocyte ghost membranes and water (promazine [288]), lipophilic–lecithin layers (chlorpromazine and promazine [289]) and phosphatidylcholine-cholesterol bilayers and water (chlorpromazine and trifluopromazine [290]). The equilibria of partition of some drugs between aqueous environmental and lipid bilayers of dimyristoyl-L-α-phosphatidylglycerol [291], dimyristoyl-L-α-phosphatidylcholine [292], bile salt/lecithin micelles [293] and phosphatidylcholine [294–296] were examined by the derivative spectrophotometric method. The second derivative spectra were used for examination of partition coefficients of some nonsteroidal anti-inflammatory drugs [297] between Egg yolk phosphatidylcholine multilamellar vesicles and water. Recently the derivative spectrophotometric technique was used for determination of stability constants of Pd–PAR and Zn–PAR complexes [298]. The application of this method allowed to minimise the error [298] caused by the presence of an excess of used colour reagent in equilibrated mixture.

6. 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 7.

Table 7
The applications of derivative spectrophotometry for kinetic studies

Investigated reaction	Characteristic of the method	Reference
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	[299]
Degradation of indomethacin in alkaline solution	The monitoring of the degradation product using its four derivative spectra at 360 nm	[300]
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	[301]
Degradation of 3-bromo-*N*-bromo-*N*-(3,4-dimethyl-5-isoxazolyl-4-amine) 1,2-naphthoquinone in etanolic solution	The values at 258 nm of the second derivative spectra of main compound	[302]
Degradation reaction of 3-chloro-*N*-chloro-*N*-(3,4-dimethyl-5-isoxazolyl)-4-amine-1,2-naphtoquinone	The values at 256 nm of the second derivative spectra of studied compound were used for study the kinetics of its degradation	[35]
Photochemical degradation of nisoldipine	The first and the second derivative spectrophotometric methods at 285 and 291 nm were proposed for investigation of photodegradation reaction	[303]
Acidic hydrolysis of nordazepam	The amplitude between 244–251 nm of the fourth-order derivative spectra of nordazepam were used	[304]
Decomposition of omeprazole in aqueous solution	The values at 313 nm of the first derivative spectra of omeprazole were used	[305]
The reaction of trifluoperazine degradation process in presence of hydrogen peroxide	The first derivative spectra at 268.4	[47]
The photodegradation of thioridazine	The second derivative spectra at 280 nm were used for examination of kinetics of degradation of thioridazine	[306]
Stability of 2-hydroxy-*N*-4-methyl-5-isoxazyl-1,4-naphtoquinone-4-imine in presence of cyclodextrin	The second derivative spectra were used for kinetic investigation. The investigations were done by measurements of second derivative amplitude at 322 nm	[307]

7. 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 optimisation 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. The appropriate selection of mathematical parameters of derivatisation allows to obtain intense and shapely derivative spectra of analyte while the spectra of others (matrix) undergo quenching. So the application of this technique required careful selection the mathematical parameters as well as working parameters of spectrophotometer. The close dependence of derivatisation results on the instrumental conditions of acquisition of spectra lowers the reproducibility of the elaborated methods. It is possible to obtain the same results only when the same instrumental parameters, given in an experimental section, are used. Otherwise the proposed procedure should be re-optimised and adopted to existing apparatus.

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 changes in its composition requires the re-optimisation and selection of new parameters of derivatisation. Based on the scientific literature, a lack of the uniform protocol of optimisation of the instrumental and derivatisation parameters is noticed. Some authors have used for derivatisation of zero-order spectra the build-in controlling program package and these parameters are not described in published articles. Such presentation of results does not allow the elaborated method reproduction using another kind of software and/or spectrophotometer.

8. Conclusions

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 spectrophotometrs resulted in the extensive number [9–281] 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 [108,145], liquid chromatography [153,156,157], flow analysis [50,53,223] or IR-spectrometry [281]. As derivatisation separates signals hidden in zero-order spectrum, this property allows to join this technique with internal standard (IS) method [267–271]. 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 minimise 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 [282–298] or kinetics [299–307] without disturbing their run.

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