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Recent Applications of Kinetic Methods in Multi-Component Analysis

M. Bahram[a] and A. Afkhami[b,*]
[a]*Department of Chemistry, Faculty of Science, Urmia University, Urmia, Iran*
[b]*Faculty of Chemistry, Bu-Ali Sina University, Hamadan, Iran*

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This review on multi-component kinetic-based determinations covers most publications in this field during the period 2000-2007. The methodologies applied during recent years have been based on differential reaction rates for simultaneous multi-component analysis. The literature shows a great attempt to apply chemometric methods, such as partial least squares regression, artificial neural networks, H-point standard addition and a new method involving mean centering of ratio spectra in this field. This review also describes some applications of advanced multiway analysis such as PARAFAC and NPLS from 2000 in the multi-component kinetic analysis.

Keywords: Kinetic methods, Multi-component analysis, Simultaneous determination, Chemometrics

INTRODUCTION

The development of kinetic methods in analytical chemistry can be attributed to the need to analyze very small amounts of substance, to gain better knowledge of reaction mechanisms and especially the great advancement in instrumental techniques, particularly in the field of computerization [1]. These methods have the advantages of high sensitivity, extremely low detection limit, good selectivity, rapid analysis rate, and inexpensive instruments.

The best classification of kinetic methods is that distinguishing between catalytic and non-catalytic methods. In turn, each of these categories can also be classified according to whether they are applied to the determination of a single species or of several components in a mixture. The present degree of development in kinetic methods, particularly for multi-component determinations relies heavily on recent breakthroughs in instrumental design, especially, the incorporation of microcomputers into analytical chemical configurations as well as the application of chemometric techniques.

Simultaneous kinetic analysis of mixtures is based on the different rates at which two or more species interact with a common reagent, allowing for the simultaneous analysis of species without prior separation. Numerous differential kinetic methods have been reported for the determination of mixtures of closely related components without prior separation.

Three of the more commonly used classical differential kinetic methods include logarithmic extrapolation, proportional equations and the Roberts and Reagan method. Recent approaches avoid the primary shortcomings of classical differential reaction rate methods (*e.g.*, the logarithmic extrapolation and proportional equation), namely their inability to accurately resolve mixtures of components with rate constant ratios approaching unity [2].

Currently, chemometric techniques are increasingly used in multi-component kinetic determinations on the grounds of the high computational power of modern computers, which

*Corresponding author. E-mail: afkhami@basu.ac.ir

allow the processing of the huge amounts of information produced by experimental kinetic work. The advantage of most of chemometric methods over those using classical differential reaction rates is their model-free strategy that has made them powerful techniques in multi-component kinetic determinations.

Reviews on kinetic determination can be found frequently in the literature [3-5] and several reviews on chemometrics have also been published [6-9]. However, the kinetic-based multi-component analysis has seldom been reviewed. The only review on kinetometrics was published by D. Prez-Bendito and M. Silva in 1996 [10].

Most of the kinetic-based methods of analysis reported over the last couple of decades are related to the catalytic kinetic determinations that were applied to a variety of real samples in order to exploit their generally high sensitivity and acceptable selectivity [11-52]. Most of these methods are related to single component analysis based on their catalytic effect on an indicator reaction.

In this article, kinetic-based determinations using chemometric methods reported since the year 2000 are reviewed. Literature reviews show that in this period, in addition to classical techniques, the H-point standard addition method (HPSAM), and some chemometric approaches including mean centering of ratio spectra, partial least squares regression (PLSR), artificial neural networks (ANN) and multiway analysis have been used for the resolution of multi-component mixtures by kinetic methods. Here we describe some of these works.

Proportional Equations Method

The proportional-equations method is a mathematical technique widely used in the differential kinetic resolution of closely related species. This method depends on changing the ratio of two rate constants by varying the reaction medium or the conditions [1].

For the simultaneous analysis of periodate and iodate, their reaction with iodide in the presence of methylene blue allows for spectrophototometric monitoring of the decrease in absorbance at 665 nm [53]. The linear range was 0.1-1.0 and 0.1-1.3 μg ml^{-1} for determination of periodate and iodate, respectively.

Salicylamide and paracetamol in mixture were determined through the spectrophotometric measurement of the increase in absorbance at 510 nm due to their oxidation by Fe^{3+} ion in the presence of 1,10-phenanthroline as an indicator [54]. Two time periods are monitored, one in which only paracetamol is oxidized by Fe^{3+} ion and the other in which both drugs are oxidized by Fe^{3+} ion. The data are evaluated by the proportional equations method, which allows for the simultaneous determination of paracetamol and salicylamide at the respective concentrations ranges of 0.5-20 and 1-40 μg ml^{-1} with relative standard deviations of 3.47 and 2.58%.

Recently, a method has been proposed for the determination of ternary mixtures of periodate-iodate-bromate based on their reaction with iodide ion at different pH values [55]. The absorbance is measured at 352 nm at three sets of reaction conditions. Only periodate reacts with iodide in the first set, periodate and iodate react with iodide in the second set, and in the third set the three ions react with iodide. Thus, individual determinations of periodate, iodate and bromate can be achieved in concentration ranges of 0.05-8.0 μg ml^{-1}, 0.05-5.0 μg ml^{-1} and 0.2-12 μg ml^{-1}, respectively. The data are then evaluated using simultaneous equations solutions.

H-Point Standard Addition Method

Presented in 1988, HPSAM is based on the principle of dual-wavelength spectrophotometry and the standard addition method [56-58]. HPSAM can be applied to the resolution of mixtures using the kinetic profiles of the known spectra of interferent species, thereby, allowing for simultaneous kinetic-based analysis. Widely used for simultaneous analysis of binary mixtures, the requirements for this application of HPSAM include knowledge of the analyte kinetic profiles, which should demonstrate linear dependency *vs*. the concentration of the analyte. Thus, although HPSAM cannot be used for catalytic-based reactions, it can be used for the simultaneous analysis of binary mixtures in their first order, or pseudo first order, competition reactions. Table 1 presents the application of HPSAM for simultaneous kinetic analysis published during the years 2000-2007 [59-75].

Mean Centering of Ratio Spectra

Recently, A. Afkhami and M. Bahram have presented a new approach for the simultaneous analysis of binary and ternary mixtures called mean centering of ratio spectra [76-

Table 1. Spectrophotometric HPSAM for Simultaneous Kinetic Analysis

Species	Basis of the method and comments	Dynamic range	Type of sample	Ref.
Levodopa and carbidopa	The difference in the rate of oxidation of these compounds with Cu(II)-neocuproine system and formation of Cu(I)-neocuproine complex at pH 5.5. The absorbance of the Cu(I)-neocuproine complex was monitored at 453 nm	0.8-4 5 μg ml^{-1} for levodopa and 0.2-1.5 μg ml^{-1} and carbidopa	Pharmaceutical samples	[59]
Fe(II) and Fe(III) or selective determination of Fe(II) in the presence of Fe(III)	The difference in the rate of complex formation between iron in two different oxidation states and methylthymol blue (MTB) at pH 3.5 in mixed cetyltrimethyl-ammonium bromide (CTAB) and Triton X-100 micellar medium	0.25-2.5 μg ml^{-1} for Fe(II)	Spiked real environmental and synthetic samples	[60]
Sb(V) and Sb(III) or Sb(V) in the presence of Sb(III)	The differences between rate of complexation of pyrogallol red with Sb(V) and Sb(III) at pH 2	0.3-2.0 μg ml^{-1} for Sb(V)	River and spring water	[61]
Periodate-bromate and iodate-bromate	The difference between the rates of their reactions with iodide in acidic media	Ratio 1:15-12:1 for periodate-bromate and 15:1-1:15 for iodate-bromate	Water and synthetic samples	[62]
Semicarbazide and hydrazine	The reduction of Cu^{2+} to Cu^{+} by semicarbazide and hydrazine in the presence of neocuproine (Nc) and the subsequent complex formation between Cu^{+} and Nc produced a sensitive spectrophotometric method for indirect determination of semicarbazide and hydrazine. The difference in the rate of reduction of Cu^{2+} with semicarbazide and hydrazine in cationic micellar media is the basis of this method	0.5-3.75 μg ml^{-1} for semicarbazide and 0.5-5 μg ml^{-1} for hydrazine	Synthetic mixtures	[63]
Fe(II) and Fe(III)	The difference in the rate of complex formation of iron in two different oxidation states with gallic acid (GA) at pH 5	0.02-4.50 μg ml^{-1} for Fe(II) and 0.05-5.00 μg ml^{-1} for Fe(III)	Environmental and synthetic samples	[64]

Table 1. Continued

Fe(III) and Fe(II) or selective determination of Fe(III) in the presence of Fe(II)	The difference in the rate of two processes; reduction of Fe(III) with Co(II) and subsequent complex formation of resultant Fe(II) with 1,10-phenanthroline, and direct complex formation between Fe(II) and 1,10-phenanthroline in pH 3 and cetyl trimethyl ammonium bromide, CTAB, micellar media	0.75-5.13 μg ml^{-1} Fe(III) in the presence of excess Fe(II)	Synthetic mixtures	[65]
V(IV) and V(V) or determination of V(IV) in the presence of V(V)	The difference in the rate of complex formation between vanadium in two different oxidation states and xylenol orange at pH 2	0.2-5 μg ml^{-1} for V(IV)	Synthetic mixtures	[66]
Paracetamol (PAR) and *p*-aminophenol (PAP)	PAR and PAP react with Fe(III)/1,10-phenantroline complex (ferriin) and result in the formation of the colored complex, Fe(II)/1,10-phenantroline, and ferroin. The difference in the rate of reaction of PAR and PAP with ferriin makes their simultaneous determination feasible by using HPSAM	0.8-20.0 μg ml^{-1} for PAR and 0.2-10.0 μg ml^{-1} for PAP	Paracetamol formulations	[67]
Beryllium and aluminium	The difference between their rates of reactions with chrome azurol S in cetyltrimethylammonium bromide micellar media	10-200 for beryllium and 10-300 ng ml^{-1} for aluminium	Environmental, geochemical and alloy samples	[68]
Hydrazine and acetylhydrazine	The difference between the rates of their reactions with N,N-dimethylamino-benzaldehyde (DAB) in the presence of sodium dodecyl sulfate (SDS) in acidic media	0.020-0.70 mg l^{-1} for hydrazine and 0.20-5.0 mg l^{-1} for acetylhydrazine	Synthetic mixtures and plasma and water samples	[69]
Ascorbic acid (AA) and L-cysteine (Cys)	Excess amounts of iron(III) is quantitatively reduced to iron(II) by AA or Cys, which in turn, in the presence of phenanthroline (phen), produces a colored iron(II)-phen complex showing maximum absorbance at 510 nm	0.50-4.00 μg ml^{-1} AA and 1.00-8.00 μg ml^{-1} for Cys	-	[70]
V(IV) and Fe(II)	The difference of in the rate of reaction of Fe(II) present in the sample with 1,10-phenantroline and the rate of reaction of F(II) that is produced as a result of the redox reaction of V(IV) and Fe(III)	0.17-6.60 μg ml^{-1} for V(IV) and 0.05-3.85 μg ml^{-1} for Fe(II)	Water, planet tissue	[71]

Table 1. Continued

Citric acid and ascorbic acid	The difference in the rate of their reaction with Cu(II)-ammonia complex	(0.80-1.15) × 10^{-2} mmol l^{-1} for citric acid and 0.70-10.00 mmol l^{-1} for ascorbic acid	Powdered drink and vitamin C	[72]
Isoniazide and hydrazine	The difference between the rates of their reactions with N,N-dimethylaminobenz-aldehyde (DAB) in the presence of sodium dodecyl sulfate (SDS) in acidic media	0.01-0.1 μg ml^{-1} for isoniazide 1.0-80 μg ml^{-1} for hydrazine	Commercially isoniazideformulations	[73]
Nb(V) and Ta(V)	The difference between the rates of their reactions with PAR in the presence of tartaric acid	0.10-5.0 μg ml^{-1} for Nb(V) and 0.5-12.0 μg ml^{-1} for Ta(V)	Alloy samples	[74]
Cr and Co	The difference of their catalytic effect in luminol-hydrogen peroxide chemi-luminescence reaction	0-10 μg ml^{-1}	Water samples	[75]

82]. Inspired by the successive derivative of ratio spectra method using two steps, [83], the mean centering method uses mean centering of ratio spectra instead of derivative of them. By eliminating derivative steps, signal-to-noise ratio is enhanced dramatically. The precise strategy of this method for simultaneous kinetic analysis is delineated in the literature [78-79].

Mean centering of the ratio kinetic profile is well-suited for binary mixtures of Co(II) and Ni(II) based on their complexation reactions with 1-(2′-pyridylazo)-2-naphthol in micellar media [77], iodate-periodate based on their reaction with iodide ion [78], Sn(II) and Sn(IV) based on the difference in the rate of their reaction with pyrocatechol violet at pH 4.0 [82] and ternary mixtures of hydrazine, phenyl hydrazine and acetyl hydrazine based on their condensation reactions with *p*-(dimethylamino)benzaldehyde (DAB) in micellar sodium dodecyl sulfate (SDS) media without any preliminary separation [79].

Partial Least Squares Regression

The methods presented so far are processed using graphical methods, which yield good results provided that the kinetic model for the system concerned is accurately known. This requirement is partly avoided by multivariate calibration methods such as PLSR. PLSR methodology is applicable to non-linear systems and requires no prior knowledge of the rate constants involved [84].

PLSR can be envisioned as a blend of classical least squares regression (CLSR) and principal component regression (PCR). While CLSR focuses on a single factor that correlates data, such as kinetic profiles, with weightings based on the initial concentrations, PCR makes use of factors that best describe the trends, or variance, in the data. PLSR looks for factors that both describe the variance in the data and associate weightings to the data. In this way, PLSR is not as susceptible to error from significant fluctuations in variables that are unrelated to the weights [85].

Widely used to obtain multivariate regression models, several publications on the application of PLSR for simultaneous kinetic analysis are listed in Table 2 [82,86-97].

Recently, L.A. Tortajada-Genaro and P. Campíns-Falcó [98] presented a multivariate standardization for non-linear calibration range in the chemiluminescence determination of chromium. Non-linear principal component regression (NL-PCR) and non-linear partial least square regression (NL-PLS) were chosen for modeling the relationship signal-concentration of transferred registers.

A novel flow-based strategy for implementing differential kinetic analysis was demonstrated in relation to an improved spectrophotometric catalytic determination of iron and vanadium in Fe-V alloys. The method makes use of the

Table 2. Partial Least Squares Regression (PLSR) for Simultaneous Spectrophotometric-Kinetic Analysis

Species	Base of the method and comments	Dynamic range	Type of sample	Ref.
Sn(II) and Sn(IV)	The difference in the rate of their reactions of with pyrocatechol violet at pH 4.0	0.1-1.80 mg l^{-1}	Fruit juice and water	[82]
CN^- and SCN^-	The difference in the rate of the reaction between CN^- and SCN^- ions with chloramine-T in a pH 4.0 buffer solution	10.0-900.0 μg ml^{-1} for CN^- and 50.0-1200.0 ng ml^{-1} for SCN^-	Water	[86]
Se(IV) and Te(IV)	The catalytic effect of these cations on the reaction of toluidine blue with sulfide	0.02-0.24 μg ml^{-1} for Se(IV) and 0.01-0.08 μg ml^{-1} for Te(IV)	Synthetic mixtures	[87]
Iodate and periodate	The reaction pyrogallol red in sulfuric acid media	0.1-12 μg ml^{-1} for iodate and 0.1-14 μg ml^{-1} for periodate	In water	[88]
Fe(II) and Fe(III)	The difference observed in the rates of the complex formation of iron in its two oxidation states with 1,2-naphthaquinone-2-thiosemicarbazone-4-sulphonic acid (NQT4S) at pH 4.0 in cetyltrimethyl-ammoniumbromide (CTAB) as micellar media, respectively	0.10-2.10 μg ml^{-1} for Fe(II) and 0.25-2.25 μg ml^{-1} for Fe(III)	Environmental samples	[89]
Carbidopa, levodopa and methyldopa	The reaction between a common oxidizing agents such as tris(1,10-phenanthroline) and iron(III) complex (ferriin, $[Fe(phen)_3]^{3+}$) in the presence of citrate	0.2-7.0 μg ml^{-1} for carbidopa, 0.2-6 μg ml^{-1} for levodopa and 0.1-6 μg ml^{-1} for methyldopa	Human serum, pharmaceutical sample	[90]
Iodate and periodate	The method was established on the different kinetic behaviors of the analytes which react with starch-iodide in the presence of sodium chloride in sulfuric acid medium	0.1-1.2 mg l^{-1} for both iodate and periodate		[91]

Table 2. Continued

Pesticides, carbaryl and phoxim	The inhibitory effect of the pesticides on acetylcholinesterase (AChE) and the use of 5,5′-dithiobis(2-nitro-benzoic) acid (DTNB) as a chromo-genic reagent for the thiocholine iodide (TChI) released from the acetyl-thiocholine iodide (ATChI) substrate	detection limits of carbaryl and phoxim were 4.7 and 0.59 μg l^{-1}, respectively	Spiked town-water	[92]
Cobalt(II) and copper(II)	The catalytic effect of Co^{2+} and Cu^{2+} on the chemiluminescence reaction of luminol-H_2O_2	Co:0.0002-0.4 and Cu^{2+}:0.02-20 μg ml^{-1}	Real water samples	[93]
Glucose (GLU), fructose (FRU) and lactose (LAC)	Their oxidative reaction with potassium ferricyanide ($K_3Fe(CN)_6$) as the oxidant. The reaction data were recorded at the analytical wavelength (420 nm) of the $K_3Fe(CN)_6$ spectrum	2.96-66.7 mg l^{-1} for glucose, 3.21-67.1 mg l^{-1} for fructose and 4.66-101 mg l^{-1} for lactose	Commercial food samples	[94]
Levodopa and benserazide	Their oxidation reaction with KIO_4 in an acidic medium. Both species instantly oxidize, giving rise to compounds which present maximum values of absorbance close to 400 nm	$(2.4\text{-}4.0) \times 10^{-4}$ mol l^{-1} for levodopa and $(4.6\text{-}7.8) \times 10^{-5}$ mol l^{-1} forbenserazide	Commercial, pharmaceutical preparations	[95]
Acetaminophen and phenobarbital	The different kinetic rates of the analytes in their oxidative coupling reaction with 3-methylbenzothiazolin-2-one hydrazone (MBTH) in the presence of hydrochloric acid and the Fe(III) oxidant. The absorbance was measured and recorded from 440 to 740 nm every 60 s from 15 to 435 s	2.00-20.00 mg l^{-1} for both analytes	Pharmaceutical preparations	[96]
Ascorbic acid and L-cysteine	These compounds react differentially with Fe(III) in neutral medium and the product of reduction, Fe(II), will form a colored compound with chromogenic reagent 1,10-phenanthroline, (monitored at 510 nm)	2.00-11.82 μg ml^{-1} for ascorbic acid and 1.50-14.99 μg ml^{-1} for L-cysteine	Pharmaceutical preparations	[97]

influence of Fe(II) and V(IV) on the rate of iodide oxidation by Cr(VI) under acidic conditions, thus requiring the Jones reductor. The sample is inserted into an acidic KI stream that also functions as carrier stream, and a Cr(VI) solution was added by confluence. Performed during sample passage through the detector, each successive measurement relates to a different yet reproducible condition for reaction development, with data treatment involving multivariate calibration by the PLS algorithm [99].

Rosa García *et al*. [100] presented a method to enable multi-component determination using addition-generated reagent profiles and PLSR. The oxidation of cysteine, methionine and homocysteine with dichromate in acidic medium was used as the chemical system for experimental verification of some theoretical suppositions. The methodology takes advantage of the differences in kinetic behavior. The continuous addition of the reagent dichromate to a sample of amino acids provides experimental data when the visible signal from dichromate is followed over time with a diode array spectrophotometer typically using concentrations of amino acids between 10^{-4} and 10^{-3} M. Some validation with pharmaceutical products has been accomplished.

The use of the Fenton's reagent (FR), a mixture of H_2O_2 and Fe^{2+}, for the kinetic determination of individual chemical species was proposed by G. López-Cueto and coworkers [101]. The potential of this reagent arises from the oxidant power of intermediate species generated during the slow oxidation of Fe^{2+} by H_2O_2, but there are very few analytical applications of the reagent in the literature. The oxidation of organic compounds (known as the Fenton reaction) is actually an induced chain reaction that proceeds to an extension. As the process is influenced by the reaction conditions, some optimizations have been made for the analytical application. The pesticide atrazine has been used as an analyte to test the analytical possibilities of the FR, with PLS applied to the reaction profiles between 206 and 270 nm as an algorithm in designing the calibration model. Using atrazine concentrations from 0.46 to 13.4 × 10^{-5} M for calibration, mean errors under 2.5% both for calibration and validation were achieved. The method has been applied for the determination of atrazine in several commercial atrazine-based pesticide preparations.

The simultaneous kinetic determination of cobalt, nickel, and iron using PCR and PLS methods was discussed by I.A. Pettas and M.I. Karayannis [102]. PCR and PLS extract information using the kinetic differences between the complexes of these metals after reacting them with a common ligand. Stopped-flow (SF) combined with charged couple device (CCD) detection produces massive quantities of data requiring the use of data-reduction techniques. These methods have been effectively used in the simultaneous determination of these metals in alloys.

Guillermo López-Cueto *et al*. [103] presented a method using PLS analysis of multiwavelength reaction profiles, acquired by the adding a reagent continuously to a binary mixture of analytes, resulting in fast reactions. The methodology is effective in the simultaneous determination of constituents of the mixture.

Octacyanomolybdate(V) [Mo(V)] has been used as a reagent for mixtures of hydroquinone (HQ) and pyrogallol (PG) in acidic medium. When the reaction profiles are followed spectrophotometrically at several wavelengths, and they are handled with PLS, the mixture can be resolved. The final spectrum of the mixture, after reaction with Mo(V), is enough to predict the HQ concentration; however, in the case of PG, successive spectra along the reaction are necessary to properly predict the concentration.

A fluorometric-enzymatic method for bilirubin, based on chemically modified bilirubin-oxidase (BOX) and multivariate calibration, was studied by Yolanda Andreu *et al*. [104]. The chemical derivatization of BOX with a fluorescein derivative (FS) results in the chemically modified enzyme (BOX-FS), possessing excitation and emission maxima of 487 and 520 nm, respectively. When oxygen oxidizes bilirubin, in the presence of BOX-FS, the change in the fluorescence of the modified enzyme depends on the concentration and type of bilirubin(free, conjugated and albumin-bonded bilirubin). This effect was used for analytical purposes for the determination of bilirubin up to 12 mg l^{-1}). PLSR was used for the simultaneous determination of direct and total bilirubin from a single run. Furthermore, a semi-quantitative speciation of the three forms of bilirubin may also be simultaneously obtained.

Artificial Neural Network

ANNs have been used frequently for simultaneous kinetic analysis. As mentioned for the PLS method, ANNs requires no prior knowledge of the rate constants involved. In addition,

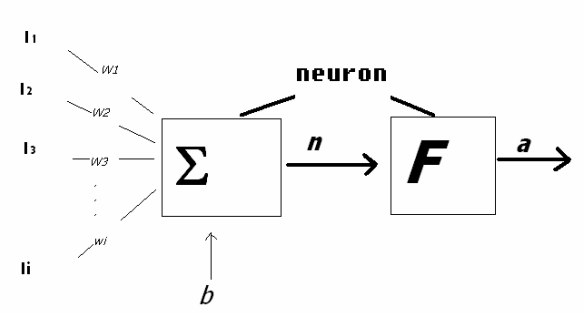

Fig. 1. Schematic description of a neuron.

ANNs are the least restrictive choice regarding reaction conditions; in fact, the sole requirement for an analytical system to be accurately defined by an ANN is the use of a large enough number of calibration samples. The primary element of an ANN is the neuron. Arranged in input and output layers sandwiching one or more "hidden" processing layers, neurons act as weighted transfer functions and can have single or multiple inputs. Applying a weighted sum of their inputs, processing neurons transfer the result to the output. Often the transfer function is non-linear, with sigmoid functions most often being used. A diagram of a neuron is shown in Fig. 1, where **Ii** is an input, **Wi** is the weighting associated with input I, **b** is the bias introduced into the summation, **n** is the output of the weighted sum and **a** is the output of the transfer function (**F**), following the formula:

$$a = F (Wi + b)$$

During the training or calibration phase, the weightings are adjusted to accurately fit the calibration data. Often principle components (PCs) are used as inputs to the network instead of experimental variables, immensely reducing the necessary number of neurons [85].

Some applications of ANN for simultaneous kinetic analysis are listed in Table 3 [90-92,94,96,105-114]. For most of the presented works, principal component analysis has been used for data compression prior to ANN analysis.

It has been shown that, in many cases, ANNs give results similar to PLSR and PCR. While the major advantage of ANNs is their applicability for analysis of non-linear data, they do have the disadvantage, however, of requiring more calibration samples for proper training [85,115,116].

Multiway Analysis

Multiway analysis is concerned with higher order data, for example as defined by Henk Kiers [117]. Higher-order data can be arranged in boxes as opposed to two-way data and matrices, which can be arranged in Tables. Multiway data often results from modern instrumental developments, therefore, recent multiway data analysis is typically applied to new advanced instrumental data. For example, kinetic data collection using a photo-diode array spectrophotometer can produce three-way data. However, in some situations, multiway data are rearranged into matrices and analyzed using ordinary multivariate data analysis and two-way analysis [118].

Various descriptions of multiway analysis methods are found in the literature [119,120]. In the following section, reports on multiway analyses published during 2000-2007 for simultaneous multi-component kinetic analysis will be reviewed.

The simultaneous determination of levodopa and benserazide in pharmaceutical formulations has been described, based on the application of multidimensional PLSR to the kinetic-spectrophotometric data provided by diode-array detection within a stopped-flow injection method where analytes react with periodate [95].

A method for the simultaneous determination of the pesticides, carbofuran, isoprocarb and propoxur in fruit and vegetable samples has been investigated and developed. Based on reaction kinetics and spectrophotometry, results are interpreted with the aid of chemometrics. The analytical method relies on the differential rates of coupling reactions between the hydrolysis product of each carbamate and 4-aminophenol in the presence of potassium periodate in an alkaline solution. The optimized method was successfully tested by analyzing each of the carbamates independently, and linear calibration models have been described. In ternary mixtures of carbamates simultaneous determination uses kinetic and spectral data processed either by three-way data unfolding or decomposed by trilinear modeling. ANNs, N-way partial least squares (NPLS), parallel factor analysis (PARAFAC) calibration models constructed using synthetic ternary mixtures of the three carbamates have been validated with a separate set of mixtures [114].

For the purpose of quantifying adrenaline and

Table 3. Artificial Neural Network (ANN) for Simultaneous Spectrophotometric-Kinetic Analysis

Species	Base of the method and comments	Dynamic range	Type of sample	Ref.
Carbidopa, levodopa and methyldopa	The reaction between a common oxidizing agents such as tris(1,10-phenanthroline) and iron(III) complex (ferriin, $[Fe(phen)_3]^{3+}$) in the presence of citrate	0.2-7.0 μg ml^{-1} for carbidopa, 0.2-6 μg ml^{-1} for levodopa and 0.1-6 μg ml^{-1} for methyldopa	Human serum, pharmaceutical sample	[90]
Iodate and periodate	The method was established on the different kinetic behaviors of the analytes which react with starch-iodide in the presence of sodium chloride in sulfuric acid medium	0.1-1.2 mg l^{-1} for both iodate and periodate	-	[91]
Pesticides, carbaryl and phoxim	The inhibitory effect of the pesticides on acetylcholinesterase (AChE) and the use of 5,5′-dithiobis(2-nitrobenzoic) acid (DTNB) as a chromogenic reagent for the thiocholine iodide (TChI) released from the acetylthiocholine iodide (ATChI) substrate	Detection limits of carbaryl and phoxim were 4.7 and 0.59 μg l^{-1}, respectively	Spiked town-water	[92]
Glucose (GLU), fructose (FRU) and lactose (LAC)	Their oxidative reaction with potassium ferricyanide ($K_3Fe(CN)_6$) as the oxidant. The reaction data were recorded at the analytical wavelength (420 nm) of the $K_3Fe(CN)_6$ spectrum	2.96-66.7 mg l^{-1} for glucose, 3.21-67.1 mg l^{-1} for fructose and 4.66-101 mg l^{-1} for lactose	Commercial food samples	[94]
Acetaminophen and phenobarbital	The different kinetic rates of the analytes in their oxidative coupling reaction with 3-methylbenzothiazolin-2-one hydrazone (MBTH) in the presence of hydrochloric acid and the Fe(III) oxidant. The absorbance was measured and recorded from 440 to 740 nm every 60 s from 15 to 435 s	2.00-20.00 mg l^{-1} for both analytes	Pharmaceutical preparations	[96]
Cu(II) and Ni(II)	The catalytic action of these ions on the reduction of resazurin by sulfide	0.5-6 mg l^{-1} for Cu(II) and 1-15 mg l^{-1} for Ni(II)	Electroplating solutions	[105]
Tryptophan (Trp), tyrosine (Tyr) and histidine (His)	The different kinetic rates of the analytes in their oxidative reaction with potassium ferricyanide ($K_3Fe(CN)_6$) in alkaline medium	10-55 μg ml^{-1} for tryptophan, 10-60 μg ml^{-1} for tyrosine and 10-40 μg ml^{-1} for histidine	Synthetic and water samples	[106]

Table 3. Continued

Glycine and lysine	The difference in the rate reaction of glycine and lysine with 1,2-naphthoquinone-4-sulfonate (NQS) in slightly basic medium	1-25 μg ml^{-1} for glycine: 1-19 μg ml^{-1} for lysine	Synthetic samples	[107]
Sulfide and thiocyanate	The catalytic effects on the reaction between iodine and azide	60-700 ng ml^{-1} for sulfide and 20-400 ng ml^{-1} for thiocyanate	Tap, waste and river waters	[108]
Sulfite and sulfide	The reaction between brilliant green (BG) as a colored reagent and sulfite and/or sulfide in buffered solution (pH 7.0) and monitoring the changes of absorbance at maximum wavelength of 628 nm	0.05-3.6 μg ml^{-1} for both analytes	Water samples	[109]
V(IV) and Co(II)	The difference of the chemical reaction rate of V(IV) and Co(II) with Fe(III) in the presence of chromogenic reagent, 1,10-phenanthroline. The reduced product of the reaction, Fe(II), can form a colored complex with 1,10-phenanthroline and make a visible spectrophotometric signal for indirect monitoring of the V(IV) and Co(II) concentrations	0.1-4.0 μg ml^{-1} for both analytes	Synthetic and water samples	[110]
V(IV) and Fe(II)	V(IV) and Fe(II) were simultaneously determined based on their catalytic effects on the redox reaction of bromate with methyl orange	50 -500 ng ml^{-1} for V(IV) and 100-1000 ng ml^{-1} for Fe(II)	Tap water and mineral water samples	[111]
Se(IV) in the presence of Te(IV)	Catalytic effect of Se(IV) and inhibition effect of Te(IV) on the oxidation reaction of hydrazinium dichloride with potassium bromate in the presence of Ponceau S as an indicator	50-400 ng ml^{-1} for Se(IV) and 100-2000 ng ml^{-1} and Te(IV)	Tap water and mineral water samples	[112]
Cysteine and homocysteine	The complexation of bivalent iron with 2,2'-bipyridin (bipy). Iron(III) is quantitatively reduced to iron(II) with cysteine and homocysteine in the presence of 2,2'-bipyridin producing iron(II)-bipy complex (λ_{max} = 522 nm) and it can be used as a visible spectrophotometric signal for indirect simultaneous determination of the cysteine and homocysteine concentrations	0.10-5.50 μg ml^{-1} for cysteine and 0.1-5.00 μg ml^{-1} for homocysteine	-	[113]
Carbofuran, isoprocarb and propoxur	Reaction kinetics and spectrophotometry; results are interpreted with the aid of chemometrics	About 0.6-10.0 mg l^{-1} of each pesticide	Fruit and vegetable samples	[114]

noradrenaline concentrations from mixtures of catecholamine standards, a method has been shown to derive selectivity from the different rates, at which the fluorescing 3,5,6-trihydroxyindole derivatives (lutines) of catecholamines are formed and degraded. Measured at consecutive time points, fluorescence landscapes for every sample create a four-way data array. It has been shown that the raw dataset can be dramatically reduced in size without losing significant information speeding up calculation and reducing the instrumental performance requirements. The data follow a two-component four-way PARAFAC model, from which quantitative information has been also obtained. Two-component multilinear PLSR (NPLSR) was also employed for the quantification of the catecholamines. The results for PARAFAC and NPLSR were very similar with root mean squared errors of cross-validation (RMSECV) ranging from 24 to 30 nmol l^{-1} [121].

The bidimensional multivariate regression procedures, multiple linear regression (MLR), PCR, PLS continuum regression (CR), several N-way methods such as N-way PLS (nPLS) and PARAFAC, have been tested as calibration methods for the kinetic-spectrophotometric determination of ternary mixtures in a pseudo first-order kinetic system. The different calibration procedures have first been applied to computer simulated kinetic-spectrophotometric data where the effect of spectral overlap and the differences in the kinetic constants were evaluated at a low level of experimental noise. They were later applied to the SF kinetic-spectrophotometric simultaneous resolution of Co(II), Ni(II) and Ga(III) using 4-(2-pyridylazo)resorcinol (PAR) as a chromogen. In spite of a high degree of spectral overlap and similar rate constants, accurate estimations of concentrations with relative standard errors of prediction of about 8% have been obtained. The influence of experimental noise on the 3-component system justifies the difference between simulation and experimental results for various calibration procedures. Where PARAFAC and MLR did not allow the resolution of the proposed 3-component system, CR provided slightly better results than those obtained by PLS, PCR and NPLS [122].

Other Methods

A simultaneous kinetic determination, based on measurement of the rate at two points during the course of the successive reactions, is referred to as a two-rate method. The performance of the method is evaluated by successive reactions of epinephrine and norepinephrine with potassium hexacyanoferrate(III) [$K_3Fe(CN)_6$] for the determination of binary mixtures of the two catecholamines. Mixtures of the two catecholamines (>2 × 10^{-5} mol l^{-1} each) with different ratios are resolved within a relative error of <5%, while other data processing methods fail to give reliable results [123].

Another simultaneous kinetic method employing the measurement of two rates at two points during the course of the successive reactions also applied to the determination of epinephrine and norepinephrine [124], involves the reaction of tris(1,10-phenanthroline)iron(III) with epinephrine and norepinephrine at similar concentrations (10^{-5} to 10^{-4} mol l^{-1}).

An additional two-rate method and differential kinetic method for simultaneous analysis of ascorbic acid (AA) and L-cysteine (Cys) takes advantage of their reaction with Fe(III) in neutral medium [125]. Here, the product of reduction, Fe(II), also forms a colored compound with the chromogen 1,10-phenanthroline and is monitored at 510 nm.

Simultaneous determination of copper(II) and zinc(II) mixtures made use of a flow injection (FI) arrangement with a synchronized double injection of the same sample solution and a single spectrophotometric detector. Employing a metal-zincon complex formation, kinetic differences in the ligand substitution reaction of these complexes with aminopolycarboxylic acids [126], gave a linear range of 0.2-9.7 μg ml^{-1} for zinc and 0.2-3.5 μg ml^{-1} for copper.

Grudpan *et al*. [127] proposed a simultaneous determination of phosphate and silicate by a technique involving a laboratory-made semi-automatic flow injection analyzer in the stopped mode with a LED-based photometer. Based on the kinetic separation of phosphate and silicate using molybdenum blue, the proposed procedure has been applied to the analysis of water samples.

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