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# A Simple Photometer Based on a New Tri-Colour Light-Emitting Diode

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**Abstract.** Light-emitting diodes which can produce blue, green, and red light and therefore cover most of the visible range have recently been introduced. Such a device is used in the construction of a simple and compact photometer for molecular absorbance measurements in analytical chemistry.

## Introduction

The use of light-emitting diodes (LEDs) in analytical chemistry was first reported by *Flaschka et al.* in 1973 [1]. The limited spectral bandwidth is generally sufficiently narrow to dispense with any wavelength discriminating devices such as monochromators or optical filters. By using a photodiode as detector transmittance measurements can be achieved with a single operational amplifier and many simple and inexpensive analytical instruments based on LEDs have been reported in the scientific literature. The technique is well proven as evidenced by the fact that dedicated LED photometers for the analysis of certain parameters in drinking, waste, or pool waters are commercially available. Absorbance measurements rather than the common transmittance measurements can be carried out with little extra effort by using a logarithmic amplifier [2][3]. Photometric measurements in solutions with LEDs has been discussed in two review articles [2][4].

One limitation of these devices to date has been the inflexibility of the emitted wavelength range. A change of colour could generally only be achieved by physically changing the LED mounted in the instrument. Fibre optic couplers may be

used to guide the light from several LEDs into one optical cell but this adds expense and bulk [5][6]. Bi-colour LEDs which are based on two semiconductor chips in a single housing have been available and used for a dual wavelength photometric device [7]. The combination of such an LED with a number of identical single colour LEDs arranged concentrically for coupling a third colour into a photometric cell has been described [8][9], but is not ideal.

Tri-colour LEDs which are based on a combination of red and green emitters with the third colour (yellow) synthesized from the other two have been available for some time, but for spectroscopic purposes are really only dual-colour devices. Blue LEDs have been rare and true tri-colour LEDs which can emit red, green, or blue (RGB) have only recently become available. These devices may be termed RGB-LEDs for distinction from the red-yellow-green tri-colour LEDs.

The aim of this paper is to show that by using a novel RGB-LED it is possible to construct a sublimely simple photometer with unprecedented wavelength flexibility covering the entire visible range.

## Experimental

### Solutions

Standards for the Fe<sup>II</sup> determination by the phenanthroline method [10] were prepared from an appropriate amount of a stock solution of ferric alum (FeNH<sub>4</sub>SO<sub>4</sub> · 12 H<sub>2</sub>O), 15 ml of 5% hydroxylamine hydrochloride, 10 ml of 10% sodium citrate, and 10 ml of 0.2% 1,10-phenanthroline in 0.1M HCl. This was diluted to 100 ml. Standards for the nitrite determination by the *Griess* method [10] were prepared from an appropriate amount of stock solution of NaNO<sub>2</sub>, 2 ml of

0.5% sulfanilamide in 20% (v/v) HCl, 2 ml of 0.3% *N*-(1-naphthyl)ethylenediamine dihydrochloride in 1% (v/v) HCl and this was followed by dilution to 100 ml. Standards for the phosphate determination by the molybdate method [10] were made up with an appropriate amount of a stock solution of KH<sub>2</sub>PO<sub>4</sub>, 10 ml of molybdate ascorbic reagent (10 ml of 1% ammonium molybdate in 0.5M nitric acid and 10 ml of 0.7% ascorbic acid diluted to 100 ml) and made up to 100 ml. All chemicals were of analytical reagent grade.

The Everlight RGB-LED was obtained from *SCR International*, Auckland, New Zealand. The log-converter (*JCL8048*) originated from *Harris Semiconductor* (Melbourne, FL, USA). The panel meter used is a standard 3<sup>1</sup>/<sub>2</sub> digit instrument (*OEM33*) with an input range of ± 199.9 mV and was obtained from *Anders Electronics* (London, England).

The conventional calibration curves and absorption spectra were acquired on a *Shimadzu UV-160A* spectrophotometer (*Shimadzu*, Kyoto, Japan) using 1 cm cuvettes. The emission spectra of the LED were determined on a *Hitachi F-2000* spectrofluorometer (*Hitachi*, Tokyo, Japan) by mounting it in the cell holder. The spectra were redrawn from the scaled numerical output of the instruments.

The stabilities of the LED were determined by enclosing the instrument in a cardboard box and gentle heating of the assembly with a hot air gun in order to elevate the temperature by approximately 5°C. For this purpose the photodiode was connected to an operational amplifier in the current follower configuration (*OPA 121*, *Burr-Brown*, Tucson, TX, USA). The temperature was determined with a temperature sensor IC (*LM35CZ*, *National Semiconductor*, Santa Clara, CA, USA). Both signals were recorded with a *MacLab* data-acquisition system (*MacLab/4s*, *ADInstruments Pty. Ltd.*, Castle Hill, NSW, Australia) in connection with a *Macintosh Centris 650* personal computer (*Apple*, Cupertino, CA, USA). The temperature coefficients of the electronic components are negligible.

## Results and Discussion

### Design of the Instrument

The instrument is essentially based on three main electronic components only: the LED, a photodiode, and a single integrated circuit (IC). The LED serves as light source, the photodiode as detector, and the integrated circuit as a logarithmic converter. The electronic circuitry is given in *Fig. 1*. It consists of two sections. To the left of the stylized cuvette the schematic of the RGB-LED is shown together with the current limiting resistors and the rotary switch which allows selection of the emitted colour. Note that the LED contains two blue emitting semiconductor substrates in order to increase the output intensity of blue light. To the right of the cuvette a photodiode converts the transmitted light intensity into a photocurrent which is fed to the logarithmic amplifier.

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The output,  $V_o$ , of this integrated circuit device is related to the logarithm of the input current,  $I_{in}$ , according to:  $V_o = -K \times \log(I_{in})$ . If  $K$  is set to 1 by adjustment of the Gain Adjust trimmer resistor than the circuitry directly emulates Lambert-Beer's law. The output is fed to a panel meter for direct display of absorbance. The LED and the photodiode are mounted on opposite sides in a special holder for standard 10 mm cuvettes. The entire circuitry including the cuvette fits into a box of 5 x 5 x 7 cm (height x width x depth).

The instrument corresponds to a single beam instrument and therefore relies on the stability of the radiation source. LEDs are comparatively stable sources and in most reports on using LEDs in analytical instruments instabilities have not been considered. However, the emission intensities of LEDs show some dependence on the temperature of the semiconductor junction. A negative temperature coefficient of approximately 1% per degree Celsius is found [11]. The temperature coefficients determined experimentally for the blue, green, and red emitters of the device used here were found to be 0.2%/°C, 0.2%/°C, and 0.6%/°C, respectively. It is presumed that these practical values are lower than the inherent coefficient because of self-heating [11] and that fluctuations in the ambient temperature affect the semiconductor junction temperature only indirectly through alterations in the cooling efficiency. Due to the logarithmic relationship, errors of 0.2 and 0.6% in transmittance correspond to errors of 0.9 and 2.7%, respectively, in absorbance. Small and slow drifts due to temperature fluctuations may therefore be encountered. These may be corrected by occasional re-zeroing of the instrument. Note, that a drift in intensity of the light source does not affect the gradient of the calibration curve in absorbance measurements. The slight temperature dependence of the device should generally not be a problem in routine applications in analytical chemistry. If higher precision is required a referenced device similar to the ones described elsewhere may be constructed albeit for the price of added complexity and cost [3][6][12].

### Emission Spectra

The emission spectra for the LED are shown in Fig. 2. Three bands are found corresponding to the three colours blue, green, and red with peaks at 463, 556, and 632 nm. As expected for blue LEDs the bandwidth is somewhat wider for this colour than for the others. The emission of the three bands is well distributed over the entire visible range from ca. 400–700 nm.

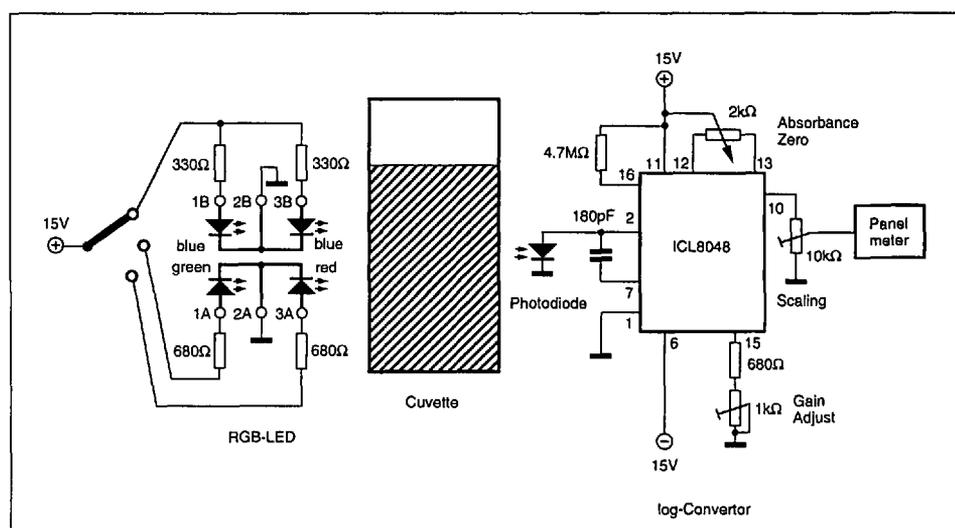


Fig. 1. Electronic circuitry for the instrument also showing the optical arrangement

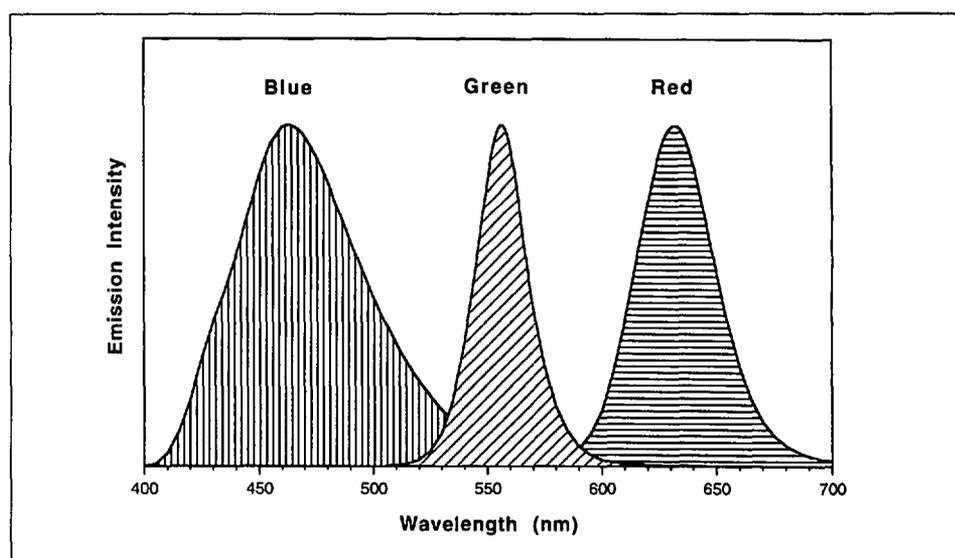


Fig. 2. Emission spectra for the three colours produced by the light-emitting diode (LED)

### Calibration Curves

Calibration curves were obtained for three photometric procedures. These are common methods used on a routine basis in many analytical laboratories and the standard prescriptions were adhered to [10]. One method was chosen for each of the three spectral region covered by the LED but it was deliberately avoided to pick methods that would give a close match of peak emission and absorbance wavelengths. In Fig. 3 the calibration curve obtained for the determination  $Fe^{II}$  by the phenanthroline method is shown. Also given is the calibration curve obtained in the conventional way by using a spectrophotometer at the wavelength of maximum absorbance. Some loss of sensitivity is encountered for the LED-based transducer. As can be seen from the absorption and emission bands of the LED and the coloured complex, respectively, which are also shown in Fig. 3, this is due to a less

than perfect match of the two peaks. A similar result is obtained for the nitrite determination method, but, as is seen in Fig. 4, the calibration for the LED shows a pronounced curvature over the entire range. This effect is common when using LEDs in photometry and is caused by variations of the absorptivity over the emission band of the LED [6]. However, curved calibration plots are not a problem in the application of the device. The third method, the common determination of phosphate with the molybdate method, yielded again a sensitivity approaching that of the monochromator, as can be seen in Fig. 5.

### Precision

After allowing about 10 min for warming up, a precision of 0.002 absorbance units (standard deviation,  $n = 5$ ) could be achieved throughout. This is close to the resolution of the read-out (0.001 absorb-

Fig. 3. Calibration curves for the Fe<sup>II</sup> determination by the phenanthroline method obtained by the LED transducer and the spectrometer. Emission spectrum of the LED and absorption spectrum of the coloured complex.

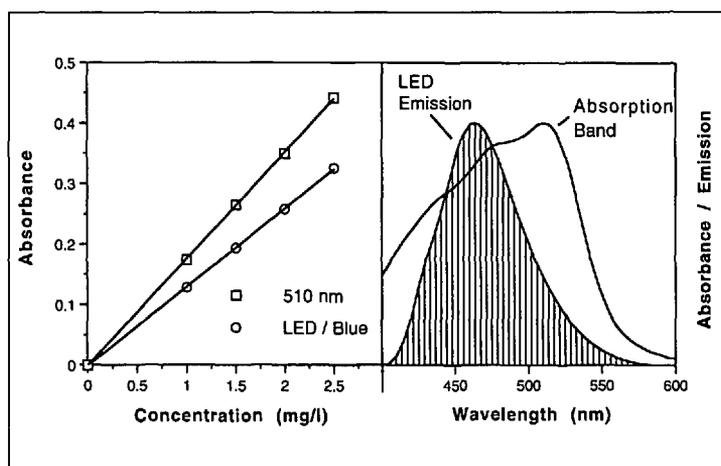


Fig. 4. Calibration curves for the nitrite determination by the Griess method obtained by the LED transducer and the spectrometer. Emission spectrum of the LED and absorption spectrum of the coloured complex.

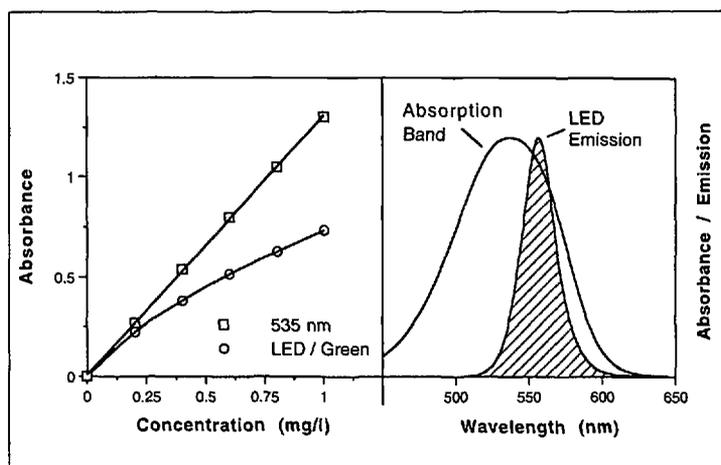
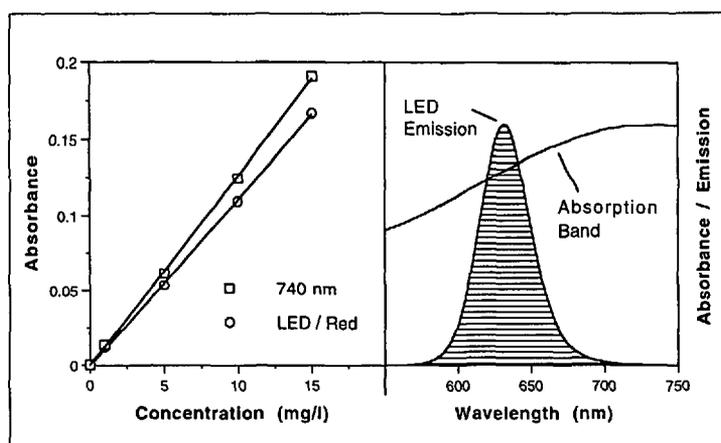


Fig. 5. Calibration curves for the phosphate determination by the molybdate method obtained by the LED transducer and the spectrometer. Emission spectrum of the LED and absorption spectrum of the coloured complex.



tion is very high. This may be surprising, but is corroborated by reported results for other LED devices [3][12] and is due to the fact that the device is based on a restricted number of components. As evidenced by the results for the iron and phosphate determinations it works well even for methods which show a peak absorbance far removed from any of the emission maxima of the LED ( $\Delta\lambda$  for Fe<sup>II</sup> 47 nm, for phosphate 108 nm). It can therefore be safely concluded that due to the generally wide absorbance bands encountered in analytical molecular photometry the instrument would work well with most quantitative methods which employ the visible range. The relative lack of spectral selectivity compared to a conventional spectrophotometer introduces an increased susceptibility to interference by coloured samples. However the wide acceptance of LED devices (albeit based on single colour LEDs) indicates that this is not a practical limitation.

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ance units) and comparable to or better than the precision obtainable with conventional spectrophotometers. This relates to confidence limits of  $\pm 1\%$  (for 95% certainty) in concentration at measured absorbances of 0.2 and it translates to lower limits of detection of 0.05, 0.007, and 0.6 mg/l for iron, nitrite, and phosphate, respectively. If the temperature varies during measurements these values may be higher (see above).

**Conclusions**

The instrument shows an unprecedented simplicity, compactness, and low cost while incorporating wavelength flexibility. Its performance indicates that it is suitable as a replacement for conventional spectrophotometers for commonly used photometric analytical procedures. A loss of sensitivity will usually be encountered but this is not of significance as the preci-