C190-E233A

SHIMADZU
Excellence in Science

Technical Report

Improved Linearity and Quantification Using the SPD-M40 Photodiode Array Detector

- Analytical Intelligence Part 4 -

Masato Watanabe[1], Hidetoshi Terada[1]

Abstract:

In principle, stray light generated during the UV-VIS and PDA detection process has a great influence on the linearity of the detector's response linearity. This report explains the influence of stray light upon detection and introduces the SPD-M40 photodiode array detector, which completely reduces the influence of stray light and achieves a linearity of 2.5 AU as a specification value (typical value is more than 2.5AU). Furthermore, in the low signal range, noise reduced noise has improved the detection accuracy of low concentrations, enabling the quantification of a wide concentration range. This enables simultaneous analysis and quantification of major components and impurities with different concentration ranges.

Keywords: Dynamic range, linearity, absorbance, stray light, noise

1. Principle of UV-VIS and PDA detectors

Unlike a UV-VIS detector, which separates light spectrally from a light source and irradiates the flow cell with only a specific wavelength to measure the absorbance of the target component, a PDA detector directly irradiates the flow cell with light from a light source containing various wavelengths (white light) and separates the light spectrally after passing through the flow cell. The optical flow diagrams are shown in Fig. 1.

A PDA detector can simultaneously measure the absorbance and the absorption spectrum, and can be used not only for quantitative analysis, but also for qualitative analysis.

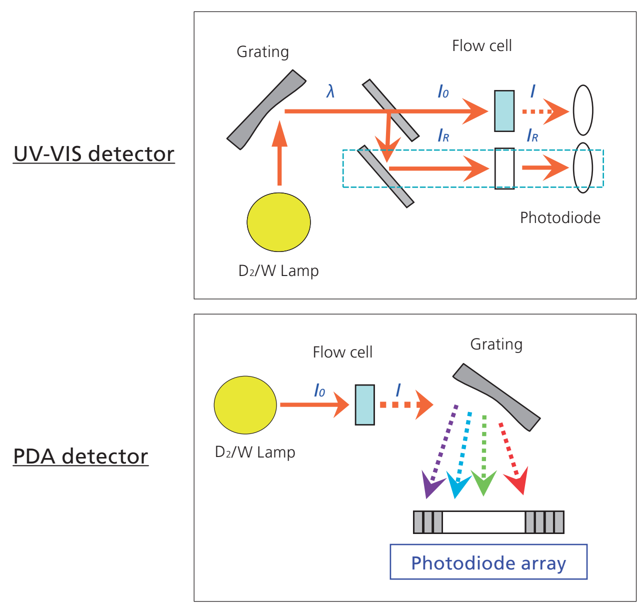

Fig. 1 Principle of UV-VIS and PDA detectors

2. Effect of stray light on absorbance

In general, absorbance is expressed in terms of the intensity of incident light on the flow cell and the intensity of transmitted light through the sample cell, according to Lambert-Bert's law.

$$A = -\log\frac{I}{I_0}$$

A : Absorbance
I : Real-time light intensity transmitted through the flow cell
I_0 : Incident light intensity

If the unexpected light is emitted by the spectroscope, the correct absorbance cannot be measured. Unexpected light during detection is commonly referred to as "Stray Light". The influence of stray light on the absorbance is expressed by the following equation.

$$A = -\log\frac{I+\Delta}{I_0+\Delta}$$

Δ: stray light intensity

If the absorbance in the flow cell is high, the transmitted light intensity from the cell will be small. In such cases, the effect of stray light intensity on the absorbance is more pronounced.

Fig. 2 illustrates the influence on the absorbance of stray light when the ratio of stray light intensity to incident light was changed to 0 - 0.5%. In cases when the stray light intensity is larger, the calculated absorbance value is smaller than the ideal value, and the linearity will be affected especially in the region exceeding 2AU.

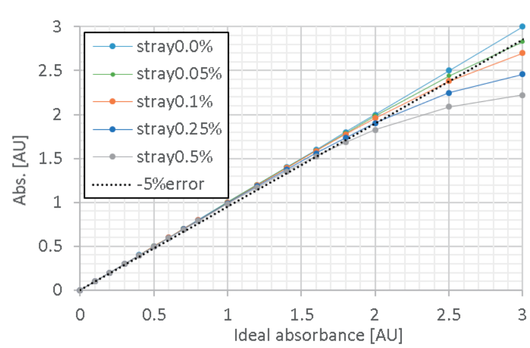

Fig. 2 Effect of stray light on absorbance

1 Analytical & Measuring Instrument Division Life Science Business Department LC Business Unit

Fig. 3 shows the effect of stray light intensity on absorbance as error rate using the results of Fig. 2. For example, when trying to obtain an absorbance linearity error within 5%, if the stray light has an intensity of 0.25% with respect to the incident light, the upper linearity limit is 2 AU; if the intensity is 0.1%, the upper limit is 2.5 AU.

Thus, the intensity of stray light greatly affects the quantitation of the target component.

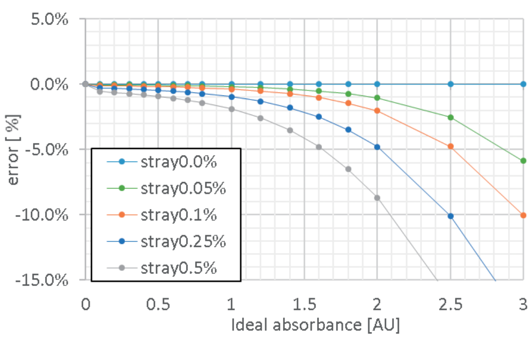

Fig. 3 Stray light intensity and absorbance error rate

3. Causes of stray light generation and reduction

Causes of stray light include reflection and scattering of light by the optical element itself and dirt attached to the optical element, reflection and scattering of light at the spectrometer, and unexpected reflection and dispersion of light at the grating.

In particular, a PDA detector emits white light from the lamp to the cell, and the transmitted light is dispersed and detected, so there is generally more stray light than for a UV-VIS detector.

Designed to reduce the effect of these causes of stray light, the SPD-M40 reduces overall stray light to a third of that in previous PDA detectors. It thereby achieves a linearity of 2.5 AU as a specification value, comparable to that of a UV-VIS detector (the actual value is typically more than 2.5 AU).

4. Noise reduction

The factor that predominantly determines the linear upper limit of absorbance is stray light. In contrast, the lower limit is primarily determined by the noise of the detector response. The SPD-M40 minimizes noise through e.g. optimization of the electrical system layout.

Fig. 4 shows a comparison of detector noise between the SPD-M40 and a conventional detector. When the time constant is small, the noise value is reduced significantly.

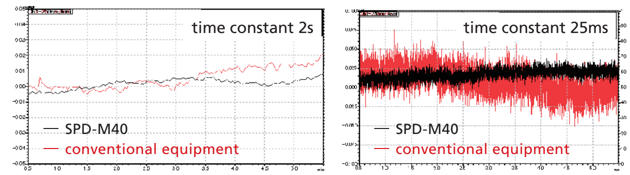

Fig. 4 Noise reduction

5. Improved dynamic range

Fig. 5 shows a chromatogram of a standard solution of ketoprofen, prepared by adjusting the analytical conditions and concentration to obtain a peak height with approximately 2.5 AU. Fig. 6 shows the calibration curve within a wide concentration range of 0.5 - 800 mg/L. With the SPD-M40, the linearity specification value is 2.5 AU; however, in practice, the value is significantly better. By reduced noise, it has become possible to simultaneously analyze high-concentration main components and trace impurities of 1 mAU or less with high accuracy. The coefficient of variation of the area value was 1% or less, even for the impurity with content that is about 0.1% quantified by area percentage, and good reproducibility was achieved.[1)]

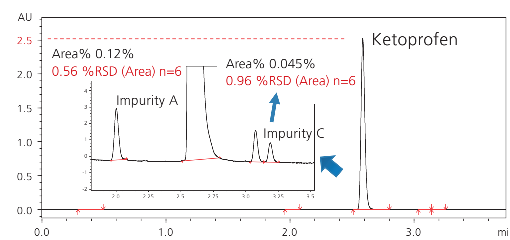

Fig. 5 Ketoprofen and impurity analysis

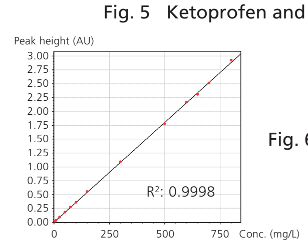

Fig. 6 Linearity of ketoprofen

6. Conclusion

- Stray light generated in the detection process has a significant effect on a detector's linearity range.
- The SPD-M40 photodiode array detector is designed to completely reduce the effects of stray light and offers wide linearity.
- In addition, it features significantly reduced noise. As a result, it is effective for analysis from low to high concentrations.

1) Application News No. L 538 "Impurity Analysis in Pharmaceutical Products with the Advanced Photodiode Array Detector SPD-M40"

First Edition: May, 2019

SHIMADZU

Shimadzu Corporation

www.shimadzu.com/an/