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SHORT COMMUNICATION

Elimination of additive interference effects by H-point calibration curve method

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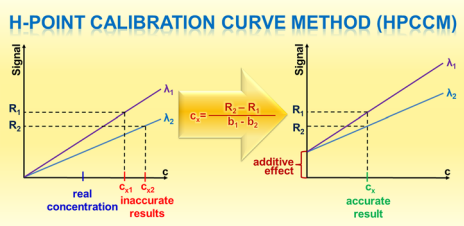
Abstract

As is known, the calibration method most commonly used in analytical practice is the calibration curve method (CCM). However, the main drawback of this approach is that it leads to the analytical results being affected by serious systematic error when the interference effect occurs. In this work it is shown how the CCM can be modified in order to eliminate the additive interference effect. The concept, termed H-point calibration curve method (HPCCM), is based on the measurements of both the standard solutions and the samples at two different conditions (e.g. wavelengths) selected in such a way to change the signals for an analyte keeping the signal for the interferents constant. Under such conditions the analyte in a sample may be determined with the use of two calibration graphs much more accurately than using a single calibration graph. It has been shown that HPCCM is equally effective but more time-efficient than the alternative approach known in the literature, i.e. the H-point standard addition method. The method was verified on the example of the spectrophotometric determination of Fe(II) in the presence of Fe(III) in various water samples.

Graphical abstract



Keywords Iron · Analytical calibration · Flow analysis · Interference Effects · Spectrophotometry

Introduction

Among from the calibration approaches known in analytical chemistry the Calibration Curve Method (CCM) is undoubtedly most often used in analytical practice. As is known, in this method a set of standard solutions is prepared separately from the sample solution. A consequence is, however, that the final analytical result can be affected by serious systematic errors since the potential interferents present in the sample matrix are as a rule not present in the standard solutions [1].

If the sample components cause the multiplicative (specific) interferences, they can be eliminated by another calibration approach—the standard addition method (SAM) [2, 3]. The calibration procedure comprises the addition of known amounts of an analyte to the same portions of a sample and measurement of the analytical signal for total analyte in each portion. By doing so the analytical results can be obtained with improved accuracy in comparison with those obtained by CCM.

A special problem is when the interferences occurring in the analytical system assayed have the additive (unspecific)

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character revealing as a constant change of the measured signal regardless of the analyte concentration. In such a case both the CCM and SAM applied to calibration in their basic versions (described above) are not able to provide accurate results.

The unique calibration approach frequently used to correct additive interferences in univariate analysis is the H-point standard addition method (HPSAM). In the original procedure (related to spectrophotometric analysis), the method consists of double determination of an analyte by SAM at two wavelengths selected in such a way that the signals measured for the analyte in the calibration solutions are significantly different and the signals produced by the interferent are the same [4]. Under such conditions, the calibration graphs constructed according to the SAM rules are crossed at a point (H-point) indicating both the additive effect and the analyte concentration being corrected for this effect. Since 1988 HPSAM have been modified to various versions, including kinetic HPSAM [5], generalized HPSAM [6], ternary HPSAM [7], K-ratio HPSAM [8], H-point curve isolation method (HPCIM) [9], ratio HPSAM [10], and chemical HPSAM [11]. Some versions of HPSAM (e.g. kinetic or chemical) are able to be applied effectively even in such cases when the sample components caused additive interferences are completely unknown.

The practical limitation of the SAM and HPSAM calibrations is that each sample analysed has to be individually dosed by the standard solutions. As a consequence, the number of samples is greater and the calibration procedure is more laborious and time-consuming. This is the main reason of both that SAM is in general of less popular than CCM and that HPSAM in any version is also very rarely used in analytical practice.

In this paper it is, however, proved that the additive interference effect can be overcome by the calibration based not only on SAM but also on CCM. The procedure developed, described and tested here is very simple, but according to our best knowledge, it has been never described before in the literature. The method, based on the same principle as HPSAM and termed consequently HPCCM, was experimentally verified on the example of the spectrophotometric determination of Fe(II) in the presence of Fe(III) in water samples. A dedicated flow injection system was designed for this purpose.

Results and discussion

The HPCCM procedure is shown in Fig. 1 with the example of analysis of the synthetic sample containing Fe(II) as the analyte and Fe(III) as the interferent in concentrations 5.00 and 20 mg dm^{-3}, respectively.

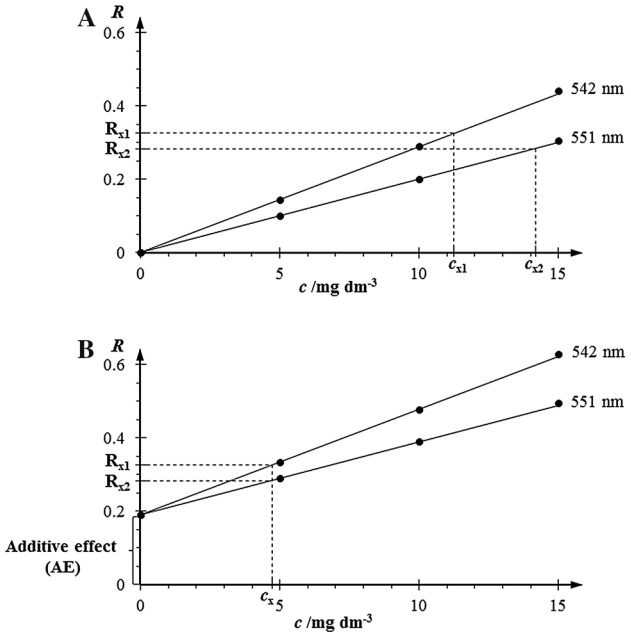

Fig. 1 The principle of HPCCM on the example of the determination of 5 mg dm^{-3} Fe(II) in the presence of 20 mg dm^{-3} Fe(III) in the synthetic sample

On the basis of the measurement data obtained for the standard solutions at two wavelengths, 542 and 551 nm, two calibration curves of the equations, $R = 0.0288c + 0.014$ and $R = 0.0199c + 0.012$, respectively, were formulated (Fig. 1a). The signals measured for the sample, $R_{x1} = 0.325$ and $R_{x2} = 0.283$, at 542 and 551 nm, respectively, were related to the calibration curves (in accordance with the CCM method), and two values of the Fe(II) concentration in the sample, $c_{x1} = 11.24$ and $c_{x2} = 14.17$ mg dm^{-3}, were obtained. It was assumed that the reason for the statistically significant difference between both values was the additive interference effect (AE) caused by Fe(III). The effect was able to be eliminated in the way presented in Fig. 1b, i.e. by relocation of the calibration curves along the signal axis to a point (H-point) allowing a single value of the analyte concentration, $c_x = 4.72$ mg dm^{-3}, to be obtained from R_{x1} and R_{x2}. The c_x value, considered as the final analytical result, was calculated from equation $c_x = (R_{x1} - R_{x2})/(b_1 - b_2)$, where b_1 and b_2 are the slopes of the calibration curves (here: 0.0288 and 0.0199, respectively). The results obtained by HPCCM in the synthetic samples and in the real water samples are shown in Table 1 in comparison with those obtained conventionally (i.e. by CCM) and by HPSAM.

The results of the determination of Fe(II) in the synthetic samples obtained by CCM were different from each other and from expected ones. They were also significantly less than those obtained by both HPSAM and HPCCM. All of these differences confirmed strong interference effect caused by Fe(III). As HPSAM (in contrast to HPCCM) is able to

Table 1 Results obtained by the CCM (c_{x1} and c_{x2}, see Fig. 1), HPSAM, and HPCCM methods in synthetic and real water samples

Sample	Expected concentration/mg dm^{-3}		Obtained concentration/mg dm^{-3}			
	Fe(II)	Fe(III)	CCM		HPSAM	HPCCM
			c_{x1}	c_{x2}		
I synthetic	1.00	5.00	2.90 ± 0.02	3.77 ± 0.03	0.95 ± 0.02	1.00 ± 0.07
II synthetic	5.00	10.00	8.26 ± 0.01	9.76 ± 0.06	4.91 ± 0.01	4.88 ± 0.09
III synthetic	5.00	20.00	11.24 ± 0.01	14.17 ± 0.00	4.73 ± 0.04	4.72 ± 0.01
Zdrój Jagielloński	–	–	4.75 ± 0.18	4.70 ± 0.25	4.73 ± 0.22	4.66 ± 0.22
Zdrój Lajkonik	–	–	4.66 ± 0.30	4.62 ± 0.55	4.63 ± 0.04	4.60 ± 0.07
Zachodnia	–	–	33.81 ± 0.27	34.16 ± 1.17	31.20 ± 0.61	33.59 ± 0.41
Ruczaj	–	–	12.92 ± 0.07	17.41 ± 0.18	5.79 ± 0.52	5.73 ± 0.32
Wisła	–	–	2.19 ± 0.02	3.17 ± 0.13	0.54 ± 0.14	0.55 ± 0.18
Wilga	–	–	3.34 ± 0.09	5.06 ± 0.22	1.08 ± 0.12	0.97 ± 0.18
Drwinka	–	–	3.10 ± 0.15	4.51 ± 0.25	0.84 ± 0.07	0.91 ± 0.18

eliminate both the multiplicative and additive interferences, the effects of both kinds could be theoretically suspected. However, the similarity of the results obtained by HPSAM and HPCCM has proved that the signal measured for the analyte was influenced by the interferent in the additive way only. As seen, the proposed method (HPCCM) was able to overcome this effect even when the Fe(III) concentration in a sample was several times greater than the analyte concentration and to eliminate the potential systematic error greater than 200% (in the case of the first synthetic sample).

The results obtained by all three methods for the water samples taken from spring sources (Zdrój Jagielloński, Zdrój Lajkonik) and drilled well (Zachodnia) were statistically equal to each other. Apparently, the concentration of Fe(III) in these samples was too small to produce notable interferences and, therefore, the analyte was able to be determined with presumably good accuracy independently from the calibration approach used.

In contrast to the previous real samples, the river samples (Wisła, Wilga, Drwinka) have contained Fe(III) in concentrations great enough to cause significant interferences. Apparently, the effects had additive character [probably caused mainly by the Fe(III) ions] as the HPSAM and HPCCM methods provided similar determination values. Although in some cases the concentrations obtained by CCM were biased with especially great systematic errors (see, e.g. the c_{x2} value for Wisła river), the HPCCM method was able to eliminate them effectively.

The analytical performance of HPCCM was quite good. Similarity of the CCM results to the expected ones in the case of the synthetic samples and to the HPSAM results obtained for the real samples is a proof of their good accuracy. In addition, the analyte was determined with satisfactory precision that was comparable with those characteristic for HPSAM.

The differences between the HPSAM and HPCCM methodologies have an impact on the time that is needed for the whole analytical procedure, including preparation of the standard and sample solutions and their triplicate measurements. Analysis of a single sample using HPCCM and HPSAM took up to 25 and 30 min, respectively, while in the case of seven samples (as above) this difference was much greater, namely 1 h and 3.4 h, respectively. This reflects the fact that the HPCCM calibration allows, in contrast to HPSAM, a single set of standards to be used for all samples assayed.

Conclusions

The presented study shows that the developed calibration approach, HPCCM, is an effective and helpful analytical tool. Due to the possibility of eliminating the additive interference effect under well-defined instrumental conditions it offers—similarly to HPSAM—the determination of an analyte with improved accuracy and with precision comparable to those characteristic for HPSAM. Furthermore, it allows the analytical result to be estimated by two independent values, which can verify the presence of this effect in the analytical system assayed. The important advantage of HPCCM over HPSAM is the possibility of using the same calibration graphs for the determination of an analyte in a set of samples containing the same components caused the additive interferences (even if the concentrations of these components in the samples are different).

As a simple and fast calibration approach HPCCM can be recommended to be used in analytical practice. There are also no obstacles to develop, test and use this method routinely in various versions characteristic for HPSAM (e.g. kinetic or chemical one) as well as to adapt it to the

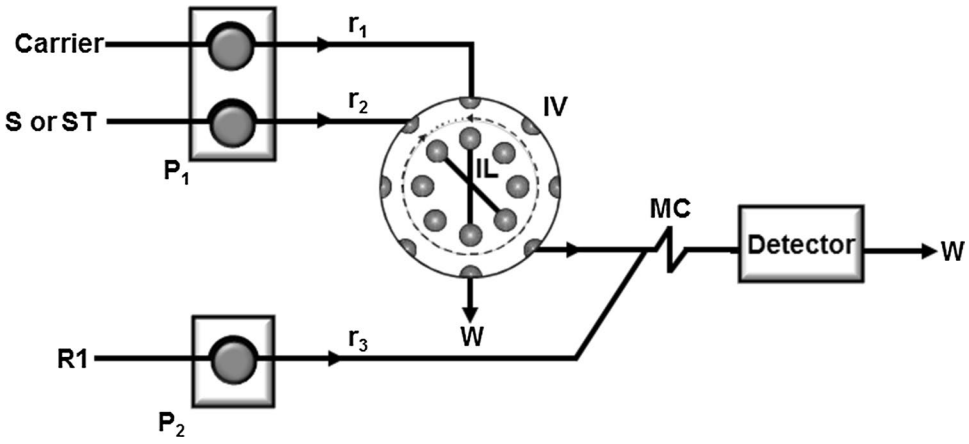

Fig. 2 Scheme of the constructed flow-injection manifold: *S* sample, *ST* standard solution, *R* reagent, r_1, r_2, r_3 flow rates, *P1 P2* peristaltic pumps, *IV* injection valve, *MC* mixing coil, *W* waste

determinations by other than spectrophotometric analytical methods (e.g. by electrochemical ones).

Experimental

Reagents and solutions

The following reagents were used to prepare the appropriate solutions: phenantroline monohydrate (Lachner, Czech Republic), salicylic acid (Fabryka Odczynników Chemicznych—Gliwice, Poland), iron(III) nitrate nonahydrate (Sigma Aldrich, Germany), ammonium iron(II) sulfate hexahydrate (Chempur, Poland), 37% fuming hydrochloric acid (Merck, Germany), 96% ethanol (POCH, Gliwice, Poland) and potassium hydrogen phthalate (Fabryka Odczynników Chemicznych—Gliwice, Poland). All reagents were of analytical grade.

Stock iron solutions containing 1000 mg dm^{-3} Fe(II) and Fe(III) were prepared by water-dissolving of an adequate amount of $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$, respectively. Stock solution of mixture of 1,10-phenantroline monohydrate and salicylic acid was prepared by dissolving 0.843 g and 0.575 g of these reagents, respectively, in 10.0 cm^3 of ethanol and adjusting the volume to 100 cm^3 with distilled water. The use of ethanol was utilized to increase the solubility of salicylic acid. Buffer solution (pH = 3.0) was prepared by mixing appropriate volume of 0.2 M solutions of potassium hydrogen phthalate and hydrochloric acid. All stock solutions were prepared fresh daily. The ultrapure water (18.2 MΩ cm) from HLP 5 system (Hydrolab, Poland) was used throughout the work.

Samples

The proposed method (HPCCM) was tested with the use of three synthetic samples of different known concentrations of Fe(II) and Fe(III) (see Table 1). In addition, seven real water samples taken from spring sources (Zdrój Jagiellonski, Zdrój Lajkonik), a drill well (Zachodnia) and different rivers situated in Krakow (Ruczaj, Wisła, Wilga, Drwinka) were analysed. The analysed samples of natural water were collected in polyethylene bottles. Before the sample collection 1.5 cm^3 of HCl (1:1,v/v) was added to obtain pH around 2–3. All of the samples were analysed on the same day. Moreover, the samples were stored prior to analysis in a cold and dark place.

Instrumentation

The instrumental flow-injection manifold dedicated to the proposed calibration method is presented in Fig. 2. It consisted of an eight-port injection valve equipped with a homemade, electric switching system, two peristaltic pumps (Minipuls 3, Gilson, France) and 16-channel controller UVCTR-16 (KSP Electronics Laboratory, Poland). Lambda 25 spectrometer (Perkin Elmer, USA) equipped with a glass flow cell with path length equal 10 mm, was utilized as the detector. The operation of pumps and injection valve was controlled by Valve and Pump Controller Software (KSP Electronics Laboratory, Poland).

The working parameters of the flow-injection manifold, such as flow rate, reaction loop length and the volume of injected sample, were optimized. The following parameters were chosen: flow rates (r_1, r_2, r_3)—2.0 cm^3 min^{-1}, the length of the reaction coi—200 cm and the volume of injected sample—0.2 cm^3. The linearity concentration range for Fe(II) was found as 0–25 mg dm^{-3}.

Procedures

Samples or standard solutions were prepared by adding 1 cm^3 of buffer solution and 7 cm^3 of samples or appropriate volume of stock solutions of Fe(II) and Fe(III) to 10 cm^3 volumetric flask and made up to mark with deionized water. The concentration of Fe(II) in the calibration solutions was

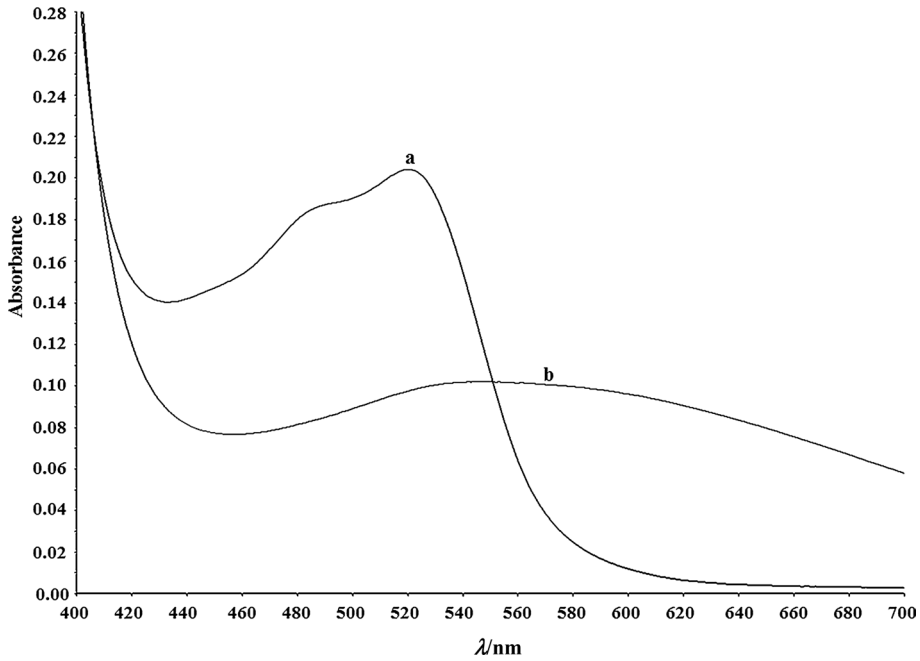

Fig. 3 Absorption spectra of **a** 5 mg dm^{-3} Fe(II) and **b** 10 mg dm^{-3} Fe(III) with the mixed reagents at pH = 3

in the range of 0–25 mg dm^{-3} (with 5 mg dm^{-3} step). The sample or standard solution was injected into a stream of water, which was connected with a stream of mixture of phenantroline and salicylic acid (R in Fig. 3), resulting in the formation of an orange or purple derivative complex of Fe(II) and Fe(III), respectively. The formed product was directed towards the detector where absorbance was recorded at two selected set wavelengths.

Based on the spectra of 1,10-phenantroline and salicylic acid complexes with Fe(II) and Fe(III) (Fig. 3), the following pair of wavelengths was chosen in accordance with principle of the method: 542 and 551 nm. The signals measured for a set of samples (synthetic and real) were related to the single pair of calibration graphs. The signals were measured in the peak height mode. Each determination was repeated three times under the same instrumental conditions.

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