

Technical Report

High-precision analysis of the photodegradable compound Naproxen using the UV cut-off filter of the photodiode array detector SPD-M40

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Abstract:

Analysis using a photodiode array (PDA) detector makes use of a broad spectrum of wavelengths, allowing qualitative analysis of a wide range of compounds. However, since the light irradiated on a sample includes ultraviolet light (UV light) in the short wavelength region, there is the concern that UV light may cause photolysis of photodegradable compounds. The SPD-M40 is equipped with a UV cutoff filter* which blocks UV light in the short wavelength region. This suppresses the photolysis of components in the PDA and enables highly-accurate analysis.

Keywords: Photodiode array detector, UV cut-off filter, Naproxen

1. Photodegradable Compounds

Photodiode array (PDA) detectors make use of light over a wide range of wavelengths and can be used for qualitative and quantitative analysis of a variety of compounds. Since ultraviolet light (UV light) is included in the short wavelength region, it may cause photolysis in the analysis of photodegradable compounds. There have been many reports on the analysis of photodegradable compounds, especially pharmaceuticals (Table 1).

Table 1 Reported cases of photodegradable compounds

Compound type	Compound name	References
Non-steroidal anti-inflammatory drugs	Diclofenac	Packer J.L. et al., 2003, <i>Aquat. Sci.</i> , 65, 342-351.
	Ibuprofen	Jacobs L.E. et al., 2011, <i>Water Res.</i> , 45, 4449-4458.
	Naproxen	Hsu Y.H. et al., 2006, <i>Biomed Chromatogr.</i> , 20, 787-793.
	Sulindac	Kawabata K. et al., 2018, <i>Chromatogr.</i> , 39, 139-146.
Calcium channel blockers	Nifedipine	Hayase N. et al., 1994, <i>J. Pharm. Sci.</i> , 83, 532-538.
	Amlodipine	Ragno G. et al., 2002, <i>J. Pharm. Miomed. Anal.</i> , 27, 19-24.
Steroid hormones	17 β -estradiol	Lin A.Y.-C. et al., 2005, <i>Environ. Toxicol. Chem.</i> , 24, 1303-1309.
	Testosterone	Young R.B. et al., 2013, <i>Environ. Sci. Technol.</i> , 47, 8416-8424.
Vitamins	Vitamin C (Ascorbic acid)	Mori Y. et al., 1969, <i>J. Jpn. Soc. Food Nutr.</i> , 22, 12-16.
	Vitamin B12 (Cyanocobalamin)	Taylor R. et al., 1973, <i>Arch. Biochem. Biophys.</i> , 156, 521-533.

When photodegradable compounds decompose in PDA detectors, their quantitation may be inaccurate.

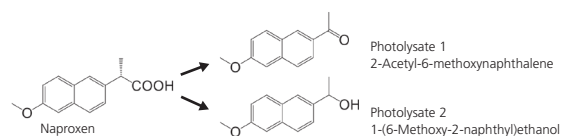


Fig. 1 Photolysis of photodegradable compounds (Naproxen)¹⁾

2. SPD-M40 UV Cut-off Filter

The SPD-M40 uses a UV cut-off filter to block short-wavelength UV light. This suppresses the decomposition of compounds in the flow cell to aid in the accurate quantitative determination of target components.

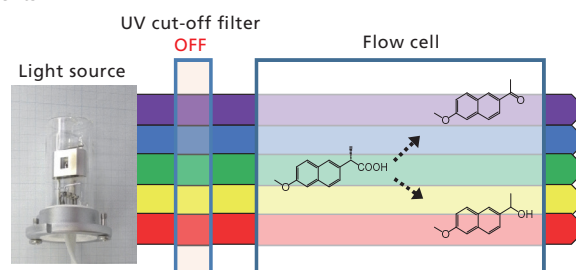


Fig. 2 Flow cell without a UV cut-off filter

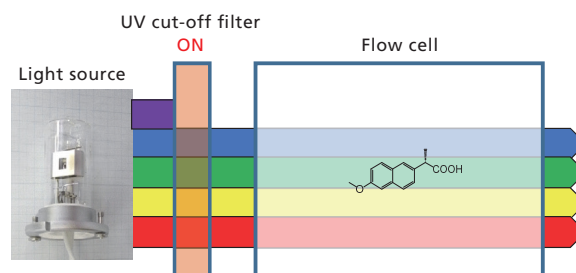


Fig. 3 Flow cell with a UV cut-off filter

Fig. 2 shows a illustration of a flow cell without a UV cut-off filter. Some of the target compounds irradiated with UV light in the flow cell are photodegraded and converted to photolysates. Fig. 3 shows an image of a flow cell using a UV cut-off filter. When the UV cut-off filter is used, the flow cell is not irradiated with high-energy short-wavelength UV light and photolysis of the target compound detected is suppressed.

3. Effect of the UV Cut-off Filter On the Calibration Curve of Naproxen

Naproxen samples were analyzed both without and with a UV cut-off filter and the results are shown in Fig. 4 and Fig. 5 respectively.

Table 2 Analytical conditions for Naproxen samples

Column	Shim-pack VP-ODS (150 mm × 4.6 mm I.D., 5 μm)
Temperature	40 °C
Mobile phase	50 % MeOH (including 0.1 % acetic acid)
Flow rate	1.0 mL/min
Injection volume	20 μL
Detection wavelength	230 nm

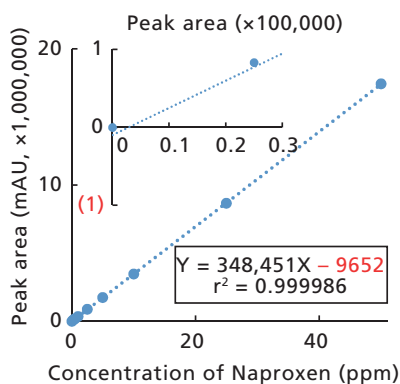


Fig. 4 Calibration curve without a UV cut-off filter

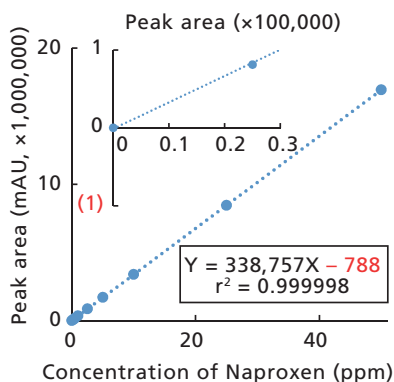


Fig. 5 Calibration curve with a UV cut-off filter

When the UV cut-off filter was not used, Naproxen was photodegraded in the low concentration region, resulting in a very negative intercept on the calibration curve. The use of the UV cut-off filter is demonstrated to mitigate these effects. It can be seen that the use of UV cut-off filters for PDA detector analysis allows accurate quantification of photodegradable pharmaceuticals.

4. Effect of the UV Cut-off Filter When Changing Analytical Conditions

In general, the lower the concentration of the sample solution, the higher the photolytic reactivity. In the analysis of Naproxen samples, it was investigated whether the UV cut-off filter could suppress photodegradation which might occur when the injection volume of sample was reduced. The results are shown in Table 3. They indicate that the UV cut-off filter mitigated the drop in the intercept value of the calibration curve by suppressing photodegradation.

Table 3 Dependence of the calibration curve of Naproxen on injection volume with and without a UV cut-off filter

Injection volume (μL)	Without UV cut-off filter		With UV cut-off filter	
	Gradient	Intercept	Gradient	Intercept
5	91794	-16321	83854	-2973
10	173067	-10561	168200	-1801
20	344560	-8414	337882	-719
40	688032	-2826	663833	5499

In addition, decreasing the pump flow rate increases the time that the sample remains in the flow cell. Table 4 and Fig. 6 show the analysis of whether the UV cut-off filter could suppress the extra photodegradation. The results indicate that the UV cut-off filter suppressed photodegradation of Naproxen in the low concentration region, especially under low flow rate conditions, which improved the accuracy of the calibration curve.

Table 4 Dependence of the calibration curve of Naproxen on flow velocity with and without a UV cut-off filter.

Flow rate (mL/min)	Without UV cut-off filter		With UV cut-off filter	
	Gradient	Intercept	Gradient	Intercept
0.25	1399666	-182475	1359458	-8904
0.5	700124	-33047	677326	-4975
1	350301	-9970	338615	-1137
2	175124	-1355	170787	1954

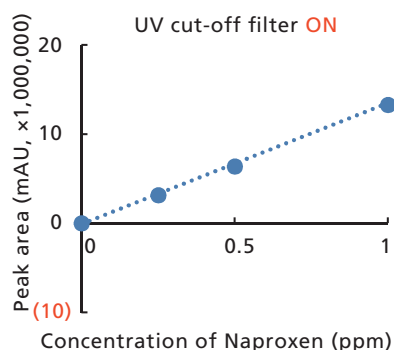
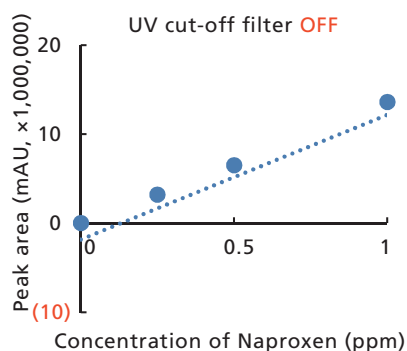


Fig. 6 Calibration curve of Naproxen at a flow rate of 0.25 mL/min (low concentration region)

5. Conclusions

- The SPD-M40 uses a UV cut-off filter that does not transmit high-energy UV light in the short wavelength region.
- The UV cut-off filter suppresses photolysis when photodegradable compounds are analyzed. In particular, it is effective even at low concentrations where photolysis progresses easily and enables accurate analysis of small-volume photodegradable samples.
- Even when analytical conditions such as injection volume and flow rate are changed, the UV cut-off filter is effective at preventing photolysis, enabling highly-accurate analysis.

References

- 1) Kawabata K, Mizuta Y, Ishihara K, Takato A, Oshima S, Akimoto S, Inagaki M, Nishi H Structure Determination of Naproxen Photoproducts in the Tablet Generated by the UV Irradiation. *Chromatography*, 2019, 40 (3), 157-162.