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Sequential injection system for simultaneous determination of sucrose and phosphate in cola drinks using paired emitter-detector diode sensor

Phoonthawee Saetear [a,b], Kittiwut Khamtau [a,b], Nuanlaor Ratanawimarnwong [a,c], Kamonthip Sereenonchai [a,d], Duangjai Nacapricha [a,b,*]

[a] Flow Innovation-Research for Science and Technology Laboratories (FIRST Labs), Thailand
[b] Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Bangkok 10400, Thailand
[c] Department of Chemistry, Faculty of Science, Srinakharinwirot University, Sukhumvit 23 Road, Bangkok 10110, Thailand
[d] Department of Chemistry, Faculty of Science and Technology, Thammasat University, Paholyothin Road, Pathumthani 10120, Thailand

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ABSTRACT

This work presents the simultaneous determination of sucrose and phosphate by using sequential injection (SI) system with a low cost paired emitter-detector diode (PEDD) light sensor. The PEDD uses two 890 nm LEDs. Measurement of sucrose in Brix unit was carried out based on the detection of light refraction occurring at the liquid interface (the schlieren effect) between the sucrose solution and water. Phosphate was measured from the formation of calcium phosphate with turbidimetric detection. With careful design of the loading sequence and volume (sample–precipitating reagent–sample), simultaneous detection of sucrose and phosphate was accomplished with the single PEDD detector. At the optimized condition, linear calibrations from 1 to 7 Brix sucrose and from 50 to 200 mg PO_4^{3-} L^{-1} were obtained. Good precision at lower than 2% RSD ($n=10$) for both analytes with satisfactory throughput of 21 injections h^{-1} was achieved. The method was successfully applied for the determination of sucrose and phosphate in cola drinks. The proposed method is readily applicable for automation and is found to be an alternative method to conventional procedures for on-line quality control process in cola drink industry.

1. Introduction

Light emitting diodes (LEDs) are commonly used as a light source for portable spectrometers due to the low power consumption and brightness [1]. Their emission spectra are rather narrow (about ± 40 nm), allowing specific selection of wavelengths without an expensive monochromator or filter. However, LEDs can also be used as a light detector [2,3]. Paired emitter-detector diode (PEDD) is an inexpensive optical sensor that consists of a pair of LEDs where one LED is used as a light emitter (LED emitter) and the other LED as a light detector (LED detector). Use of PEDD as detector of light is attractive in terms of costs, size and broad range of wavelengths from UV to near-infrared region (ca. 380–900 nm). Unfortunately, LED as detector generates very small photocurrent. Diamond's group [4–6] demonstrated the accurate and precise measurement of the photocurrent using a threshold detector and timer circuit. The principle is based on measurement of the time taken for the photon-induced current to discharge the reverse-biased LED from an initial 5 V to 1.7 V. Later, another approach was proposed by using direct measurement of the voltage generated at the LED detector [7,8]. This method is very simple and convenient employing a common pH-meter or a digital multimeter with high input impedance.

The use of PEDD for absorbance measurement has been reported as early as 2004 when Diamond et al. employed the device as optical sensor for colorimetric analysis of dyes for pH measurement [4]. Since then, application of PEDD detector has been broaden to environmental field such as detection of heavy metals [9] and phosphate [10] in water samples as well as to bioanalytical field, such as detection of hemoglobin [11] and alkaline phosphatase activity [12–14]. PEDD has also been adopted as a detector in post column HPLC [15] and IC [16,17]. Recently, PEDD compatible with optosensing films has been developed for sequential injection (SI) system [18,19]. Prussian Blue film was used as a model optical chemoreceptor to detect hydrogen peroxide [18]. Determination of glucose in serum was demonstrated for this application [19]. With different configurations, the PEDD can also be used for fluorescence detection. The first report

* Corresponding author at: Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand. Tel./fax: +66 2 2015127.
E-mail addresses: duangjai.nac@mahidol.ac.th, dnacapricha@gmail.com (D. Nacapricha).

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of LED as fluorescence detector was in 2010 for the determination of quinine in beverage drinks [20]. Another application of fluorometric PEDD was the detection of calcium using complexation reaction with calcein [21,22].

The phenomena of light refraction and light scattering are alternative detection methods useful in analytical practice, especially with colored sample. This is because they can employ wavelengths at which that the colored solution does not absorb the light. Detection of light refraction at the liquid interface (the schlieren effect) was employed as detection in liquid chromatography using deflection of a laser beam [23] and in capillary electrophoresis [24]. In addition, the schlieren effect was also applied to flow analysis for quantitation of sucrose [25,26], alcohol [27] and glycol [28]. Another approach for analysis of colored sample is detection based on light scattering of colloidal particles (turbidimetry) [29] has been widely used through the formation of solid particles using suitable precipitating reagents. With coupling to flow-based system, it provides automation for several applications such as in environmental [30], biological [31] and food [32] samples.

In this work, implementation of PEDD for detection of the schlieren effect and the turbidity in liquid-flow system is presented. We selected sucrose and phosphate as model analytes to demonstrate this application for possible quality control in cola drink industry. The work used a sequential injection (SI) system [33]. With optimized selection of the loading sequence, simultaneous detection of the two analyte is carried out with one PEDD detector. The system is thus simple and compact.

2. Experimental

2.1. Chemicals and reagents

All solutions were prepared in deionized water (Barnstead EASYpure II, USA). The sucrose standard used in this work was commercial grade sugar (Mitr Phol, Thailand). A 50 Brix (Bx) stock sucrose solution was prepared by dissolving exactly 50.00 g of solid sucrose in 50.00 g of deionized water with stirring on a magnetic stirrer until the solid has completely dissolved. The stock solution was stored at 4 °C and used within one week.

A 5000 mg PO_4^{3-} L^{-1} stock phosphate solution was prepared by dissolving 0.7157 g of potassium dihydrogenphosphate (Fluka, Switzerland), previously dried at 60 °C for 2 h and kept in a desiccator, in 100.00 mL with deionized water. Working standard solutions used for calibration were mixed standards of sucrose and phosphate, prepared in deionized water by appropriate dilution of the stock solutions.

The precipitating reagent (R in Fig. 1) was a solution of 0.08 mol L^{-1} $CaCl_2$ in 0.1% (w/v) polyvinyl alcohol (PVA). This solution was prepared by weighing 0.888 g of calcium chloride (Merck, USA) and 0.10 g of PVA (Merck, USA), dissolving in approximately 90 mL of 0.3 mol L^{-1} ammonium buffer pH 10 and heating on a hot plate with magnetic stirring until all solids dissolved. After cooling to room temperature, ammonium buffer was added to make 100.0 mL. The buffer was prepared by dissolving 0.1338 g of ammonium chloride (Ajax Finechem, New Zealand) and 0.9 mL of 30%(w/w) ammonia (density 0.892 g L^{-1}, Panreac, Spain) in deionized water to give 100 mL.

2.2. Sample preparation

Regular and sugar-free cola drink samples were purchased from supermarkets in Bangkok, Thailand. All samples were degassed in an ultrasonic bath for 15 min. Dilutions of samples with water (1:1) were carried out prior to analysis. Five synthetic samples were also analyzed. These samples were prepared by dissolving analytical grade sucrose (UNIVAR, Australia) and potassium dihydrogenphosphate (Fluka, Switzerland) in deionized water (Table 2).

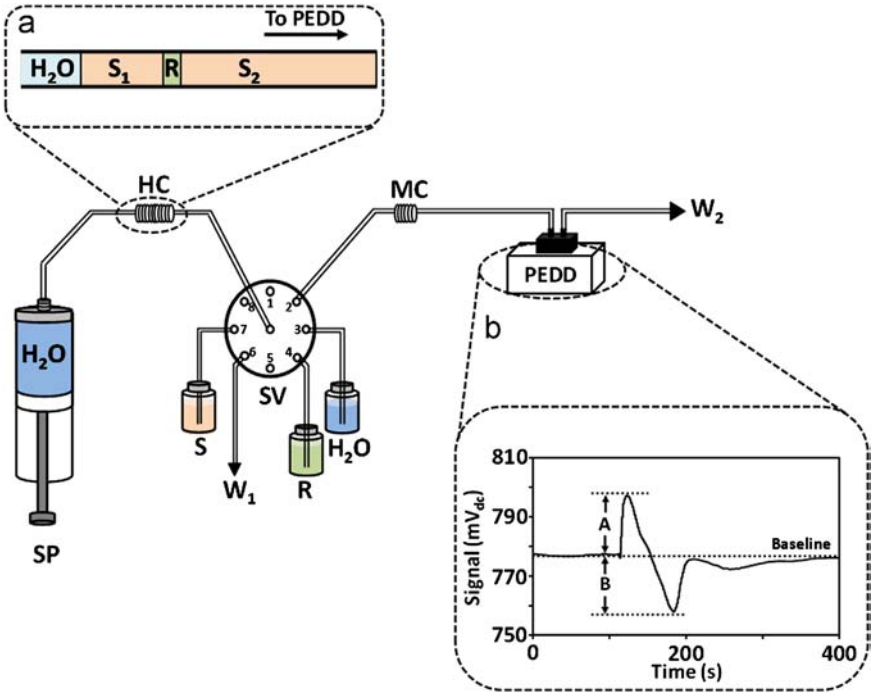

Fig. 1. Schematic diagram of the SI-PEDD system for simultaneous determination of sucrose and phosphate in cola drinks: S_1, 1st aspirated sample zone; R, precipitating reagent 0.08 mol L^{-1} $CaCl_2$ with 0.1%(w/v) PVA in ammonium buffer pH 10; S_2, 2nd aspirated sample zone; W, waste; SP, syringe pump; SV, selection valve; HC, 4.6-mL holding coil (i.d. 1 mm, 588 cm long); MC, mixing coil (i.d. 1 mm, 144 cm long); inset (a), sequence of the detection zone in HC; inset (b), signal profile of a mixed standard of sucrose and phosphate.

Table 1
The steps in the SI-PEDD operation for simultaneous determination of sucrose and phosphate in cola drinks.

Step	Mode of syringe pump	Volume (mL)	Flow rate (mL min^{-1})	Port no.	Action	Duration (s)
1	Aspirate	4.00	4.0	3	Aspiration of water carrier	60
2	Aspirate	0.50	4.0	7	Aspiration of 1st sample zone (S_1)	7.5
3	Aspirate	0.10	4.0	4	Aspiration of precipitating reagent (R)	1.5
4	Aspirate	1.75	4.0	7	Aspiration of 2nd sample zone (S_2)	26
5	Dispense	6.35	5.0	2	Dispense of all zones to detector and waste (W_2)	76

Total analysis time is 171 s.

Table 2
Comparison of accuracy obtained from analysis of synthetic samples by using the developed and conventional methods. The numbers in parenthesis are %RSD for six replicate injections.

Nominal values of synthetic sample	Sugar (Brix)		Phosphate (mg PO_4^{3-} L^{-1})	
	Our method	Refractometric method[a]	Our method	Spectrophotometric method[b]
5 Brix+200 mg PO_4^{3-} L^{-1}	5.16 ± 0.14 (2.7)	5.16 ± 0.05 (1.0)	197.7 ± 3.0 (1.5)	202.7 ± 2.1 (1.0)
7 Brix+200 mg PO_4^{3-} L^{-1}	6.42 ± 0.12 (1.9)	6.47 ± 0.07 (1.1)	200.0 ± 2.5 (1.3)	199.0 ± 2.1 (1.1)
10 Brix+300 mg PO_4^{3-} L^{-1}	9.79 ± 0.14 (1.4)	9.94 ± 0.10 (1.0)	300.7 ± 2.5 (0.8)	296.3 ± 2.6 (0.9)
10 Brix+300 mg PO_4^{3-} L^{-1}	10.44 ± 0.22 (2.1)	10.27 ± 0.10 (1.0)	299.9 ± 3.9 (1.3)	303.9 ± 3.0 (1.0)
12 Brix+300 mg PO_4^{3-} L^{-1}	11.95 ± 0.24 (2.0)	12.31 ± 0.14 (1.1)	300.7 ± 3.3 (1.1)	306.4 ± 4.3 (1.4)

[a] Refractometer 30PX/GS. Mettler Toledo, USA.
[b] See Ref. [35].

2.3. The SI-PEDD system and its operation

2.3.1. The SI-PEDD system

The SI system, shown in Fig. 1, consisted of a syringe pump (SP) equipped with an eight-port selection valve (SV) (Kloehn Versa Pump 6, USA). A 10-mL zero dead volume syringe (Kloehn, USA) was fitted to the pump. PTFE tubings with 1.0 mm i.d. (Cole Parmer, USA) were used as holding coil (HC) and mixing coil (MC). The syringe pump and selection valve were computer controlled by means of an in-house software written using LabVIEW 8.0™. The simple paired emitter-detector diode (PEDD) was made of two gallium–aluminium arsenide NIR-LEDs (890 nm, Model OP291, OPTEK Technology Inc., USA). A dc power supply (Model PS-1502DD, BEST, China) was used to supply the 5 V to the LED emitter. A 100 Ω resistor was used as a current-limiting load to the LED emitter. A 6-digit digital multimeter with 10^{12} Ω impedance (Model 8845A, Fluke, USA) was used to measure voltage signal from the LED detector. Data was recorded and stored on a computer via RS-232 port with in-house software written using LabVIEW 8.0™. A 10-mm path length, 18-μL volume, quartz flow-through cell (PerkinElmer, USA) was placed in a cuvette holder between the two LEDs.

2.3.2. System operation

A water carrier plug (4.0 mL) was introduced into the holding coil (HC in Fig. 1) followed by plugs of sample and reagent (1st aspirated sample zone (S_1), reagent (R) and 2nd aspirated sample zone (S_2)). These detection zones are finally driven forward to the PEDD detector to give a sequence of signal peaks. Details of the operation steps are given in Table 1.

2.4. Data analysis

For a PEDD, the LED detector generates a voltage, which is linearly proportional to the logarithm of the intensity of light illuminating on the LED. When there is alteration in light intensity due to light refraction or light scattering, such as in this work, the monitored voltage is changed accordingly. Thus a plot between the voltage measured versus time is obtained, as the sample zone passes through the flow-through cell. Example of signal profile is shown in Fig. 1b.

The baseline signal is obtained when water carrier flows passing through the PEDD. The signal for sucrose is the difference of the voltage between the apex of peak and baseline ('A' in Fig. 1b). The signal for phosphate is the difference of the voltage between the baseline and the minimum of the second peak ('B' in Fig. 1b). Two calibration curves were constructed by plotting the values of A and B against the analyte concentrations.

For validation of the method, the results were compared to measurements obtained from refractometric method for sucrose [34] and spectrophotometric method based on molybdenum blue reaction [35] for phosphate, respectively.

3. Results and discussion

3.1. System design and its signal profile

A simple SI system, shown in Fig. 1, was employed to study the use of the PEDD detector for simultaneous detection of the schlieren and turbid effect within one cycle of operation. The system starts by aspirating the detection zone, with the precipitating reagent (R in Fig. 1a) inserted in the middle of the mixed standard solution containing sucrose and phosphate (S_1 and S_2 in Fig. 1a), into the HC, followed by dispensing to the PEDD detector. As the laminar flow is driven towards the PEDD detector, this right hand end of S_2 (Fig. 1a) becomes the leading parabolic interface between sample and water, which is responsible for the schlieren signal. Positive signal profile in Fig. 1b demonstrates this phenomenon. After the zone head has moved through the PEDD, the middle zone containing suspension of the calcium phosphate precipitate enters the flow cell. These calcium phosphate particles scatter light, giving rise to a decrease in the signal. If there is appreciable inhomogeneity within the zone, small negative signal is observed when the zone tail travels through the light path. Normally this negative signal is only observed at sucrose concentration greater than

5 Brix. The complete signal profile obtained for one sample is shown in Fig. 1b.

The observed schlieren effect has been explained in great details [26]. To summarize, the interface of the carrier and sugar solution forms a lens. In this case, where $n_{sample} > n_{carrier}$ (n=refractive index), we may expect a significant population of light rays to bend towards the LED light sensor. As a result, the absorbance decreases. Thus, the signal voltage from the LED light sensor increases with decreasing absorbance. So the signal profile increases with the passage of the sugar zone (the signal change 'A' in Fig. 1b), which is the inverse of the regular signal profile using photodiode as light sensor with log amplifier (see Ref. [26] for example). For the turbidity profile, suspending particle causes light scattering away from the LED light sensor. Therefore there is an increase in absorbance which for our LED light sensor means a decrease in the signal profile (the signal change 'B' in Fig. 1b).

3.1.1. Interference between sucrose and phosphate measurements

In this study, the concentrations of phosphate were varied up to 200 mg PO_4^{3-} L^{-1} whereas the concentration of sucrose was fixed at 7 Brix. We found no effect of phosphate concentration on the sucrose measurement. Thus the refractive index (RI) of standard/sample depends mainly on the concentration of sucrose with no contribution from the concentration of phosphate.

On the other hand, sucrose had a significant negative effect on the phosphate measurement at aspirated volumes of S_1:R:S_2 of 0.5:0.1:0.5 mL (see data in Fig. 2 for S_2=0.5 mL). This might be from inhomogenity in the calcium phosphate zone due to the viscosity of sucrose (7 Brix). Normally, increasing the mixing coil length of the SI system improves mixing. But for our system which requires efficient mixing only in the mid-zone, but not at the leading zone, this is not a suitable choice. Therefore, enhancement of the mid-zone dispersion was investigated by increasing the aspirated volume of the second sample segment, S_2. In this way, mixing of the reagent and sample zones is promoted by increasing the longitudinal dispersion along the tube. The results are shown in Fig. 2. The signal height for phosphate in pure water increased with increasing volume of S_2 from 0.5 to 0.75 mL indicating more precipitation had occurred. With larger volume dilution effect dominated and signal decreased drastically. For phosphate dissolved with sucrose, the same trend was found but with smaller signals for segment volume of S_2 between 0.5 and 1.5 mL. However equal signals for solution using pure water and sucrose solution were found for volume of 1.75 mL and larger. Therefore, in order to eliminate the interference effect of sucrose, the volume of segment S_2 of 1.75 mL was selected.

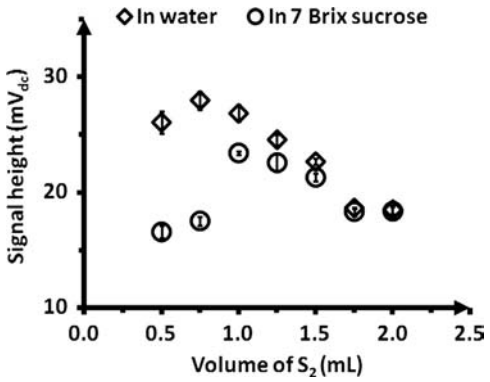

Fig. 2. Effect of volume of S_2 on signal height of 200 mg PO_4^{3-} L^{-1} in water (◇) and in 7 Brix sucrose (○). Each point is the result from triplicate injections for volumes of S_1:R fixed at 0.5:0.1 mL.

3.1.2. Light source and sensor for PEDD detector

Cola drink has a dark brown color and the wavelength of the detector must be carefully chosen to ensure that only the schlieren and turbidity effects are observed. The visible absorption spectrum of these drinks were measured and found to have absorbance only in the wavelength range of 350–700 nm. Therefore, NIR LED emitter with wavelength of 890 nm was selected as the light source. The same LED was employed as detector for maximum response. A stable output voltage at 0.8 V was found for water. Signal changes in the range of $\pm$ 0.05 V were observed for samples containing sucrose and phosphate.

Flow cell with small volume (18 μL) was used for our experiment since it provided sharper schlieren signal than the normal 80 μL-flow cell. The larger i.d. of the 80 μL-flow cell produces greater dispersion of the sample zone, which is not suitable for measurement based on the schlieren effect.

3.2. Optimization

3.2.1. Flow rate

Flow rate is an important parameter which affects the sensitivity and sample throughput. The flow rate in the final step for driving all the liquid zones to the PEDD detector was varied from 1 to 10 mL min^{-1}. It was observed that at lower flow rate higher sensitivity was achieved for both phosphate and sucrose measurements. A flow rate at 5 ml min^{-1} was chosen as compromise between sensitivity and throughput.

3.2.2. Parameters for calcium phosphate precipitation process

The effect of various concentrations of $CaCl_2$ was studied using concentration range from 0.04 to 0.12 mol L^{-1}. Results are shown in Fig. 3a. The signal B (Fig. 1b) increased with increasing concentration of $CaCl_2$, reaching a plateau value for concentrations greater than 0.06 mol L^{-1}. The concentration of 0.08 mol L^{-1} $CaCl_2$ was chosen to ensure excess Ca^{2+} ion for production of the $Ca_3(PO_4)_2$ precipitate.

Buffer concentrations ranging from 0.2 to 6.5 mol L^{-1} were investigated. The results in Fig. 3b showed that buffer concentration of 0.3 mol L^{-1} gave the highest sensitivity. At buffer concentration lower than 0.3 mol L^{-1}, the buffer capacity was not sufficient to neutralize the acid in the sample. High concentration of buffer has large ionic strength, resulting in less precipitation [36]. In this work 0.3 mol L^{-1} buffer was chosen. The pH of buffer solution was also investigated (Fig. 3c). The sensitivity significantly increased to pH 10 and then decreased. Therefore a pH 10 buffer was selected for maximum sensitivity.

Generally, turbidity measurement requires addition of a stabilizer to control uniformity of the particle size for reproducibility. In this work, PVA was used and the effect of PVA concentration in the range of 0.02–0.30%(w/v) was studied. The results in Fig. 3d showed that 0.10%(w/v) PVA provided the highest sensitivity which decreased significantly when concentration of PVA was more than 0.1%(w/v) because increasing concentration of PVA can cause decreased number of nucleation sites of $Ca_3(PO_4)_2$, and hence lower number of scattering particles [37]. Hence the concentration of PVA of 0.1%(w/v) was selected as optimum condition.

The volume of the calcium chloride solution (R) was also investigated in the range of 50–200 μL. It was found that sensitivity increased, with increasing volume, to maximum value at 100 μL. Therefore, the volume of 100 μL was selected because it offered highest sensitivity with least reagent.

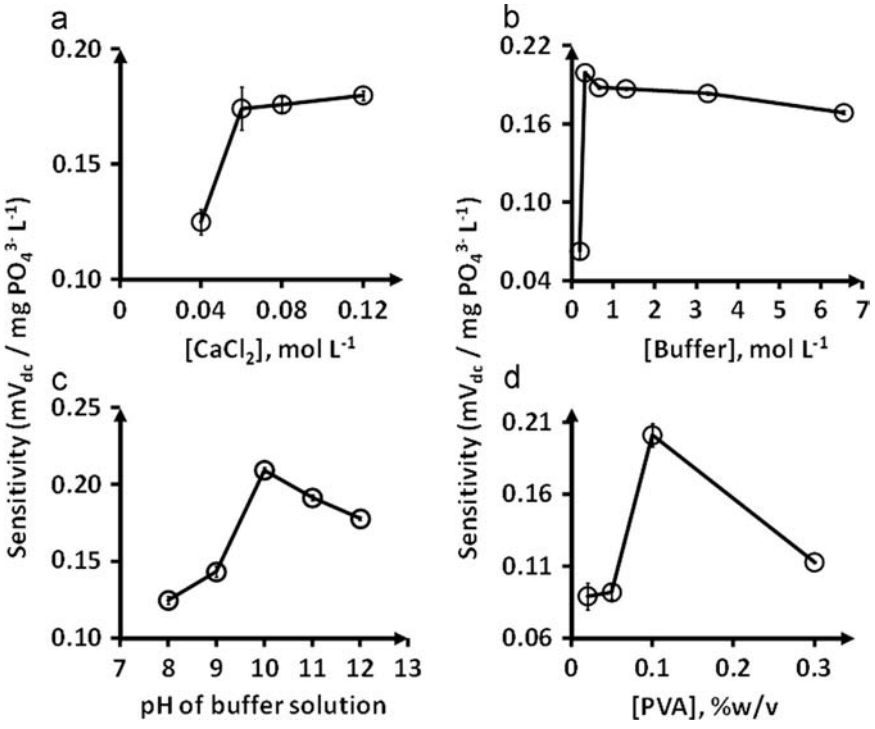

Fig. 3. Effect of the precipitating reagent on the sensitivity of phosphate analysis. Triplicate injections for each point in the graph.

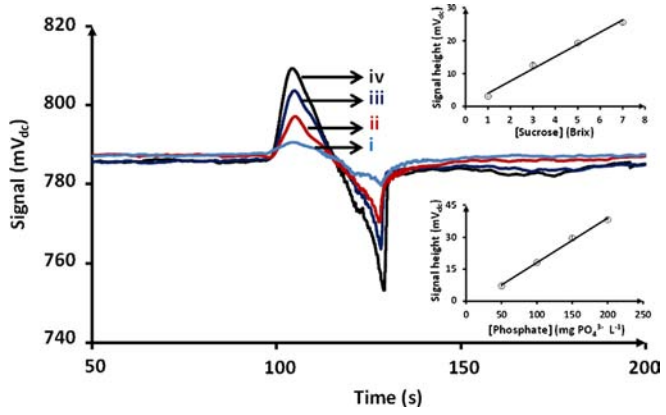

Fig. 4. Example of signal profiles obtained from mixed standards of sucrose and phosphate at (i) 1 Brix+50 mg PO_4^{3-} L^{-1} (ii) 3 Brix+100 mg PO_4^{3-} L^{-1} (iii) 5 Brix +150 mg PO_4^{3-} L^{-1} (iv) 7 Brix+200 mg PO_4^{3-} L^{-1}, using the developed system, and calibration plots for sucrose and phosphate. Each point in the calibrations was from triplicate injections.

3.3. Analytical features and application to cola drink samples

Using the optimum condition, representative SI-signal profiles and calibration plots are shown in Fig. 4. Calibration curve is linear in the range of 1–7 Brix sucrose ((signal height, mV_{dc})=(3.14 ± 0.03)[Brix]+(0.14 ± 0.13), $r^2=0.999$) and of 50–200 mg PO_4^{3-} L^{-1} ((signal height, mV_{dc})=$((1.85 \pm 0.04) \times 10^{-1})$[mg PO_4^{3-} L^{-1}]–(1.96 ± 0.51), $r^2=0.999$). Detection limits (3S/N) at 0.5 Brix sucrose and 20 mg PO_4^{3-} L^{-1} were obtained. Ten replicate injections of the mixed standard of 5 Brix sucrose and 150 mg PO_4^{3-} L^{-1} were carried out to provide system precision of 0.9% and 1.7% (RSD), respectively. Reasonable throughput of 21 injections h^{-1} was achieved.

Five synthetic samples were prepared and analyzed by our method and reference methods (Table 2). Analysis of sucrose and phosphate was compared with refractometric method and the conventional molybdenum blue method, respectively. The results show that the precision of our methods are comparable with the reference methods. The developed SI-PEDD system was subsequently applied to regular and sugar-free cola drinks (Table 3). According to the paired *t*-test, the results in Table 3 show significant agreement between the proposed method and the conventional methods for all the samples (sugar: $t_{observed}=1.285$, $t_{critical}=2.306$ at $P=0.05$; phosphate: $t_{observed}=0.005$, $t_{critical}=2.178$ at $P=0.05$) [38].

4. Conclusions

In this work, the PEDD sensor was employed as a single flow-based detector for measuring the schlieren effect and turbidity of sample in a SI system for automation of liquid handling. It was shown that the SI-PEDD flow system had sufficient sensitivity to detect light refraction at interface of sucrose and water or so-called the schlieren effect, as well as the light scattering of the colloidal particles of calcium phosphate, when the output of the LED detector was monitored by a high-impedance digital multimeter.

Simultaneous analysis of sucrose and phosphate in cola drinks was selected to demonstrate this application. With two fold sample dilution, the measurements were carried out using NIR-PEDD (890 nm) sensor without sample pretreatment to remove the color. At the optimum condition, the observed signal comprised one positive peak for sucrose and a second negative peak for phosphate. These two signals are well separated. Thus the contents of sucrose and phosphate were successfully determined with no interference. The developed SI-PEDD flow system has advantages in terms of simplicity, robustness and costs. Moreover, the system is environmentally friendly since only small amounts of non-toxic $CaCl_2$ in ammonium buffer solution were used. The SI-PEDD system was successfully applied to the measurement of sucrose and phosphate in commercial cola drinks and is also suitable for on-line quality control processing plants.

Table 3
Analysis of cola drinks by SI-PEDD system as compared with conventional methods. The numbers in parenthesis are %RSD for six replicate injections.

Sample	Sugar (Brix)		Phosphate (mg PO_4^{3-} L^{-1})	
	Our method	Refractometric method[a]	Our method	Spectrophotometric method[b]
Cola 1	9.55 ± 0.11 (1.2)	9.75 ± 0.05 (0.5)	341.5 ± 6.1 (1.8)	342.4 ± 3.6 (1.1)
Cola 2	9.09 ± 0.09 (1.0)	9.14 ± 0.06 (0.7)	338.2 ± 1.7 (0.5)	347.6 ± 5.6 (1.6)
Cola 3	9.96 ± 0.13 (1.3)	9.82 ± 0.10 (1.0)	340.5 ± 7.0 (2.1)	330.0 ± 3.1 (0.9)
Cola 4	9.73 ± 0.14 (1.4)	9.84 ± 0.10 (1.0)	377.7 ± 1.8 (0.5)	375.8 ± 4.4 (1.2)
Sugar-free cola 1	nd	nd	348.0 ± 5.3 (1.5)	351.7 ± 1.4 (0.4)
Sugar-free cola 2	nd	nd	343.3 ± 9.3 (2.7)	332.7 ± 5.3 (1.6)
Sugar-free cola 3	nd	nd	356.0 ± 6.1 (1.7)	347.4 ± 6.0 (1.7)
Sugar-free cola 4	nd	nd	342.5 ± 7.3 (2.1)	351.3 ± 3.6 (1.0)

nd: not detected.

[a] Refractometer 30PX/GS. Mettler Toledo, USA.

[b] See Ref. [35].

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References

[1] P.K. Dasgupta, I.Y. Eom, K.J. Morris, J. Li, Anal. Chim. Acta 500 (2003) 337–364.
[2] R.H. Lindsay, B.E. Paton, Am. J. Phys 44 (1976) 188–189.
[3] F.M. Mims III, Appl. Opt. 31 (1992) 6965–6967.
[4] K.T. Lau, S. Baldwin, R.L. Shepherd, P.H. Dietz, W.S. Yerzunis, D. Diamond, Talanta 63 (2004) 167–173.
[5] M. O'Toole, K.T. Lau, D. Diamond, Talanta 66 (2005) 1340–1344.
[6] K.T. Lau, S. Baldwin, M. O'Toole, R. Shepherd, W.J. Yerazunis, S. Izuo, S. Ueyama, D. Diamond, Anal. Chim. Acta 557 (2006) 111–116.
[7] L. Tymecki, M. Pokrzywnicka, R. Koncki, Analyst 133 (2008) 1501–1504.
[8] L. Tymecki, R. Koncki, Anal. Chim. Acta 639 (2009) 73–77.
[9] K.T. Lau, E. McHugh, S. Baldwin, D. Diamond, Anal. Chim. Acta 569 (2006) 221–226.
[10] M. O'Toole, K.T. Lau, R. Shepherd, C. Slater, D Diamond, Anal. Chim. Acta 597 (2007) 290–294.
[11] E. Mieczkowska, R. Koncki, L. Tymecki, Anal. Bioanal. Chem. 399 (2011) 3293–3297.
[12] L. Tymecki, L. Brodacka, B. Rozum, R. Koncki, Analyst 134 (2009) 1333–1337.
[13] L. Tymecki, K. Strzelek, R. Koncki, Talanta 79 (2009) 205–210.
[14] K. Strzelek, R. Koncki, L. Tymecki, Talanta 96 (2012) 127–131.
[15] M. O'Toole, K.T. Lau, B. Shazmann, R. Shepherd, P.N. Nesterenko, B. Paull, D. Diamond, Analyst 131 (2006) 938–943.
[16] L. Barron, P.N. Nesterenko, D. Diamond, M. O'Toole, K.T. Lau, B. Paull, Anal. Chim. Acta 577 (2006) 32–37.
[17] M.O' Toole, L. Barron, R. Shepherd, B. Paull, P. Nesterenko, D. Diamond, Analyst 134 (2009) 124–130.
[18] M. Pokrzywnicka, D.J. Cocovi-Solberg, M. Miró, V. Cerdà, R. Koncki, L. Tymecki, Anal. Bioanal. Chem. 399 (2011) 1381–1387.
[19] D.J. Cocovi-Solbera, M. Miró, V. Cerdà, M. Pokrzywnicka, L. Tymecki, R. Koncki, Talanta 96 (2012) 113–120.
[20] M. Pokrzywnicka, R. Koncki, L. Tymecki, Talanta 82 (2010) 422–425.
[21] L. Tymecki, M. Pokrzywnicka, R. Koncki, Analyst 136 (2011) 73–76.
[22] M. Pokrzywnicka, M. Fiedoruk, R. Koncki, Talanta 93 (2012) 106–110.
[23] J. Pawliszyn, Anal. Chem. 58 (1986) 3207–3215.
[24] J. Pawliszyn, Anal. Chem. 60 (1988) 2796–2801.
[25] S. Teerasong, S. Chan-Eam, K. Sereenonchai, N. Amornthammarong, N. Ratanawimarnwong, D. Nacapricha, Anal. Chim. Acta 668 (2010) 47–53.
[26] T. Mantim, P. Saetear, S. Teerasong, S. Chan-Eam, K. Sereenonchai, N. Amornthammarong, N. Ratanawimarnwong, P. Wilairat, W. Meesiri, K. Uraisin, D. Nacapricha, Pure Appl. Chem. 84 (2012) 2015–2025.
[27] S.R.B. dos Santos, M.C.U. Araújo, R.A. Barbosa, Analyst 127 (2002) 324–327.
[28] A. Wijk, B. Karlberg, Talanta 41 (1994) 395–400.
[29] D.A. Skoog, D.M. West, Principles of Instrumental Analysis, second ed., Saunders College, West Washington Square, Philadelphia, PA, USA294–299.
[30] R.B.R. Mesquita, S.M.V. Fernandes, A.O.S.S. Rangel, J. Environ. Monit. 4 (2002) 458–461.
[31] B.M. Simonet, F. Grases, J.G. March, Fresenius J. Anal. Chem. 369 (2001) 96–102.
[32] J.L.F.C. Lima, A.O.S.S. Rangel, M.R.S. Souto, E.A.G. Zagatto, Anal. Chim. Acta 356 (1997) 259–265.
[33] J Ruzicka, G.D. Marshall, Anal. Chim. Acta 237 (1990) 329–343.
[34] M. Bhuyan, Measurement and Control in Food Processing, CRC Press, Taylor & Francis, Boca Raton, USA179–182.
[35] E.W. Rice, R.B. Baird, A.D. Eaton, L.S. Clesceri, Standard Methods for the Examination of Water and Wastewater, twenty second ed., American Public Health Association, Washington, USA, 2012 4-155–156.
[36] Y. Song, H.H. Hahn, E. Hoffmann, Chemosphere 48 (2002) 1029–1034.
[37] C.O. Costa-Neto, A.V. Pereira, C. Aniceto, O. Fetibello-Filho, Talanta 48 (1999) 659–667.
[38] J.N. Miller, J.C. Miller, Statistics and Chemometrics for Analytical Chemistry, fifth ed, Pearson Education Limited, Gosport, 2005.