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A multichannel photometer based on an array of light emitting diodes for use in multivariate calibration

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Abstract

The development of a multichannel photometer based on an array of eight light emitting diodes (LED) as light sources is described. Optical fibre bundles were employed to guide the light radiation of the LED to the measuring cell and from the cell to the photodiode detector. The instrument was controlled by a microcomputer and was designed to perform absorbance measurements in a single wavelength continuously as well as in all wavelengths (470, 500, 562, 590, 612, 636 and 654 nm) sequentially, allowing its application in multivariate analysis methods. The photometer presented a drift lower than $2\,\mu V\,h^{-1}$, allowing absorbance measurements with a precision better than 0.003 units. The instrument was applied for the simultaneous determination of Zn(II) and Cu(II) in pharmaceutical and metallic alloy samples, whose pH adjustment followed by the addition of xylenol orange complexing agent were accomplished by employing a monosegmented flow system. Solutions containing both metal ions in the concentration range from 1.0 to 4.0 mg L^{-1} were employed to constructed the calibration model based on multiple linear regression (MLR), providing root mean square errors of prediction of 0.06 and 0.12 mg L^{-1} for Zn(II) and Cu(II), respectively. The results obtained by employing the photometer were compared with those obtained by flame atomic absorption spectrometry, showing no significant differences at the 95 % confidence level.

Keywords: Multichannel photometer; Multivariate calibration; LED; MLR; Zinc; Copper

1. Introduction

Molecular absorption spectrophotometry in the UV–vis region is an analytical technique that has been widely employed for the determination of organic and inorganic species. Good precision and accuracy with a cost significantly lower than other techniques are some of the reasons that contribute to the widespread use of UV–vis spectrophotometry in many fields, principally in routine analysis. Despite these advantages, the methods based on UV–vis spectrophotometry usually present poor selectivity that impairs their application in both mono- and multielement analyses.

The use of multivariate calibration methods, such as multiple linear regression (MLR) and partial least square (PLS), associated with instrumentation based on multichannel detection, such as diode array and CCD array spectrophotometers, has renewed the interest of many researches in the application of UV–vis spectrophotometry in simultaneous determinations. The reliable results obtained for multicomponent determinations in highly interfering chemical systems attest to the capability of this association [1].

Multichannel spectrophotometers, particularly those based on diode arrays, present many advantages, such as spectrum acquisition in a very short interval of time, good resolution and accuracy in wavelength measurements, and adequate sensitivity and dynamic range for many applications. In spite of these advantages, the measurements of absorbance intensity in many hundreds of wavelengths may be not necessary for multivariate calibration and simultaneous determination, as demonstrated by chemometric methods for variable selection, which are useful to reduce noise and to minimise redundancies [2,3].

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Considering these aspects, a multichannel photometer based on an array of light emitting diodes (LED) can be a feasible alternative to implement a multivariate calibration method for simultaneous determination, as a pre-determined number of wavelengths can be employed for measurements, providing the proper information for the construction of accurate calibration models. Moreover, an LED-based photometer is not expensive, and has low power consumption, permitting the construction of miniaturised instruments for field measurements.

LED have been frequently employed in Analytical Chemistry. Excellent stability, low consumption of energy, monochromaticity and reduced size [4] are among some of the characteristics of these devices that allow their application in commercial instruments [5] and in dedicated systems [6,7]. Nowadays, there are LED available on the market that emit from the ultraviolet to the near infrared regions, entirely covering the visible region. The great interest in the analytical applications of these devices is attested by the growing number of papers published in the literature, including review articles [4,8].

Cantrell and Ingle [9] developed a portable photometer based on an array of three LED (blue, green and red) that embodies a programmable microcontroller and a memory chip, enabling measurements at pre-determined intervals of time, for long periods, without intervention of the user. A four-LED photometer (red, orange, yellow and NIR) was constructed by Brooks et al. [10] and applied to extend the dynamic range of an optical sensor for the determination of relative humidity in air, by means of multivariate calibration based on artificial neural networks. A bicolour LED (green and red) was employed by Araújo et al. [11] for the construction of a photometer used as a detector in a flow system for clinical analysis. A similar LED was also employed by Rocha and Reis [12] in a photometer for speciation of inorganic nitrogen. The use of LED in the development of detection systems for field measurements have been also described. Liddy Meaney et al. [13] utilised an ultra-bright red LED (650 nm) in the construction of a photometer employed as detector in a portable flow injection system for mapping the concentration of phosphate ions in marine waters. Hauser et al. [6] employed a LED that emits in the NIR region for monitoring nickel ion in industrial processes. A multichannel photometer based on an array of seven LED was developed by Hauser and Rupasinghe [14] and applied to the simultaneous determination of metal ions in binary mixtures by means of calibrations at two wavelengths, in which the metal complexes absorbed differently.

Multichannel photometers can be easily constructed by employing optical fibre bundles as waveguides for the radiation of each LED. These distinct bundles can be then merged and connected to the cell, allowing measurements at different wavelengths without moving the LED. As a LED presents very short response times, all the elements of an array can be sequentially actuated in a short interval of time, by employing a microcomputer, which can fully control the photometer. This work describes the construction of a photometer based on an array of eight LED, which emit radiation at 470, 500, 525, 562, 590, 612, 636 and 654 nm. In order to assess its multichannel capability, the photometer was applied for the simultaneous determination of Zn(II) and Cu(II) in pharmaceuticals and metallic alloys, by using xylenol orange as chromogenic reagent and multiple linear regression for the multivariate calibration.

2. Experimental

2.1. Construction of the photometer

Ultrabright LED (RS Components, UK), with diameters of 5 mm and transparent plastic bodies were employed. The heads of the LED were sanded and polished to the proximity of the semiconductor junction in order to minimise the loss of radiation. Each LED was fixed in a fibre optic bulkhead connector (RS 655-010) and the array was mounted on an acrylic plate. Bundles of four plastic optical fibres (250 μm diameter, Toray, UK), fixed in a fibre optic connector (RS 655-004), were employed to guide the light emitted by each LED and randomly combined in a single bundle of 32 fibres, which was then connected to the holder of the measurement cell. Another 32-fibre bundle was utilised to guide the light from the cell to the detector (photodiode RS 308-067).

Fig. 1 shows the electronic circuits employed to turn on each LED of the array and to amplify the signal from the detector before analog-to-digital conversion. The variable resistor R_v was employed to control the intensity of radiation emitted by the LED, allowing adjustment of the detector signal to the same value for all LEDs when the cell was filled with water (reference signals).

The LED array, the detector and respective electronic circuits were placed in a box (200 mm × 180 mm × 90 mm). A

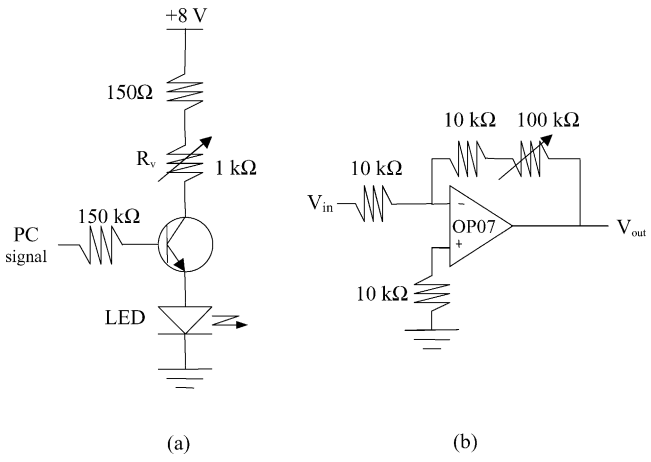

Fig. 1. Electronic circuits for (a) actuation of LED and (b) for amplification of signal from photodiode detector.

25-pin female DB connector was installed in the rear panel of the photometer box to receive the TTL signals from the microcomputer necessary to actuate the LED.

Software to control the instrument and for data acquisition through a parallel interface PCL-711S (Advantech Co.) was written in Microsoft VisualBasic 3.0. Absorbance measurements can be performed in up to eight wavelengths, determined by the user. When a single wavelength is chosen, the LED is on continuously. When two or more wavelengths are required, measurements are made from the lowest to the highest wavelength, by sequentially turning on/off all the chosen LED.

The absorbance value was calculated by the following equation:

$$A = -\log\frac{(S_a - S_d)}{(S_r - S_d)}$$

where S_a is the analytical signal, S_r is the reference signal and S_d is the dark signal (signal intensity obtained with the LED turned off).

2.2. Reagents and solutions

Analytical grade reagents and distilled/deionised water were used to prepare all solutions. Reference solutions of the metal ions were prepared by proper dilution of a 1000 mg L^{-1} stock solution (Tec-Lab). A 0.5 mol L^{-1} acetate buffer solution, pH 5.7, was prepared by using glacial acetic acid (Synth) and sodium acetate (Merck). A 3.0 mmol L^{-1} xylenol orange solution was prepared by dissolving the tetrasodium salt (Fluka) in the acetate buffer solution.

Reference solutions of Zn(II) (0.2–1.0 mg L^{-1} and 1.0–5.0 mg L^{-1}) and Cu(II) (1.0–5.0 mg L^{-1}) were prepared in 2.0 mmol L^{-1} HNO_3 (Synth) for evaluation of the instrument. For the multivariate calibration, reference solutions containing binary mixtures of Zn(II)/Cu(II) and Zn(II)/Ni(II) were prepared in 2.0 mmol L^{-1} HNO_3, according to the design depicted in Fig. 2.

Brass alloys (500 mg) were dissolved in 50% HNO_3 (v/v) and, after evaporation of the excess of the nitric acid, the volume was adjusted to 250 mL with deionised water. This solution was appropriately diluted for measurements. Pharmaceutical liquid preparations containing zinc and copper ions were acquired locally and appropriately diluted with 2.0 mmol L^{-1} HNO_3.

2.3. Apparatus

Emission spectra of the LED, as well as the absorption spectra of the metallic complexes, were acquired with a commercial diode-array (HP 8453). A flame atomic absorption spectrometer (Perkin Elmer 5100) was employed to determine Zn(II) and Cu(II) in the sample solutions for comparison purpose.

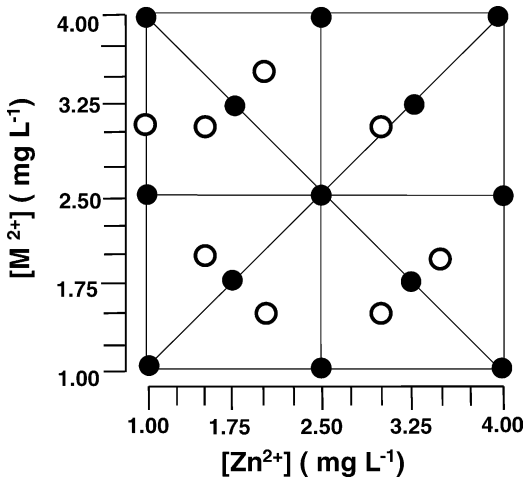

Fig. 2. Experimental design employed for calibration and validation in the simultaneous determination of binary mixtures of metal ions by MLR. [M^{2+}] represents [Cu^{2+}] or [Ni^{2+}]; (●) represents calibration samples, (○) represents prediction samples.

2.4. Procedures

Measurements were made in a monosegmented flow system, as shown in Fig. 3. Metal ion (80 μL) and buffered xylenol orange (50 μL) solutions were mixed and introduced into the flow system by means of simultaneous multiple injection [15]. Deionised water was used as carrier and the flow rate was fixed 2.0 mL min^{-1}. In these conditions, the software was able to perform six measurements for each LED (48 measurements), while the sample monosegment passed through the 1.0 cm quartz flow cell (Hellma 178.711-QS).

2.5. Multivariate calibration

Thirteen binary mixtures containing Cu(II)/Zn(II) Ni(II)/Zn(II) were used to construct the calibration model, while eight solutions constituted the external validation set, as indicated in Fig. 2. The calibration models were obtained by multiple linear regression [16], employing the software Unscrambler 7.5 (Camo).

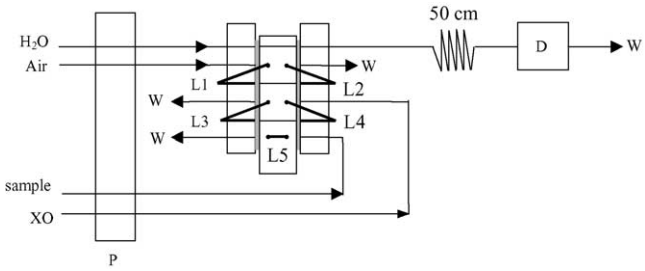

Fig. 3. Monosegmented flow system with simultaneous multiple injection approach employed to process the solutions. W, waste; L, loops; D, detector; P, peristaltic pump; XO, xylenol orange solution.

Table 1
Optical characteristics of the LED employed to construct the photometer

Manufacturer peak wavelength (nm)	Acquired peak wavelength (nm)	Bandwidth[a] (nm)
470	468	19
500	502	40
525	519	30
562	561	20
590	595	16
612	613	16
636	632	17
654	657	34

[a] Width of the peak at its half intensity.

3. Results and discussion

3.1. Evaluation of the photometer

The LED employed for the construction of the photometer do not present the same intensities of radiation at a given electric current. Moreover, the sensitivity of the photodiode detector is dependent on the wavelength. To minimise the dependence of the signal detector with regard to the intensity of emission of each LED, the variable resistor R_v, shown in the Fig. 1, was adjusted in order to obtain similar signals for all LED, when the measuring cell was filled with deionised water. These signals were taken as the reference signal for each LED, as described in the Section 2.

The spectrum of each LED was acquired with the HP 8453 spectrophotometer. Table 1 lists the maximum wavelength of emission and the bandwidth found for each LED. The slight differences relative to the maximum wavelengths indicated by the manufacturer can be attributed to the calibration of the spectrophotometer and/or to the fabrication processes, being concordant with the bandwidth values as well as to those described in the literature [4], indicating their usefulness for analytical applications. In addition to these experiments, thirty emission spectra were obtained in intervals of 3 s, in order to verify the intensity of emission of the LED in the instants after it was turned on, as exemplified in Fig. 4 for the 590 nm LED. The signal marked at "zero" was obtained immediately after turning on the LED and its intensity, usually low, depends on the synchronisation between the actuation of the LED and the acquisition of the spectrum by the spectrophotometer, as these tasks were manually initiated. It can be noted that signal intensity decreases 3–4% after reaching the maximum value, indicating the necessity of controlling the data acquisition after turning on the LED, as the absorbance value will be directly affected. Similar results were obtained for all the other LED, except for the 500 nm and 525 nm LEDs, whose intensity does not decay after reaching the maximum value.

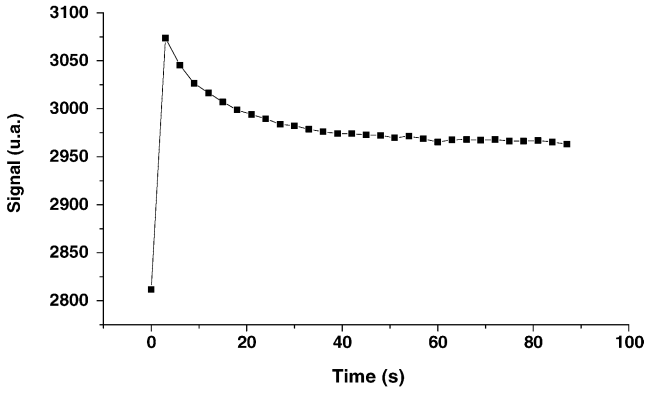

Fig. 4. Emission profile of the 590 nm LED.

Table 2
Absorbance values for a 3.0 mg L^{-1} Zn(II)/xylenol orange complex solution obtained with different modes of operation of the photometer

LED (nm)	Individually pulsed[a]	Sequentially pulsed[a]	Continuous[a]
468	0.022 ± 0.007	0.007 ± 0.003	0.024 ± 0.007
502	0.194 ± 0.004	0.203 ± 0.002	0.208 ± 0.006
519	0.275 ± 0.008	0.295 ± 0.002	0.295 ± 0.004
561	0.311 ± 0.010	0.337 ± 0.005	[b]
595	0.208 ± 0.009	0.229 ± 0.004	0.204 ± 0.003
613	0.048 ± 0.001	0.051 ± 0.001	0.044 ± 4.79E-04
632	[c]	[c]	[c]
657	[c]	[c]	[c]

[a] Average of three measurements ± standard deviation.
[b] Not evaluated (see text).
[c] Solution does not absorb.

Considering the results described above, three set of experiments were carried out by using a 3.0 mg L^{-1} Zn(II)/xylenol orange complex solution, in order to evaluate the capability of the photometer to perform measurements in a sequential manner. Firstly, absorbance intensities were measured at all wavelengths by maintaining the LED turned on continuously. Secondly, a single LED was pulsed for the measurements and, finally, the LED were sequentially pulsed for obtaining absorbance values at all wavelengths. Table 2 shows the results obtained, demonstrating that there is no mutual interference between the emission of the LED when they are sequentially pulsed during the measurements, as all the values are similar, as well as their standard deviations.

The photometer stability was evaluated by performing measurements for a period of one hour, in intervals of 1 s,

Table 3
Drifts presented by each LED of the photometer, considering the mode of operation

LED (nm)	Pulsed mode (μV h^{-1})	Continuous mode (μV h^{-1})
468	−0.5	+0.19
502	−0.5	+0.04
519	−0.2	+0.02
561	+1.9	[a]
595	+0.78	−1.6
613	+0.09	+0.19
632	+0.47	−0.89
657	+0.29	−0.98

[a] Not evaluated (see text).

Table 4
Evaluation of the photometer sensitivity compared to a commercial diode-array spectrophotometer

Wavelength (nm)	PS[a] slope	SS[a] slope	(PS/SS)[a] × 100%
502	0.109	0.144	76
519	0.168	0.168	100
561	0.191	0.233	82
595	0.128	0.109	117

[a] PS, proposed LED photometer slope; SS, commercial diode-array spectrophotometer slope.

with the cell filled with deionised water. Table 3 lists the drift values obtained for measurements performed with the LED turned on constantly and when pulsed sequentially. The 561 nm LED showed the worst performance, being employed only in the pulsed mode, as it was operated at 60 mA, a current higher than the maximum value of 30 mA recommended by the manufacturer. Using the values of dark and reference signals as constants, the precision of the photometer, evaluated as the standard deviation of the absorbance baseline, was better than 0.003 units, confirming the good performance of the instrument.

The sensitivity of the instrument was evaluated by constructing analytical curves for Zn(II) in the 1.0–5.0 mg L^{-1} concentration range and comparing these with those obtained with a commercial diode-array spectrophotometer. LED emitting at 500, 525, 562 and 590 nm were sequentially pulsed for the measurements, as the metal ion/xylenol orange complex absorbs at these wavelengths. Table 4 lists the slopes of the analytical curves obtained, demonstrating that the sensitivity of the photometer is close to that shown by the commercial instrument. At 519 nm the same sensitivity is obtained for both instruments, as the measurements were made at the "flat" region of the absorbance spectrum of the Zn(II) complex. The effect of the emission bandwidth of the LED can be noted at wavelengths in which there are pronounced variations in the molar absorption coefficient of the complex, that is 502, 561 and 595 nm. At 595 nm, the photometer shows higher sensitivity because its emission bandwidth covers regions of the spectrum in which the molar absorption coefficients of the complex are higher than those at 595 nm. Although different values for sensitivity have been found for different wavelengths, all analytical curves showed similar linearity ($0.997 \leq r^2 \leq 0.999$) in the concentration range investigated.

3.2. Simultaneous determination of binary mixtures of metal ions

Multiple linear regression is a calibration method adequate for multivariate analysis that employs a reduced number of variables. In this method, the data matrix **X**, which comprises the instrumental information, is mathematically related to the concentrations of the samples, which are contained in the matrix **Y**, by means of a new matrix **B**, constituted by the regression coefficients, which can be calculated according to the equation [16]:

$$\mathbf{B} = (\mathbf{X}^t\mathbf{X})^{-1}\mathbf{X}^t\mathbf{Y}$$

The models of calibration constructed are usually evaluated with regard to their correlation coefficients and root mean square error of prediction (RMSEP). The RMSEP value is one of the most important parameters for evaluation of a chemometric model, as it indicates the capability of prediction of this model, comparing the predicted values with those expected for a sample of known concentration [16].

For spectrophotometric methods, the prediction capability of a chemometric model is directly dependent on the spectral differences, often very slight, of the species (or related species) which are intended to be determined. As a general rule, the prediction capability of a model improves as the difference between the spectra are more noticeable. For evaluation of the instrument with respect to multivariate calibration, two metal ion mixtures were studied, Zn(II)/Ni(II) and Zn(II)/Cu(II), considering the spectral differences between their complexes with xylenol orange, as shown in Fig. 5, which also includes the spectra of the LED. The factor design shown in Fig. 2 was employed in this study. Table 5 lists some of the results obtained, when different numbers of LED were employed for calibrations. A reduced number of wavelengths was employed for calibrations as a variable selection approach [17], considering the emission spectra of the LED, the absorption spectra of the complexes and the regression coefficients provided by the MLR software. As expected, the best results were obtained for the Zn(II)/Ni(II) mixtures, since their complexes with xylenol orange show the most pronounced differences. On the other hand, the worst results were obtained for Cu(II), because the spectrum of its xylenol orange complex is virtually the same as the Zn(II) complex. In addition, the use of a smaller number of LED to obtain the calibration model was more effective for the Zn(II)/Cu(II) mixture, probably because their metal complex

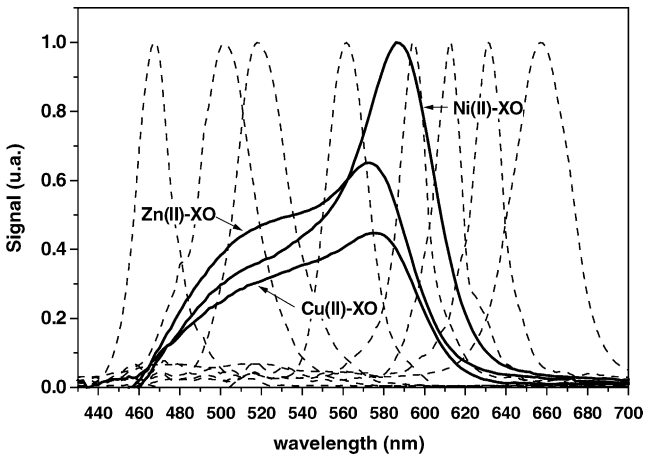

Fig. 5. Emission spectra of the LEDs employed to construct the photometer and absorption spectra of the metal ion/xylenol orange complexes.

Table 5
Evaluation of the photometer for simultaneous determination of binary metal ion mixtures using MLR multivariate calibration

Number of LEDs	Zn(II)		Cu(II)	
Correlation	RMSEP (mg L^{-1})	Correlation	RMSEP (mg L^{-1})	
8	0.998	0.062	0.967	0.314
7[a]	0.974	0.315	0.983	0.138
7[b]	**0.998**	**0.057**	**0.987**	**0.121**
5[c]	0.996	0.125	0.985	0.130
Number of LEDs	Zn(II)		Ni(II)	
Correlation	RMSEP (mg L^{-1})	Correlation	RMSEP (mg L^{-1})	
7[d]	0.998	0.061	0.994	0.081
6[e]	0.999	0.051	0.996	0.088
5[f]	0.997	0.090	0.994	0.099

[a] Without 500 nm LED.
[b] Without 562 nm LED.
[c] Without 470, 636 and 654 nm LEDs.
[d] Without 500 nm LED.
[e] Without 500 and 562 nm LED.
[f] Without 470, 500 and 562 nm LED.

Table 6
Simultaneous determination of Zn(II) and Cu(II) in pharmaceutical preparations and brass

Sample	Unit	Zn			Cu		
Photometer	FAAS	Deviation (%)	Photometer	AAS	Deviation (%)		
AD-element	mg/L	2385 ± 43	2429	−1.8	748 ± 24	723	+3.5
PED-element A	mg/L	506 ± 12	500	+1.2	145 ± 23	142	+2.1
PED-element B	mg/L	504 ± 2.0	500	+0.8	159 ± 5.2	142	+12
Zn–Cu oligosol A	mg/L	31.0 ± 1.5	33.3	−6.9	33.1 ± 4.2	35.1	−5.7
Zn–Cu Oligosol B	mg/L	31.5 ± 1.3	33.3	−5.4	32.9 ± 3.0	36.1	−8.9
Brass-1 A	mg/g	372 ± 13	356	+4.5	621 ± 16	631	−1.6
Brass-1 B	mg/g	410 ± 42	360	+14	578 ± 49	638	−9.4
Brass-2 A	mg/g	350 ± 35	351	−0.3	636 ± 49	631	+0.1
Brass-2 B	mg/g	369 ± 14	356	+3.7	647 ± 18	639	+1.3

spectra show high degrees of similarity, whose redundancies were minimised by the selection of variables [17]. Although there is no information at 654 nm, as the metal ion complexes do not absorb at this wavelength, good results were obtained when this wavelength was also included. Similar results have been described in the literature [18], indicating that the calibration model employs a non-absorbing wavelength as a kind of reference for the calculation. The RMSEP values obtained in both cases are similar to those described in the literature, when a diode array spectrophotometer was employed as detecting system [19].

In order to verify the prediction capability of the multivariate calibration models constructed with MLR algorithm, Zn(II) and Cu(II) was determined in brass alloys and pharmaceutical preparations. The calibration model employed for the predictions of the concentrations of the metal ions was that which presented the lowest RMSEP values for the validation set (marked in bold in Table 5). Table 6 lists the results obtained by employing the instrument developed in the present work and those obtained using FAAS. These results does not show significant differences at a 95% confidence level. As expected, results for Cu(II) were usually less favourable, since its concentration in the samples was lower than those of Zn(II), in addition to the characteristics of the metal ion complexes discussed above.

4. Conclusions

The multichannel photometer developed in this work is simple, easily constructed and versatile, suitable for application in multivariate calibrations and simultaneous determinations, providing acceptable errors for many applications. Although the LED employed cover virtually all the visible region of spectrum, the capability of the instrument can be further extended by employing a higher number of emitting devices. In addition, a more dedicated instrument can be also developed, if the LED are chosen according to a variable selection [17] carried out with spectral data obtained with a multichannel spectrophotometer.

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