Selective determination of acenaphthylene by flow injection analysis with tris(2,2′-bipyridine)ruthenium(II) chemiluminescence detection

Ming Li [a], Sang Hak Lee [b],*

[a] Division of Molecular and Life Sciences, Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, South Korea
[b] Department of Chemistry, Kyungpook National University, 1370 Sankyuk-dong, Buk-gu, Taegu 702-701, South Korea

Abstract

A simple, rapid flow injection chemiluminescence (FI-CL) method has been developed for selective determination of acenaphthylene (ACY), based on the CL produced in the reaction of tris(2,2′-bipyridine)ruthenium(III) ($Ru(bipy)_3^{3+}$) and ACY in an acidic buffer solution. Under the optimum experimental conditions, the calibration curve was linear over the range 5.0×10^{-3} to 4.0×10^{-7} mol L^{-1} for ACY. The detection limit ($S/N = 3$) was 2.0×10^{-7} mol L^{-1} and the relative standard deviation of 10 replicate measurements was 2.3% for 5.0×10^{-5} mol L^{-1} of ACY. Selectivity of CL reaction of ACY from other 15 polycyclic aromatic hydrocarbons (PAHs) was investigated by flow injection method. The method was applied to determine the ACY content in soil.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Acenaphthylene; Ruthenium; Chemiluminescence; Flow injection; Soil

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are hazardous organic pollutant because of their potential carcinogenic, mutagenic properties and immunotoxicities [1,2]. Major sources of PAHs in the environment are mainly due to their release from transportation vehicles, industrial wastes and personal cooking. As a consequence, most types of waters and foods contain measurable levels of PAHs, generally in the parts per billion to parts per million ranges. The US EPA identifies 16 PAH compounds as priority pollutants to be monitored. Now, PAHs have being been monitored in the marine environment, atmosphere and biological tissues for seafood safety reasons, air-quality assessment and for health-effects monitoring in the world. Acenaphthylene (ACY) has two benzene ring structures and could be used as one of light (2-3 ring structure) PAHs indicators, like benzo[a]pyrene as a heavy PAHs indicator [3,4], in a wide variety of matrices such as waters, foodstuffs, vegetable oils, sediments and human tissues, especially some plastic materials and newspapers.

Separation techniques such as gas chromatography [5,6], liquid chromatography [7–13] and capillary electrophoresis [14–16] with mass spectrometry, UV, fluorescence, CL and amperometric detection have commonly been used for the determination of PAHs in gaseous, liquid and solid samples. However, these methods based on separation techniques need complicated and time-consuming procedures unfit for their use in real-time monitoring of PAH pollutants. Conventional fluorimetry is very sensitive, however, it does not allow for the selective analysis from multicomponent mixtures [17]. Synchronous fluorescence spectrometry based on luminescent properties of PAHs has been reported [18–21] for the improvement of selectivity in PAH analysis without separation steps to overcome some of drawbacks observed with general separation techniques. Flow injection technique is potentially useful for field operation due to its portability, flexibility and low cost, so it has been shown to be well suited to real-time monitoring. However, it still suffers interferences from complex real sample matrices. For this reason more inherently selective reactions should be used. Flow injection immunosensing method [22] with a quartz crystal microbalance was reported for the determination of benzo[a]pyrene with monoclonal antibody 10c10 as sensing materials. Another continuous flow-through solid-surface phosphorescence optosensor for selective determination of benzo[a]pyrene [23] has been

---

* Corresponding author. Tel.: +82 53 950 5338; fax: +82 53 950 6330.
E-mail address: shlee@knu.ac.kr (S.H. Lee).

developed using the selection inherent properties of phosphorescence signals. The system is based on the measurement of their native phosphorescence signal when they are supported on non-ionic resin and Silica Gel. CL offers an attractive means of detection of trace analysis due to its low detection limit and wide dynamic range with relatively simple instrumentation. Peroxyoxalate CL method was widely studied for PAHs in environmental matrixes [24]. A FI-CL with CCD detection method was reported for the determination of multicomponent of PAHs using multivariate calibration without separation, and it provided quantitative information with a high degree of predictive errors [25].

Ru(bipy)$_3^{2+}$ is one of the most frequently used chemiluminogenic reagent like luminol and peroxyoxalate. A number of papers have reported for FI determination of different types of drugs such as barbiturate [26], ofloxacin [27] and ascorbic acid [28] by the CL method using electrogenerated or chemically prepared ruthenium(III) complex as oxidant. The electrogenerated ruthenium(III) CL method can offer a reliable and constant source of ruthenium(III). However, it has certain limitations including electrode fouling and the need for frequent re-conditioning of the electrode surface to maintain CL responses [29]. Advantages of the chemically prepared ruthenium(III) CL method are rapidity, simplicity and intense CL signal comparing to electro-chemiluminescence method, while it has disadvantage of the inherent instability of reagent with respect to reduction at basic conditions [30].

This paper describes development of a chemiluminometric method combination with flow injection technique for selective determination of ACY in extracted PAHs mixtures, based on ACY inherent reactivity with Ru(bipy)$_3^{3+}$ solution prepared by reaction of PbO$_2$ and Ru(bipy)$_3^{2+}$ in acidic medium. The effect of pH, concentrations of Ru(bipy)$_3^{3+}$ and organic solvent on the chemiluminescent intensity were investigated. The present method was applied to determine ACY content in soil.

2. Experimental

2.1. Apparatus

A schematic diagram of a flow injection analyzer used in the CL measurements is shown in Fig. 1 [31]. Simple two line flow system is employed in this study. A chemiluminogenic reagent solution (R1) stream and a buffer solution stream (R2) with injected sample solution segment were delivered by a peristaltic pump (Ismatec Model MS-4 Reglo/6-100, Glattbrugg-Zürich,
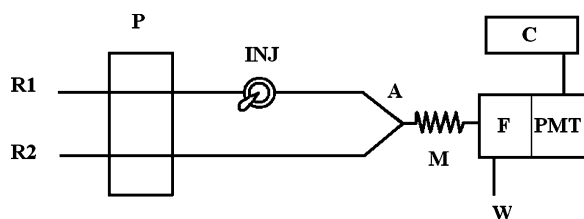
Fig. 1. FI-CL setup for ACY determination. R1 and R2, solution streams; P, peristaltic pump; INJ, injection valve; M, mixing coil; F, flow cell; W, waste; PMT, photomultiplier tube; C, computer.

Switzerland). The two streams of solution were mixed at a Y-shaped element (M) positioned at 20 mm before a coiled glass flow cell (1.0 mm i.d., 20 mm total diameter). Bran + Luebbe (Roselle IL, USA) Tygon R3603 tubing (0.51 mm i.d.) was used for connecting all the components of this system. Manual injection of sample solution was accomplished using a Rheodyne (Cotati, California, USA) Model 7125 six port valve. All CL measurements were performed using a Spex (Edison, NJ, USA) Model FL111 spectrofluorometer equipped with a Hamamatsu R238 photomultiplier. Instrumental parameters were controlled by Spex DM3000 software. For the CL measurement, the light source of the spectrofluorometer was switched off. The slit width of the emission monochromator used was 0.5 mm. The high voltage for the photomultiplier tube was set to 900 V. A Mettler Toledo (CH-8603 Schwerzenbach, Switzerland) MA235 pH/Ion analyzer was used for pH measurements.

2.2. Reagents

Acenaphthylene (ACY), other 15 kinds of PAHs (Naphthalene (Na), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fu), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo-[a,h]anthracene (DahA), benzo[g,h,i]perylene (BahiP) and indeno[1,2,3-c,d]pyrene (IPY)), potassium chloride, hydrochloric acid and potassium dihydrogenphosphate were purchased from Aldrich (Milwaukee, WI, USA). Tris(2,2′-bipyridine)ruthenium chloride were obtained from Sigma (St. Louis, MO, USA). Standard PAHs 610 mix was purchased from Supelco (Bellefonte, PA, USA). A stock solution of the ACY (5.0 mmol L^{-1}) was prepared by dissolving the appropriate amount of reagent in pure ethanol and it was stable for at least 1 month when stored at 4 °C. A stock solution of 5 mmol L^{-1} Ru(bipy)$_3^{2+}$ was prepared by dissolving the appropriate amount of reagent in 50 mmol L^{-1} sulfuric acid solution and stored at 4 °C. Ru(bipy)$_3^{3+}$ solution was prepared off-line, 0.1 g lead dioxide was added to 5 mL Ru(bipy)$_3^{2+}$ stock solution [32]. The resultant suspension was allowed to settle for 5 min followed by vigorous mixing, and filtered through a membrane filter assembly (0.2 μm). Produced Ru(bipy)$_3^{3+}$ solution was stable for 2 h in the 50 mmol L^{-1} sulfuric acid solution. Methanol, ethanol and acetonitrile were obtained from Mallinckrodt Baker (Kentucky, Paris, France). All of the chemicals used in this study were of analytical grade. All aqueous solutions were prepared by using water purified with a Milli-Q purified system.

2.3. Sample collection and pretreatment

Soil samples of surface sediment (0–2 cm depth) were collected at the Gumho riverside (Taegu, Korea) at selected sampling points. This area has a considerable amount of textile industries which will generate pollution. For sample pretreatment, a simplified one step extraction method was used with acetonitrile as a solvent. The soil sample was air dried to constant weight at ambient temperature, broken up and sieved at