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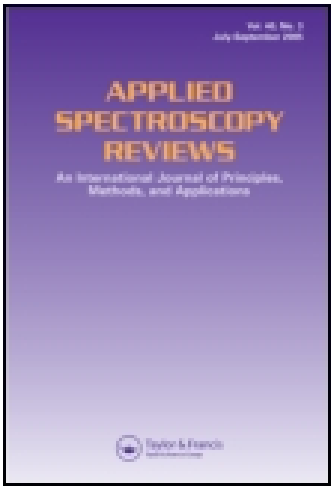

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H-Point Standard Addition Method (HPSAM) in Simultaneous Spectrophotometric Determination of Binary Mixtures: An Overview

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H-Point Standard Addition Method (HPSAM) in Simultaneous Spectrophotometric Determination of Binary Mixtures: An Overview

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Abstract: *The H-point standard addition method (HPSAM) is a modification of the standard addition method that transforms the incorrigible error resulting from the presence of a direct interferent in the determination of an analyte into a constant systematic error. This error can then be evaluated and eliminated. The method was established for resolving strongly overlapping spectra of two analytes and permits both proportional and constant errors produced by the matrix of the sample to be corrected directly. The technique is based on the principle of dual-wavelength spectrophotometry and the standard addition method. The application of the method requires only two wavelengths, and the analytical signal caused by one of the species should be constant and that of the other should differ as much as possible. This overview discusses both the theoretical and practical aspects of HPSAM applications.*

Keywords: H-point standard addition method, metal ions analysis, pharmaceutical analysis, binary mixtures

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Introduction

The requirements of a satisfactory analytical method are usually manifold, but certainly selectivity must be counted among the most important. Hence, there has always been interest in procedures that can improve the selectivity of the measurement methods themselves.

Quantitative analyses often involve the spectrophotometric resolution of mixtures of two components with partly overlapping spectra—the greater the extent of overlap, the more difficult the resolution is rendered. Not surprisingly, this topic has been the subject of a number of chemometric studies originally intended for the resolution of binary mixtures and later extended to others of three or more components (1, 2).

Derivative spectroscopy has been profitably applied to quantitative analytical applications in which the presence of a broad, unstructured background spectrum overlaps the bands of interest (3, 4). Some new calibration techniques have arisen from established

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chemical methods for modeling well-known phenomena, such as the direct multicomponent modeling of mixtures and fitting by different statistical approaches such as ordinary multiple regressions (5). The H-point standard addition method (HPSAM) method is a modification of the standard addition method, which was proposed in order to obtain an unbiased analyte concentration when both analyte and interferent are present in a sample (6).

In 1935, Foster and coworkers (7) presented the first application of a standard addition method followed by many other papers, some of which are presented below.

The aim of this report is to demonstrate the usefulness of HPSAM in all instances where the determination of two analytes requires the use of an absorbent reagent, particularly when it does not present a constant analytical signal because of its consumption. The method can calculate the concentration of one species from spectral data at two wavelengths where the other species presents the same absorbance relationship. This review focuses on HPSAM applications used for theoretical and practical aspects.

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Theoretical Aspects

Chemometric methods are defined as the chemical discipline that uses mathematical and statistical methods to relate measurements made on a chemical system to the state of the system and design or select optimal measurement procedures and experiments (8). HPSAM is a chemometrics methods often used in analytical chemistry. A modification of the standard additions method, presented by Foster et al. (7), was proposed in 1988 by Reig and Falco (6) in order to obtain an unbiased analyte concentration when both analyte and interferents are present in a sample. It also permits the determination of an interferent known to be present. HPSAM is based on the principle of dual-wavelength spectrophotometry and the standard addition method (6, 9). Although the standard addition method can remove the error resulting from the sample matrix, it cannot remove the constant error resulting from other components in the system (9). The greatest advantage of HPSAM is that it can remove the presence of an interference and reagent blank (10–14). HPSAM can determine the two components simultaneously with extensive or even coincident overlapping spectra (15). However, HPSAM can be applied in the absence of a constant bias, only the proportional bias is eliminated by this method (9) in quantifying interferents. The principles of the method should be followed. At the two selected wavelengths, the analyte signal should be linear with its concentration, whereas the interferent signals should remain equal, even if the analytical concentrations are changed. The analytical signals of the mixture composed of the analyte and interferent should be equal to the sum of the individual signals of the two compounds (Figure 1). In addition, the slope difference of the two straight lines obtained at λ_1 and λ_2 should be as large as possible, in order to obtain good accuracy (16) (Figure 2). The method uses the analytical signal data at two selected wavelengths, giving two straight lines that have a common point with coordinates H $(-C_H$ & $A_H)$, where $-C_H$ is the unknown analyte concentration and A_H is the analytical signal due to an interferent.

The theory of HPSAM can be explained as presented by Reig and Falco (6, 9): The occurrence of a constant bias due to the sample matrix (total Youden blank, TYB) was always considered in developing the method. The statistically calculated TYB was virtually zero. This is also frequently the situation with more complex samples. Moreover, when the analyte signal is only modified by the matrix effect, HPSAM allows both proportional and constant bias errors to be corrected and the latter to be calculated. In this event, the two selected wavelengths can be chosen arbitrarily due to the very nature of the TYB, and an unbiased analyte concentration can be obtained by performing a single set of experiments

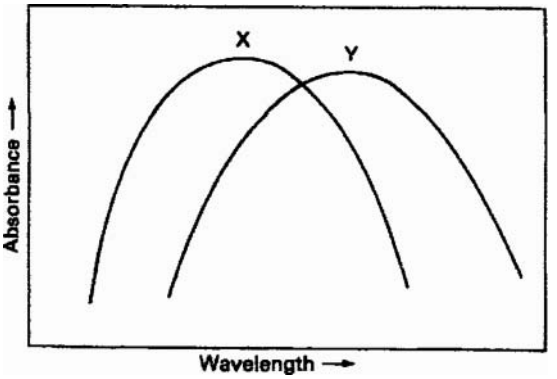

Figure 1. Absorption spectra of two compounds; *X* is the analyte and *Y* is the interferent.

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and applying the multipoint data technique. Application of the corrigible error correction (CEC) technique (17, 18), on the other hand, entails carrying out two sets of experiments.

The above considerations are expressed theoretically below.

Let us consider an unknown containing an analyte *X* and an interferent *Y* subject to a constant bias error (TYB). As previously mentioned, two wavelengths (λ_1, λ_n) from the analyte and the interferent spectra are chosen and relate them with their corresponding absorbance values through the following expressions:

$$A_i = b_i + m_i\lambda_j \left(\lambda_1 \geq \lambda_j \geq \lambda_n\right) \tag{1}$$

for the analyte (*X*) and

$$A' = b + m\lambda_j \, (m = 0) \tag{2}$$

for the interferent (*Y*), where *b* and *m* are the intercepts and slopes of the corresponding straight lines, respectively. The subscript *i* refers to the different solutions for *m* additions

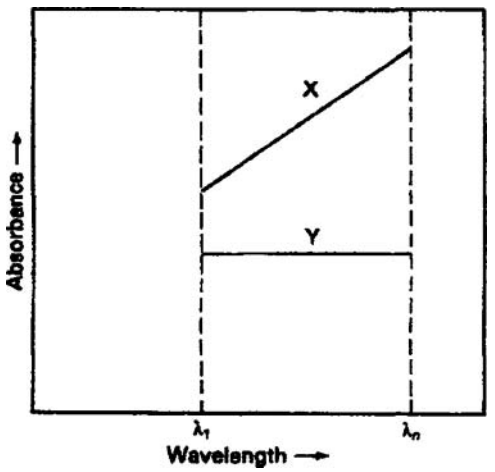

Figure 2. Required shape of the spectra of the analyte *X* and the interfering *Y* in the wavelength interval λ_1–λ_2.

of the analyte concentration prepared in order to apply the standard additions method and the subscript *j* indicates a wavelength in the λ_1–λ_n range. This condition is fulfilled because the interferent features a constant absorbance at the two selected wavelengths. Let us also consider the TYB, which will normally be the same at the two selected wavelengths; that is,

$$A'' = \text{TYB} \tag{3}$$

Hence, the overall equation corresponding to the first solution ($i = 0$) used to apply the method of standard additions (MOSA), which only contains the sample with no added analyte, will be

$$A_0 + A' + A'' = b_0 + b + m_0\lambda_j + \text{TYB} \tag{4}$$

The plot of *A versus* λ is shown in Figure 3b.

The MOSA starts by calculating the unknown concentration by extrapolation when the ordinate value is zero. Taking this into account, $A_i = 0$ for $m_i = m = 0$; this is the H-point, as shown in Figure 3a, at which the slope of the straight line of the $A = f(A)$ plot for the analyte equals that of the interferent. The overall equation will thus be reduced to:

$$b + \text{TYB} = A' + A'' = A_H \tag{5}$$

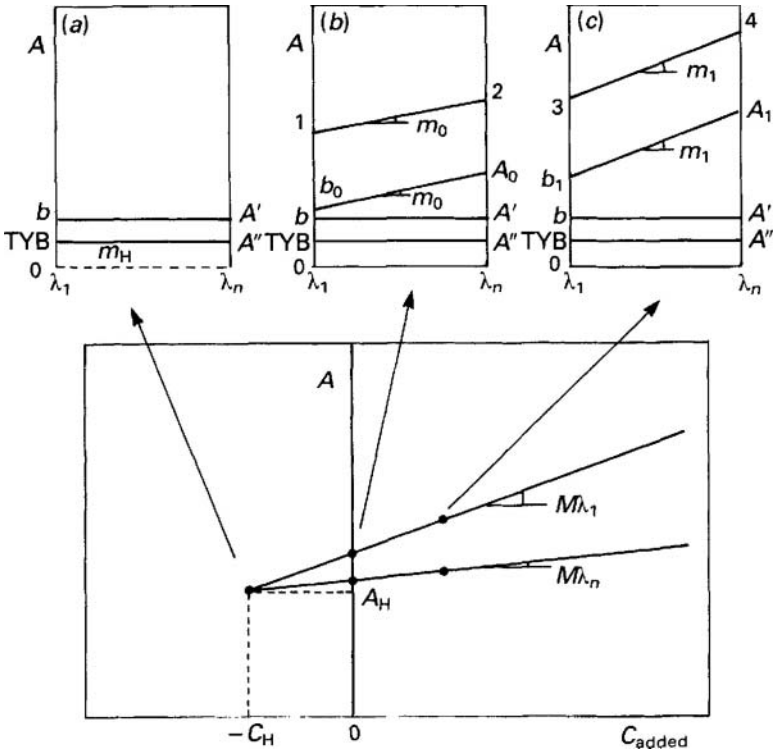

Figure 3. H-point standard additions plot.

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Obviously, for TYB = 0, $b = A' = A_H$ and, therefore, b can be related to the interferent concentration. Hence, in the absence of the interferent, TYB $= A'' = A_H$ and TYB can be determined readily.

Let us now consider the instance involving two constant systematic errors. The $A = f(\lambda)$ plot, corresponding to the first addition of the MOSA, is shown in Figure 3c and the overall equation is

$$A_1 + A' + A'' = b_1 + b + \text{TYB} + m_1\lambda_j \tag{6}$$

These concepts can be clarified by plotting the absorbance as a function of the added analyte concentration (C_i) at the two selected wavelengths (Figure 3). The MOSA equation will be

$$A\lambda_1 = b_i + b + M\lambda_1 C_i + \text{TYB} \tag{7}$$

for λ_1, and

$$A\lambda_n = A_i + A' + M\lambda_n C_i + \text{TYB} \tag{8}$$

for λ_n, where $M\lambda_1$ and $M\lambda_n$ are the slopes of the MOSA plots.

The H-point is common to the two MOSA plots and is given by:

$$b_i + b + M\lambda_1 C_i + \text{TYB} = A_i + A' + M\lambda_n C_i + \text{TYB} \tag{9}$$

or

$$C_i\,(M\lambda_1 - M\lambda_n) = A_i + A' - b_i - b \tag{10}$$

As $A' = b$; then

$$C_i = (A_i - b_i)\,/\,(M\lambda_1 - M\lambda_n) = Cx\,(M\lambda_n - M\lambda_1)\,/\,(M\lambda_1 - M\lambda_n) = -C_x = -C_H \tag{11}$$

The analyte concentration can thus be obtained free from constant and proportional bias errors.

By substituting the C_i value obtained into Eqs. (7) and (8), A_H can be determined through Eq. (12):

$$A_H = b_i + b + M\lambda_1\,(-C_H) + \text{TYB} \tag{12}$$

As $b_i = M\,\lambda_1 C_H$, then:

$$A_H = b + \text{TYB} \tag{13}$$

Hence, it is possible to obtain an unbiased analyte concentration directly on application of the HPSAM if the constant bias is the same at the two selected wavelengths.

The interferent concentration will be free from proportional, but not from constant, bias, which requires evaluation by Youden's method (19, 20) or the CEC technique (6, 9). however, it is not essential that the TYB be the same at the two selected wavelengths because it can be evaluated at both and later used to construct the HPSAM graph by plotting $A\lambda_1 - \text{TYB}\lambda_1$ and $A\lambda_n - \text{TYB}\lambda_n$, as a function of the added concentration.

HPSAM was applied to mixtures of dyes and metal ions and to organic compounds. All samples were found to have a TYB of zero. However, multicomponent mixtures and samples with complex matrices require correction of the constant bias by applying the

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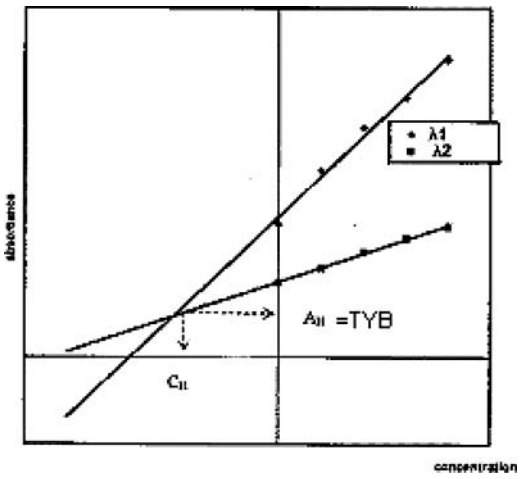

Figure 4. Plot of the H-point standard additions method. C_{added} is the added analyte concentration.

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Youden method or the CEC technique or even HPSAM by substituting the added analyte concentration by the added sample concentration (Figure 4). The A_H value thus obtained is equivalent to the TYB if this is equivalent at the two selected wavelengths. In this way, HPSAM, like the Youden method and the CEC technique, permits the occurrence of TYB to be detected; in addition, it allows one to determine whether it is constant at the two selected wavelengths.

Applications of HPSAM in Spectrophotometric Methods for Determination of Metal Ions IN Binary Mixtures

Many HPSAM applications known for the determination of metal ions in binary mixtures are related to water analysis. Metals are often introduced into the water cycle from industrial waste. Most of these ions are toxic to humans, and their release must be carefully monitored and controlled.

From a physiological point of view, calcium and magnesium, along with sodium and potassium, are the most important ions affecting cardiology, due to their role in nervous impulse conduction and cell contraction. The determination of magnesium and calcium in waters is important, because they are responsible for water hardness, and their presence at high concentrations lowers the quality of drinking waters. Taking into consideration these aspects their simultaneous determination is very useful, so Gómez et al. (21) presented, several reagents for spectrophotometric determination of these cations. They also proposed an flow injection analysis (FIA) method for magnesium and calcium determination in mineral water with arsenazo (III) at pH 8.5. The selected pairs of wavelengths were those with the highest slope in the calibration line for Ca(II) and a correlation coefficient equal or higher than 0.995. The calibration graphs best fitted to a two-order polynomial, and no dependence of the signals for Ca(II) on the Mg(II) concentration in the sample was observed (i.e., for the increment $A_{655} - r_{YZ}A_{688}$ the curve equation was $y = -0.0022\,x^2 + 0.0877x - 0.0053$, $r^2 = 0.997$, $n = 25$).

The majority of the elements and substances present in environmental samples occur in different physicochemical forms or species. The identity and concentration of the respective

element species in a given matrix are largely responsible for its mobility, bioavailability, and toxicological impact, rather than the total concentration (22–24).

Chromium can be found as Cr(III) and Cr(VI). Cr(III) is less toxic than Cr(VI). The toxicity of Cr(VI) in aerosol form has been demonstrated; it causes damage to the skin and upper respiratory system and can result in lung cancer. However, the toxic effects of Cr(VI) in drinking water have been documented (25). The distribution curves of the different chemical forms of Cr(VI) are a function of the total Cr(VI) concentration and pH. Tortajada-Genaro et al. (26, 27) proposed a new method based on the location of linear spectral intervals for the global interferent in the entire spectral region measured using generalized H-point standard addition method (GHPSAM). In this case, the selection of the three wavelengths was based on the following criteria: a distance between wavelengths of greater than 4 nm, a determination coefficient $r^2 > 0.995$, and the greatest slope for the calibration curve ($A_k - qA_j - pA_l$ vs. c) for each form of the analyte individually. The predictions were obtained by means of the slope and the intercept of the corresponding curves employing the selected absorbance increments.

Simultaneous determination of Cr(VI) and Fe(III) by partial least squares (PLS) calibration and HPSAM was described by Abdollahi (28). Mixed reagents of diphenylcarbazide and 1,10-phenanthroline in a nonionic micellar solution of Triton X-100 were used as a selective chromogenic system for determination of Cr(VI) and Fe(III). The presence of a micellar system allows one to eliminate the previous solvent extraction step that is necessary for the determination of slightly soluble metal complexes in the absence of micelles. The total relative standard error for applying the PLS method to 15 synthetic samples in the ranges 0.20–6.00 μg mL^{-1} Cr(VI) and 0.20–8.00 μg mL^{-1} was 1.5%. The results of applying the HPSAM showed that Cr(VI) and Fe(III) can be determined simultaneously with weight concentration ratios of Cr(VI) to Fe(III) varying from 15:1 to 1:30 in the mixed sample.

Iron is the fourth most abundant element in the Earth's crust. Determination of the oxidation state of iron in pharmaceutical samples is of great importance. Fe(II) is important for the transport and storage of oxygen in higher animals by means of hemoglobin and myoglobin and easily absorbed in our body, whereas Fe(III) does not bind to oxygen (29). Zarei et al. (30) proposed two reagents (1,10-phenanthroline and potassium thiocyanate, respectively) that are easily available. They were suggested as two sensitive reagents for simultaneous spectrophotometric determination of Fe(II) and Fe(III) by use of chemometric approaches such as a principal component artificial neural network (PC-ANN), polymerase chain reaction (PCR), and PLS. After parameter optimization, the individual calibration curves were constructed with several points, as absorbance vs. metal ion concentration in the range of 0.40–8.00 μg/mL for Fe(II) and Fe(III). The correlation coefficients for Fe(II) and Fe(III) are 0.9995 and 0.9987, respectively.

Iron is generally considered not to be a toxic metal in groundwater, but when dissolved above 0.3 μg/mL this may result in an unpleasant taste and formation of an unsightly brown suspension when exposed to oxygen. In water it normally exists as Fe^{2+} and Fe^{3+}; the latter is readily removed from water through precipitation. A method for iron determination was proposed by Zendera et al. (31), who suggested a method of iron extraction from water with activated carbon, wood charcoal, and garlic carbon at pH 3.0 and an Fe^{2+}: Fe^{3+} concentration ratio range of 10:1 to 1:15. Taking Fe^{2+} as the analyte the absorbance were measured at 535 and 540 nm, whereas for Fe^{3+} the absorbance was measured at 460 and 530 nm. The recovery (Fe^{2+}/Fe^{3+}) was 94.4/89.5 using activated carbon, 85.0/72.133 for wood charcoal, and 89.34/82.467 for garlic carbon.

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Hasani et al. (32) proposed a method based on the difference in the rate of complex formation of Fe(II) and Fe(III) with methylthymol blue (MTB) under acidic conditions in mixed micellar medium. Surfactants, amphiphilic molecules, which self-assemble to form micelles in solution, are used in all area of chemistry. Many advantages including sensitivity and improved selectivity in analysis can be achieved by the use of micellar system. Many surfactants have been tested: sodium dodecylsulfate (SDS) had no effect on the rate of complexation, and cetylpyridinum chloride (CPC) and cetyltrimethylammonium bromide (CTAB) caused the rate of Fe(III)–MTB complex to become very fast but had no effect on the rate of Fe(II)–MTB complex, so due to too slow rate of Fe(II)–MTB system, no appropriate condition for analysis is obtained. Triton X-100 caused the rate of complex formation of both species to increase. The concentration ranges of Fe(II) and Fe(III) for the calibration graph were 0.03–5 and 0.06–4 μg/mL^{-1}, respectively.

Beryllium and its compounds are very toxic, especially to the lung, skin, and eyes, and at high concentration can cause death (33). Afkhami et al. (34) proposed a new micelle-mediated phase preconcentration method for preconcentration of ultra-trace quantities of beryllium as a prior step to its determination by spectrophotometry. Chrome Azurol S (CAS) and cetyltrimethylammonium bromide (CTAB) were used as chelating agent and cationic surfactant, respectively. A calibration graph was constructed by measuring the absorbance change for the surfactant-rich phase as a function of beryllium concentration at a fixed wavelength of 612 nm. The analytical characteristics of the method are as follows: the limit of detection was 0.75 ng/mL^{-1}, the improvement factor was 36.5, and the relative standard deviation (RSD) for five replicate measurements of 5 ng/mL^{-1} beryllium was 2.1%.

Tin is a toxic metal that could deposit in the human body and the tissue of animals (35). There are mainly two chemical species of inorganic tin (Sn(II) and Sn(IV)) in environmental samples. Sn(II) seems to be more toxic than Sn(IV) (36). Madrakian et al. (37) discussed two different methods for the simultaneous analysis of binary mixtures of Sn(II) and Sn(IV) based on the difference in the rate of complex formation of these metal ions with pyrocatechol violet (PCV) without any preliminary separation. The methods are mean centering of ratio kinetic profiles and PLS methods. In the proposed method, Beer's law was obeyed in the concentration range 0.10–1.80 mg L^{-1} for both Sn(II) and Sn(IV) ions. The mean recoveries for simultaneous determination of these species in binary mixtures were 104 and 101% for Sn(II) and Sn(IV), respectively.

Safavi et al. (38) proposed an HPSAM application applied to kinetic data for simultaneous determination of Vanadium (IV) and V(V) or selective determination of V(IV) in the presence of V(V). The method is based on the difference in the rate of complex formation between vanadium in two different oxidation states and xylenol orange at pH = 2. Vanadium (IV) can be determined in the range 0.2–5 μg/mL^{-1} with satisfactory accuracy and precision in the presence of excess vanadium (V) and other metal ions that rapidly form complexes with xylenol orange under working conditions.

The simultaneous determination of iron and vanadium by HPSAM was described by Abdollahi et al. (39) and Abbaspour and Baramakeh (40). In the first method (39), gallic acid (GA) in a cationic micellar solution of CTAB was used for determination of iron and vanadium in different oxidation states at pH 5. The presence of a micellar system enables total iron and vanadium to be determined with improved sensitivities. The total relative standard error for applying the PLS method to 15 synthetic samples in the ranges 0.20–15.00 μg/mL^{-1} iron and 0.20–8.00 μg/mL^{-1} vanadium was 2.2%. The second method (40) is based on the difference absorbance of formed complex between Fe(III) and pyrogallol in two different wavelength at pH = 6.5. Fe(III) can be determined in the range of

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0.2–23 μg/mL^{-1} with satisfactory accuracy and precision in the presence of excess V(V) and most of other metal ions studied.

Bismuth and antimony belong to group VA of the periodic table. The principle uses of these elements are in the manufacture of alloys, pharmaceuticals, and metallurgical additives (41). Several methods have been reported for the simultaneous determination of Bi(III) and Sb(III) in rock, water, alloys, and biological samples. A new method was described by Afkhami and Zarei (42) in which simultaneous determination was performed with iodide in acidic media in different wavelength pairs, 330 and 337 nm. The calibration graph was linear in the range 0.5–10.0 mg/L^{-1} Bi(III) and 0.5–8.0 mg/L^{-1} Sb(III), respectively. The results showed that Bi(III) and Sb(III) can be determined simultaneously with concentration ratios of 15:1 to 1:20. The RSDs for four replicate measurements of the mixture of 8.0 mg/L^{-1} Bi(III) and 5.0 mg/L^{-1} Sb (III) were 1.02 and 2.7%, respectively.

Antimony is a toxic element present in the environment (43). The standard addition method could remove the error resulting from the sample matrix, but it could not remove the constant error resulting from other components in the system. For kinetic determination by applying HPSAM, two variants for the treatment of kinetic data can be use. One variant is used when one component reacts faster than the other or the latter does not take place at all. The second variant is used for two components when their rate constants are time dependent. Abbaspour et al. (44) used the first variant for treatment of kinetic data based on HPSAM when, at pH 2.0, Sb(III) formed a complex with pyrogallol red rapidly, whereas Sb(V) formed a complex very slowly. The concentration ranges of Sb(V) and Sb(III) for construction of HPSAM calibration graphs were 0.3–2.0 and 0.3–3.4 μg/mL^{-1}, respectively.

It is thought that alloys of palladium (such as Pd–Ni and Pd–Co alloys) should exhibit good tritium aging behavior and allow the metal–hydride equilibrium to be adjusted by varying the composition of the alloy. Palladium–cobalt alloys exhibit higher surface hardness and better plated connection performance than palladium–nickel alloys. Simultaneous determination of palladium and cobalt in the presence of each other is therefore of interest. Various spectrophotometric methods for the individual determination of Pd(II) or Co(II) have been reported. Two of the methods use HPSAM (45, 46). In first paper, Bagherian et al. (45) proposed a simple, sensitive, and selective spectrophotometric method for the simultaneous determination of Co(II) and Pd(II) using PLS calibration and HPSAM. The method is based on the complex formation of Co(II) and Pd(II) with 4-(2-pyridylazo) resorcinol (PAR) in acidic media and in the presence of sodium dodecyl sulfate (SDS) as a micellizing agent. Acidic media and the presence of a micellar system improve selectivity and sensitivity, respectively. By applying PLS calibration, Co(II) and Pd(II) can be determined in the range of 0.20–2.0 and 0.40–4.0 μg/mL^{-1}, respectively. The detection limits were found to be 0.021 and 0.035 μg/mL^{-1} for Co(II) and Pd(II), respectively. In the second paper, Eskandari (46) proposed disodium 1-nitroso-2-naphthol-3,6-disulphonate (nitroso-R salt) as a selective chromogenic reagent. Palladium and cobalt in the neutral pHs form red-colored complexes with nitroso-R in aqueous solutions and make spectrophotometric monitoring possible. Simultaneous determination of palladium and cobalt were performed by HPSAM-first derivative spectrophotometry. The method is able to accurately determine palladium/cobalt ratio 1:10 to 15:1 (wt/wt).

Copper and zinc are metals that occur together in many alloys and pharmaceutical samples. The determination of trace amounts of zinc and copper is important in metallurgy and environmental analytical chemistry, and there is a growing need for procedures with high sensitivity and selectivity because these elements have important roles in

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biological, industrial, and medical science. Zinc compounds have biocidal activity because they precipitate and denature the bacterial proteins. For this reason, zinc has been used in dermatology as an antiseptic and disinfectant agent in ophthalmic and mouthwash solutions and mineral–vitamin preparations (47). Cobalt is a biologically essential trace element. Although cobalt is required only in minute amounts for maintaining normal health, a lower or higher concentration may lead to deficiency or toxicity states, respectively, resulting in impairment or abnormalities of health (48). Akhalghi and Kompany-Zareh (49) proposed a procedure for the selection of wavelength pairs as part of the ternary (t-HPSAM). t-HPSAM is employed for simultaneous determination of Cu(II) and Zn(II) using murexide as chromogenic reagent. The total relative standard error (RSE) for applying t-HPSAM (coupled with the proposed selection method) to samples in the ranges of 0.00–40.00 mM Cu(II) and 0.00–16.00 mM Zn was 2.56% for Cu and 6.54% for Zn. Pouretedal and Asefi (50, 51) proposed a method based on the difference in the absorbance of methylthymol blue complexes of Zn(II) and Co(II) at pH 6 buffered solution in different wavelength pairs. Arvand et al. (52) applied HPSAM for handling spectrophotometric data for simultaneous determination of Zn^{2+} and Cu^{2+} or selective determination of the first in the presence of the second ion. The ligand used was 1-(2-pyridylazo)2-naphthol (PAN) and its metal complexes (Zn-PAN and Cu(II)-PAN) were made water soluble by the neutral surfactant Triton X-100; therefore, no extraction with organic solvents was required. The method was based on the difference in absorbance of formed complexes between Zn^{2+} and PAN, at two different wavelengths at pH = 9.2.

Applications of HPSAM in Spectrophotometric Methods for Determination of Pharmaceuticals in Binary Mixtures

Hydrazine and its derivatives are important industrial chemicals with many applications. They are used, for example, in the pharmaceutical, polymer, and dye industries and in agriculture. In addition to being reactive and explosive, various reagents (53, 54) have been used for determination of hydrazine and its derivatives by applying HPSAM. One method (53) for hydrazine and acetylhydrazine in micellar media is based on the difference between the rates of their reactions with N,N-dimethylaminobenzaldehyde in acidic medium in the concentration ranges of 0.02–0.7 and 0.2–5.0 mg/L^{-1} for hydrazine and acetyl hydrazine, respectively. The absorbances were measured at 460 nm after 5 and 20 min. Hydrazine and semicarbazide were determined in their mixture depending on their reduction of Cu^{2+} to Cu^{+} in the presence of neocuproine (Nc), and the subsequent complex formation between Cu^{+} and Nc can be used in a sensitive spectrophotometric method for indirect determination of semicarbazide and hydrazine (54). The difference in the rate of reduction of Cu^{2+} with semicarbazide and hydrazine in cationic micellar media is the basis of this method. Semicarbazide can be determined in the range of 0.5–3.75 μg/mL^{-1} with satisfactory accuracy and precision in the presence of excess hydrazine. The proposed method was successfully applied to the simultaneous determination of semicarbazide (0.5–3.75 μg/mL^{-1}) and hydrazine (0.5–5 μg/mL^{-1}) and for the selective determination of semicarbazide in the presence of hydrazine in several synthetic mixtures containing different concentration ratios of the two compounds.

Hydrazine and phenylhydrazine were determined based on the hydrazone formation reactions of hydrazine and phenylhydrazine in the presence of micellar sodium dodecyl sulfate using mixed reagents of p-(dimethylamino) benzaldehyde and p-nitrobenzaldehyde as selective chromogenic reagents (55). Beer's law was obeyed in the range 0.020–0.50 and 0.20–10.0 μg/mL^{-1} for hydrazine and phenylhydrazine, respectively. The results allowed

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simultaneous determination even at ratios of 1:500 to 1:10 hydrazine–phenylhydrazine. The method can be applied for the simultaneous determination of hydrazine and phenylhydrazine in several synthetic mixtures and plasma and water samples.

Hydrazine, one of isoniazid's principal degradation products, is considerably more toxic than isoniazid (56, 57). Two methods have been described for their simultaneous determination by applying HPSAM. The first method depends on the difference observed in the rate of Fe^{3+} reduction to Fe^{2+} with hydrazine and isoniazid in the presence of 2,2′-bipyridine and subsequent complex formation between the resulted Fe^{2+} and bipyridine in an anionic surfactant micellar medium with maximum absorption at 520 nm (58). The solutions were measured at 120 and 300 s, and the simultaneous determination could be performed even at ratios of 1:1,000 to 1:12.5 for isoniazid–hydrazine in several commercially isoniazid formulations. The second method depends on their difference between the rates of their reactions with N,N-dimethylaminobenzaldehyde in the presence of sodium dodecyl sulfate in acidic media (59). The method was applied for determination of 0.01–0.1 $\mu g/mL^{-1}$ for isoniazide and 1.0–80 $\mu g/mL^{-1}$ for hydrazine.

Paracetamol and salicylamide have been widely used as analgesic and antipyretic drugs. They are frequently prescribed in a mixture with each other or with other related drugs. Simultaneous determination could be performed with HPSAM in the ratio 0.2:5–20:1 for salicylamide–paracetamol using pH 6.0 and the wavelengths selected for the measurements were at 232 and 252 nm. The method was successfully applied to the determination of salicylamide and paracetamol in pharmaceutical preparations (60).

The use of a mixture of paracetamol and caffeine as an analgesic and antipyretic is well established in pharmaceutical formulations (61). In order to achieve better curative effects and lower toxicity, it is important to control the content of paracetamol and caffeine in pharmaceutical tablets. HPSAM was applied for simultaneous determination of paracetamol and caffeine in their binary mixture (62). The method was based on the difference in the rate of oxidation of these compounds with a Cu(II)-neocuproine system and formation of Cu(I)–neocuproine complex, which was monitored at 453 nm at pH 5.0 in the presence of the surfactant sodium dodecyl sulfate. Paracetamol and caffeine can be determined in the range of 1.5–7.0 and 0.1–3.0 $\mu g/mL^{-1}$ with limits of detection (LODs) of 0.80 and 0.05 $\mu g/mL^{-1}$, respectively. The precision of the method (RSD) for five replicate measurements of a mixture of 1.5 $\mu g/mL^{-1}$ paracetamol and 1.0 $\mu g/mL^{-1}$caffeine was 1.41 and 1.94, respectively. The method was successfully applied to the simultaneous determination of paracetamol and caffeine in pharmaceutical samples and satisfactory results were obtained.

Paracetamol and p-aminophenol were determined in their binary mixture based on the difference in the rate of reduction of Fe^{3+} with paracetamol and p-aminophenol in the presence of 2,2′-bipyridine (Bpy) and subsequent complex formation between resulted Fe(II) and 2,2-bipyridine (63). The resulting colored complex of $[Fe(Bpy)_3]^{2+}$ was monitored at 520 nm. The results showed that the simultaneous determination of paracetamol and p-aminophenol could be performed in the concentration ranges of 0.4–70.0 and 0.03–8.0 $\mu g/mL^{-1}$. The proposed method was successfully applied for the simultaneous determination of paracetamol and p-aminophenol in several commercially paracetamol formulations.

Carmoisine and ponceau 4R are synthetic dyes that contain azo and aromatic ring structures and are often used in dyeing food, drink, medicine, and cosmetics. Their species show a highly overlapped spectra. Simultaneous determination of Carmoisine and Ponceau 4R with HPSAM (64) was performed by measuring the absorbances at 460 and 549 nm (when standards of carmoisine were added) or 490 and 541 nm (when standards

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of Ponceau 4R were added) in the presence of acetate buffer solution of pH 4.5. This method was satisfactorily applied for the determination of Carmoisine and Ponceau 4R in synthetic binary mixtures and several commercial products. The total relative standard error for five synthetic samples was 3.26 or 4.96% with carmoisine or ponceau 4R addition, respectively.

Tartrazine, Sunset Yellow, and Ponceau 4R are mixtures of food colorants, which are species with highly overlapped spectra. By using HPSAM (65), the concentration of one colorant was calculated from overlapping spectra at two appropriate wavelengths, where the other two colorants were selected as interferents present the equal absorbance relationship. These wavelength pairs are generally easily found and can be selected to give the most precise analytical results. This method was satisfactorily applied to determination of colorants of Tartrazine, Sunset Yellow, and Ponceau 4R in synthetic ternary mixtures and several commercial products.

Flavonoid compounds are widespread in the plant kingdom, including flavonoid glycosides diosmin and hesperidin. Diosmin and hesperidin are always present in mixtures either from natural or synthetic origin. Most of the pharmaceutical dosage forms contain diosmin and hesperidin (e.g., Daflon 500, Servier, France) either stated on the label or not. The similarity in the chemical structure of hesperidin and diosmin represents a difficulty in determining one or both of them when present together in pharmaceutical dosage forms. HPSAM was applied successfully for spectrophotometric determination of hesperidin and diosmin in a concentration range from 5 to 40 μg/mL^{-1}, sensitivity 5 μg/mL^{-1}, and detection limit 5 μg in the presence of NaOH (66). The method was also applied was applied for the determination of both compounds in bulk powder mixture.

One of the most important pharmaceuticals, which contains both ascorbic acid and L-cysteine is a class of pharmaceuticals known as Ultra Potent-C. These formulations are based on ascorbic acid as the main ingredient and L-cysteine as a metabolite support (67). HPSAM is applied for the simultaneous determination of ascorbic acid and L-cysteine. If present in excess amounts, based on the difference of the reduction reaction rates between AA and L-cysteine with Fe(III) and subsequently reacted with phenanthroline to produce a colored Fe(II)-phenanthroline complex showing maximum absorbance at 510 nm. HPSAM in the linear dynamic ranges for the two analytes ascorbic acid and L-cysteine are 0.50–4.00 and 1.00–8.00 μg/mL^{-1}, respectively. The predictability of the method was checked by determining the two analytes in real samples (68).

HPSAM was applied to the simultaneous determination of levodopa and carbidopa. The method was based on 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. Experimental conditions such as pH, reagent concentrations, ionic strength, and temperature were optimized. Simultaneous determination of levodopa and carbidopa was performed in the range of 0.8–4 and 0.2–1.5 μg/mL^{-1}, respectively. The proposed method was applied to the simultaneous determination of levodopa and carbidopa in pharmaceutical samples, and satisfactory results were obtained (69).

Minoxidil is widely used for stimulating hair growth after topical administration. Tretinoin has been widely used in the local treatment of several skin disorders (70). It was reported that percutaneous minoxidil absorption was enhanced by tretinoin as a result of increased stratum corneum permeability (71). HPSAM is described for simultaneous determination of tretinoin and minoxidil. The results show that minoxidil and tretinoin can be determined simultaneously with the concentration ratio of tretinoin to minoxidil varying from 2:1 to 1:33 in mixed samples in the presence of phosphate buffer solution adjusted at pH 5 and measuring the absorbance at 293 and 301 nm (when standards of tretinoin

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were added). The method was successfully applied in the determination of tretinoin and minoxidil in several synthetic pharmaceutical solutions (72).

HPSAM was applied for simultaneous determination of citric acid and ascorbic acid in their binary mixture depending on their difference in the rate of their reaction with Cu(II)-ammonia complex. The method was applied for determination of (0.80–1.15) $\times$ 10^{-2} mmol L^{-1} for citric acid and 0.70–10.00 mmol L^{-1} for ascorbic acid in powdered drink and vitamin C (73). HPSAM showed that hydrochlorothiazide and propranolol could be determined simultaneously with concentration ratios varying from 1:20 to 10:1 in a mixed sample, respectively. The proposed method has been successfully applied to the simultaneous determination of hydrochlorothiazide in the presence of propranolol in some synthetic samples. Moreover, the applicability of the method was demonstrated by their determination in some biological fluids (74).

Ethinylestradiol is a semisynthetic estrogen female sex hormone, which is present at a very low dosage level (30 μg $tablet^{-1}$) in combination with levonorgestrel, an orally active synthetic progestin that is present at a level of one to four times that of estrogen (75). HPSAM has been applied for simultaneous determination of both drugs in the range of 0.50–5.00 and 0.20–8.00 $\mu g/mL^{-1}$ respectively at 237 and 224 nm in contraceptive norgestrol and ethinyl estradiol LD pill.

A urine sample containing methamphetamine always contains amphetamine due to metabolism of the former drug (76). HPSAM is described for simultaneous determination of both compounds in urine. The method was based on an extraction of these drugs with sodium 1,2-naphthoquinone 4-sulphonate using *n*-hexane-ethyl acetate in the presence of bicarbonate buffer solution adjusted at pH 10, and the absorbencies were measured at different pairs of wavelengths.

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Conclusions

HPSAM is a modification of a standard addition method that permits the constant systematic error produced by the matrix of a sample to be corrected, as an alternative method to Youden's plot. The modified method succeeded for determining unbiased analyte concentrations when a direct interferent is present and even for determining an interferent concentration when it is known to be present have been demonstrated. The method has been applied successfully for resolving binary mixtures of metal ions and pharmaceuticals with extensively or completely overlapping spectra.

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