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Simple and Practical Two-Photon Ionization Detection in High-Performance Liquid Chromatography

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A method for simple and practical two-photon ionization detection for HPLC effluents was demonstrated. A peak detector can replace a boxcar integrator. The system was applied to several types of samples and eluents.

1. Introduction

The incorporation of a laser spectrometric system into a detector for high-performance liquid chromatography (HPLC) has induced substantial improvements in detection sensitivity^{1,2)} as has been shown by laser induced fluorescence³⁻⁶⁾, thermal lens⁷⁾, photoacoustic⁸⁾, and two-photon ionization⁹⁻¹³⁾ detectors.

The two-photon ionization technique has following advantages over other techniques: (1) the conductivity method is sensitive and convenient, (2) the signal can be obtained even from nonfluorescent molecules, and (3) the signal is hardly affected by scattered and stray lights as well as mechanical fluctuation. A falling jet cell is simple and practical for analytical applications of this technique: highly sensitive detection¹⁴⁾ and a detector for HPLC¹³⁾.

A simple and sensitive method for the measurement of the pulsed photoionization current enhances the analytical application of the two-photon ionization technique. A boxcar integrator so far used is complicated and costly in practical applications. A dc current detector (picoammeter) was used to a high-repetition (90 Hz) laser photoionization in hexane¹⁵⁾. A peak detector will be more useful than a picoammeter for lower-repetition experiments.

In this paper, we have investigated feasibility of a two-photon ionization detector for its practical applications.

2. Experimental

2.1 Instrumentation

The experimental system (**Fig. 1**) is similar with the previous one¹³⁾, but a peak detection system has been added and the chromatographic effluent first passed into a UV detector and then entered the falling jet photoionization cell¹³⁾. A Moletron UV-12 nitrogen laser (2.5 mJ, 10 ns) was focused into the falling jet cell. The photoionization current was converted to voltage by a current-to-voltage converter (gain 10^7 V/A, RC time constant ~ 10 μ s).

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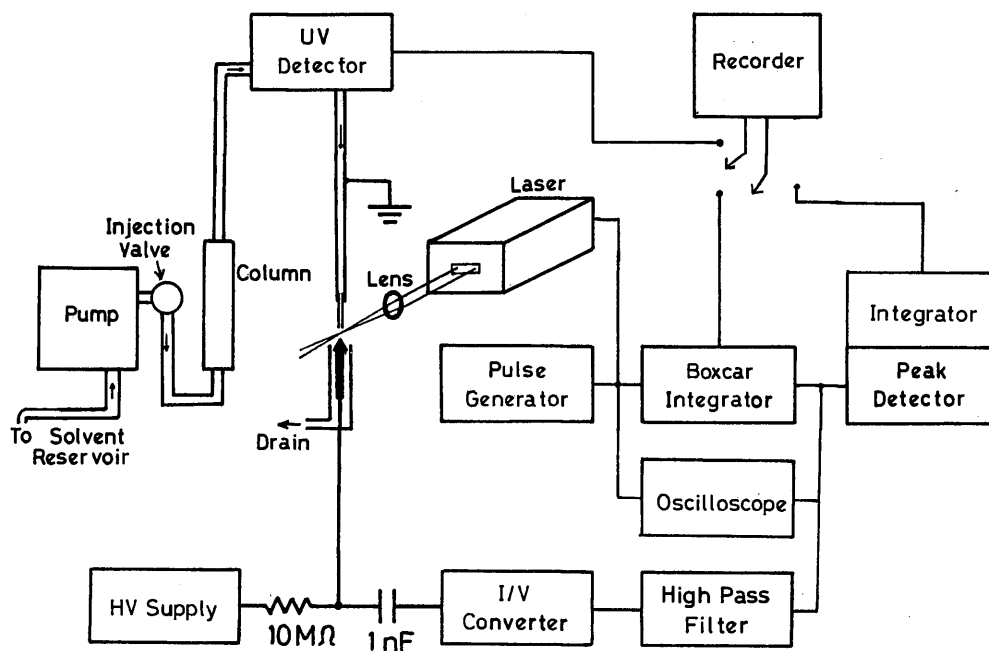


Fig. 1 Schematic diagram of the experimental apparatus.

Lower frequency noises were removed by a high-pass filter (cutoff frequency 3–5 KHz). This output signal was fed into both a peak detector¹⁶⁾ and a boxcar integrator (gate delay 6–10 μ s, gate duration 10 μ s, effective time constant 1–3 s). The peak detector consists of LF 356 and CA 3140 FET op amplifiers and a capacitor (2.2 nF) as shown in **Fig. 2** and can stretch a pulsed input signal up to ca. 300 ms. Its output was connected with a home-made integrator (μ A 741 op amplifier), whose time constant was almost identical with that of the boxcar. Outputs of both the boxcar and the home-made integrators were recorded on a dual-pen recorder.

2.2 Reagents

Pyrene (Nakarai Chemicals) was purified as described previously¹⁷⁾. Vitamin K₂ was a gift from Eisai Co., Ltd.. Other chemicals (reagent grade) were used as received.

2.3 Chromatographic measurements

The chromatographic system¹³⁾ with a Shodex Silikapack (Showa Denko, E-411) or a Zorbax ODS (Dupont) column (150 $\times$ 4.6mm i.d.) was connected to the photoionization cell. The injected volume was 10 μ l, and flow rates were 1.5–1.7ml/min.

3. Results and Discussion

3.1 Comparison of peak and boxcar detection systems

The photoionization signal has a slow signal (10–1000 ms) and a fast signal (5–100 ns),^{18,19)} however, for the purpose of highly sensitive detection it is more convenient to measure it as a single peak by using low time resolution (typically $\sim$ ms). The temporal shape and peak position of the signal varied with experimental conditions such as bias voltage, cutoff

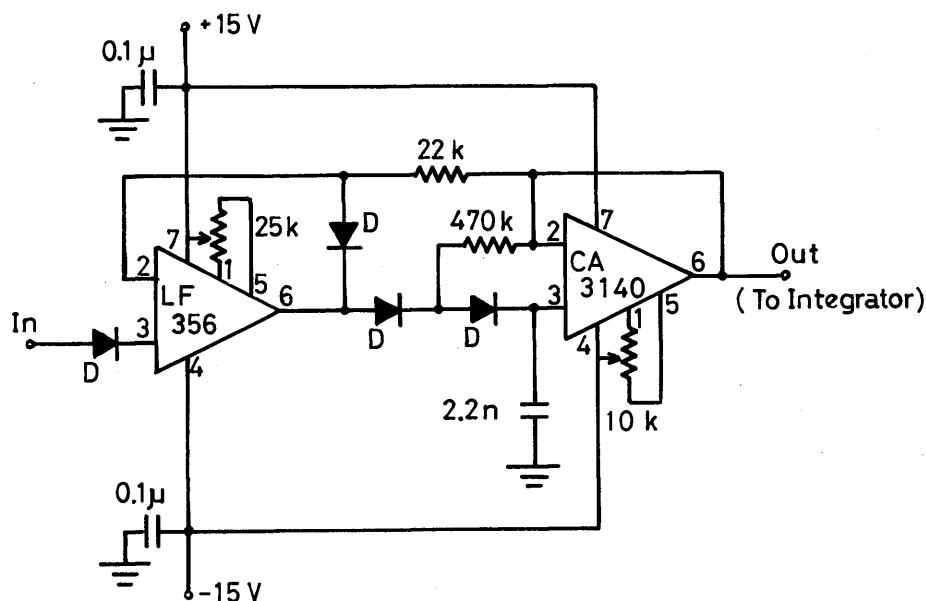


Fig. 2 Circuit of the peak detector.

frequency, or solvent. Thus, it is essential for the boxcar detection system to adjust the boxcar gate on the peak position for each experimental condition. The peak detection system as indicated in **Fig. 2** has no such drawback, since it can detect the peak position by itself and no other sophisticated time-gated equipments are necessary.

A typical set of photoionization chromatograms for a mixture of pyrene and 1-chloroanthracene in isooctane obtained by the peak detection and the boxcar detection systems are shown in **Fig. 3**. The S/N ratio and the bandwidth of the chromatograms were almost identical. A logarithmic plot of the S/N ratio versus the concentration of an analyte was satisfactorily linear; the results are shown in **Fig. 4**. Detection limits ($S/N=3$) by both detection systems are summarized in **Table 1**. The peak detection system can basically replace the boxcar detection system in terms of sensitivity, but it suffers from shot noise. Thus, the boxcar detection system is superior in terms of reproducibility for S/N ratio.

3.2 Comparison with UV detector

Figure 5 shows a typical set of photoionization and UV absorption chromatograms of a mixture of vitamin K₃ and K₅ in methanol. The UV chromatogram shows better S/N ratio, because the UV cell ($17.7 \mu\text{l}$) is larger by three orders of magnitude than the falling jet cell (14 nl). Vitamin K₃ alone shows a peak II in **Fig. 5**. Vitamin K₅ alone has two peaks I and II, probably due to decomposition; however these peaks are quite reproducible chromatographically (intensity ratios of the peak, II/I, are 1.5 for photoionization and 7 for UV absorption). These results show that both methods are compatible for the selective detection of each Vitamin in the mixture; the photoionization method is superior for a selective detection of vitamin K₅. The detection limits are summarized in **Table 1**.

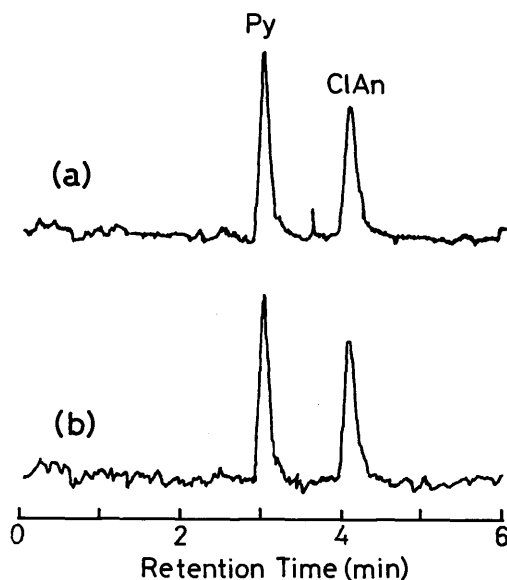


Fig. 3 Two-photon ionization chromatograms for a mixture of pyrene (Py, 0.4 $\mu\text{g/ml}$) and 1-chloroanthracene (ClAn, 2 $\mu\text{g/ml}$) in isooctane: (a) peak detection, (b) boxcar detection.

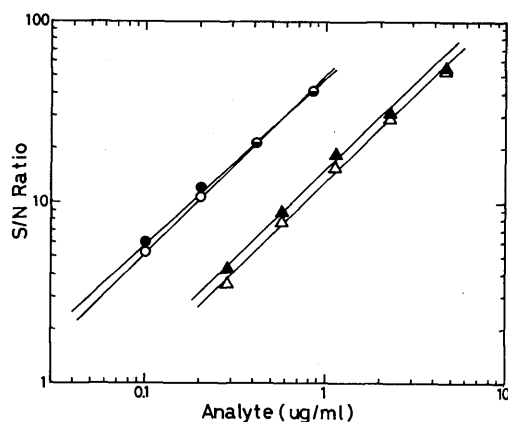


Fig. 4 Relationships between S/N ratio and analyte concentration in isooctane: Boxcar detection, (●) pyrene and (▲) 1-chloroanthracene; peak detection, (○) pyrene and (△) 1-chloroanthracene.

3.3 Chromatography in polar solvents

The photoionization detector is applicable for polar solvents by suppressing lower-frequency noises effectively¹²; typical results are also shown in **Table 1**. However, the detectability in methanol is still slightly worse than that in isooctane, mainly because of a larger fluctuation of the blank signal caused by a higher leakage current^{9,12}.

Table 1. Comparison of chromatographic detection limits ($S/N=3$).

Compound	Solvent	Detection Limit, ng/ml		
		Peak Detector	Boxcar	UV
pyrene	isooctane	60	50	8
	methanol	150	80	7
1-chloroanthracene	isooctane	240	220	30
	methanol	390	380	50
2-chloro-9,10-anthraquinone	methanol			
vitamin K ₁	methanol/dichloro-methane (80/20)	1500	1100	30
vitamin K ₂	methanol/dichloro-methane (80/20)	1500	1100	30
vitamin K ₃	methanol	2700	2300	40
vitamin K ₅	methanol	390	380	50

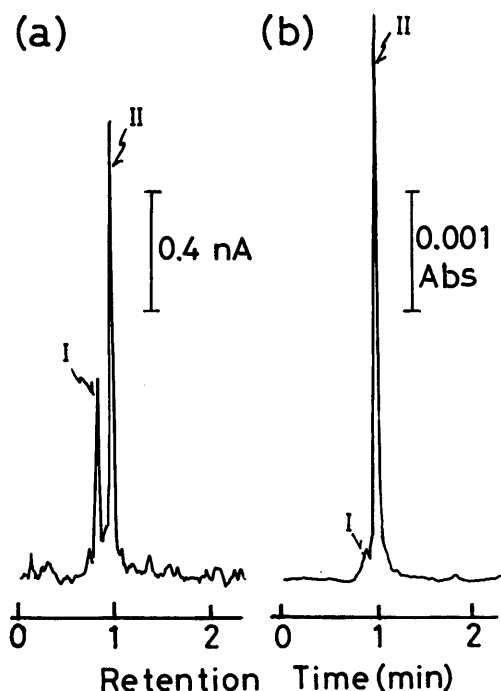


Fig. 5 Photoionization (a) and UV absorption (b) chromatograms of a mixture of vitamin K₃ (3×10^{-6} M) and K₅ (3×10^{-5} M) in methanol.

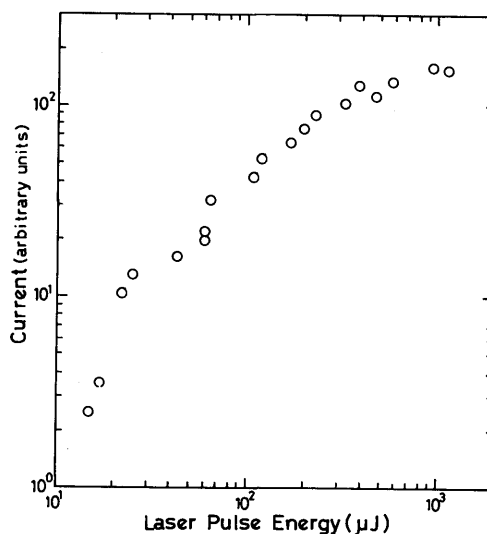


Fig. 6 Effect of laser pulse energy on the photoionization signal of pyrene (1×10^{-6} M).

3.4 Laser power

Figure 6 shows the effect of the laser pulse energy on the photoionization signal of pyrene in methanol, where another falling jet cell¹⁴⁾ is used. The signal increases sharply in the lower energy region than about 100 μ J. However, it tends to saturate in higher energy region and the intensity at 100 μ J is about half of that at 1 mJ. Thus, even a much smaller laser than the present one may be satisfactory in this cell.

4. Conclusion

We have elucidated the usefulness of a peak detector for the two-photon ionization detection of HPLC effluents, and that the present detector is applicable to various types of analytes. Thus, the combination of the falling jet cell, a peak detector, and a compact laser is promising in practicality.

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