Talanta 133 (2015) 112–119

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Direct-injection chemiluminescence detector. Properties and potential applications in flow analysis

Stanislawa Koronkiewicz *, Slawomir Kalinowski

University of Warmia and Mazury, Department of Chemistry, 10-957 Olsztyn, Poland

ARTICLE INFO

Article history:
Received 14 December 2013
Received in revised form
21 May 2014
Accepted 13 June 2014
Available online 8 July 2014

Keywords:
Chemiluminescence
Flow analysis
Solenoid micro-pumps
Direct injection detector

ABSTRACT

We present a novel chemiluminescence detector, with a cone-shaped detection chamber where the analytical reaction takes place. The sample and appropriate reagents are injected directly into the chamber in countercurrent using solenoid-operated pulse micro-pumps. The proposed detector allows for fast measurement of the chemiluminescence signal in stop-flow conditions from the moment of reagents mixing.

To evaluate potential applications of the detector the Fenton-like reaction with a luminol-H_2O_2 system and several transition metal ions (Co^{2+}, Cu^{2+}, Cr^{3+}, Fe^{3+}) as a catalyst were investigated. The results demonstrate suitability of the proposed detector for quantitative analysis and for investigations of reaction kinetics, particularly rapid reactions. A multi-pumping flow system was designed and optimized. The developed methodology demonstrated that the shape of the analytical signals strongly depends on the type and concentration of the metal ions. The application of the detector in quantitative analysis was assessed for determination of Fe(III). The direct-injection chemiluminescence detector allows for a sensitive and repeatable (R.S.D. 2%) determination. The intensity of chemiluminescence increased linearly in the range from about 0.5 to 10 mg L^{-1} Fe(III) with the detection limit of 0.025 mg L^{-1}. The time of analysis depended mainly on reaction kinetics. It is possible to achieve the high sampling rate of 144 samples per hour.

1. Introduction

Chemiluminescence (CL) is considered to be a promising mode of detection offering an excellent sensitivity and a wide dynamic range for many classes of analytes [1]. As the reactions involved are usually fast, the precision and sensitivity depend largely on the ability to mix the solutions and measure the emitted light. Flow methods are ideally suited for monitoring such reactions because they provide immediate and reproducible mixing of the sample and reagents in the vicinity of the detector. For the greatest sensitivity, the flow manifold should be configured to maximize the emission and to detect the light as soon as possible.

In flow injection analysis (FIA), the sample is inserted into a carrier (Fig. 1). The reagent, flows through a separate channel, is merged with the sample-carrier stream. The CL reaction begins upon merging these two streams [2]. Next, the light-emitting segment of the solution must be transported to the detector. Therefore, the merging point (usually a T-piece or a Y-piece) is located as close to the flow detection cell as possible. The final, effective mixing of reagents with the sample takes place in the flow cell of the detector. Very often an additional reaction coil is not used in such a configuration.

The popular flow cells used in CL detectors employ quartz, glass or a PTFE flat spiral placed in front of the photomultiplier tube [3–6]. However, this configuration has some limitations [2,7]: (1) mixing is initiated before the reacting mixture enters the flow coil; (2) the walls of tubing are curved, and therefore most of the cell surface is not flat against the photomultiplier window; and (3) the most popular and the cheapest PTFE spiral is not fully transparent. Because of these shortcomings, new types of chemiluminometric cells have been developed. The detection flow cells could be constructed by etching or milling channels in glass/polymer material and sealing that channel with a transparent window [7–10]. To increase the mixing efficiency and enlarge the volume of solution within the detection zone, meandering or serpentine channels [7] can be applied. In a double-inlet serpentine flow detector, the merging point is integrated with the flow cell. No additional T- or Y-fitting was used in this configuration. The mixing of solutions before they enter the flow cell was

* Corresponding author. Tel.: +48 895234137/+48 895234801; fax: +48 895234801.
E-mail address: stankor@uwm.edu.pl (S. Koronkiewicz).

http://dx.doi.org/10.1016/j.talanta.2014.06.077
0039-9140/

minimized. However, the serpentine needs time to fill up completely. After initiation of the CL signal, the first portion of the reacting mixture is transported through the serpentine. Following the first part of the mixture, all the subsequent portions are gradually and smoothly introduced into the serpentine. The CL signal, which appears at the beginning, overlaps the signals derived from the following mixed segments of the reagents. This mechanism can influence the CL signal especially when the CL reaction is fast and the intensity of the CL is changing during the serpentine filling. Therefore, kinetic studies of the fast reactions are not possible using this detector.

Other designs of the flow CL cells have also been developed. One of the most original ones is the fountain cell with novel flow geometry [11]. Here the reacting mixture enters the center of an open thin cylindrical space and drains into a ring-shaped edge with an outlet hole. Another example is the bundle cell containing a bundled PTFE tube packed into a plastic cuvette [12]. The other flow cell designs are: sandwich membrane cell [13], vortex configuration flow cell [14], droplet detector [15] or coiled polyethylene cell sandwiched between two large area photodiodes [16]. Many authors highlight the fact that the closeness of the confluence point to the detection zone is essential for enhancing the sensitivity of detection.

Apart from the typical flow methods, the chemiluminescence detection is applied in a hybrid flow-batch analysis (FBA) [17,18]. The main component of such manifolds is the mixing chamber, into which different solutions can be introduced sequentially or simultaneously using a peristaltic pump in a typical configuration. The mixing chamber is usually equipped with a magnetic stirrer. The mixtures prepared in the mixing chamber are usually sent to a detector. The CL detection system as a part of the mixing chamber has been also developed [18,19]. In such systems, the CL detector (photomultiplier [19] or photodiode [18]) is located at the top of the mixing chamber [18] or close to the side wall fitted with the quartz window [19]. Unfortunately, the mixing process usually takes several seconds, which is a problem when investigating a very fast reactions. To our knowledge, the CL detector exploited the solenoid micro-pumps as a dispensing and mixing element has

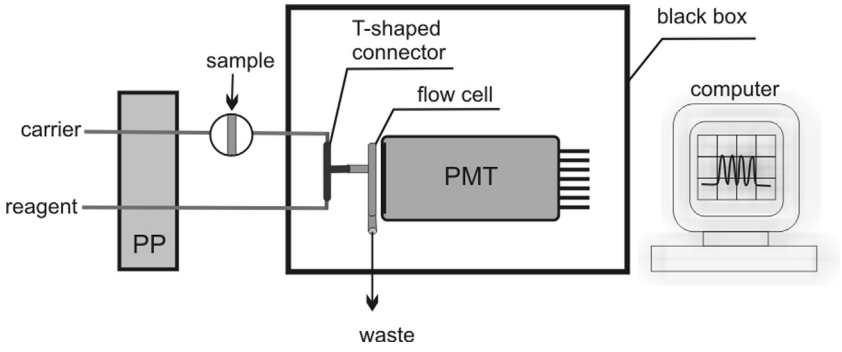

Fig. 1. Schematic diagram of a typical FIA system used in combination with chemiluminescence detection. PP—peristaltic pump; PMT—photomultiplier tube.

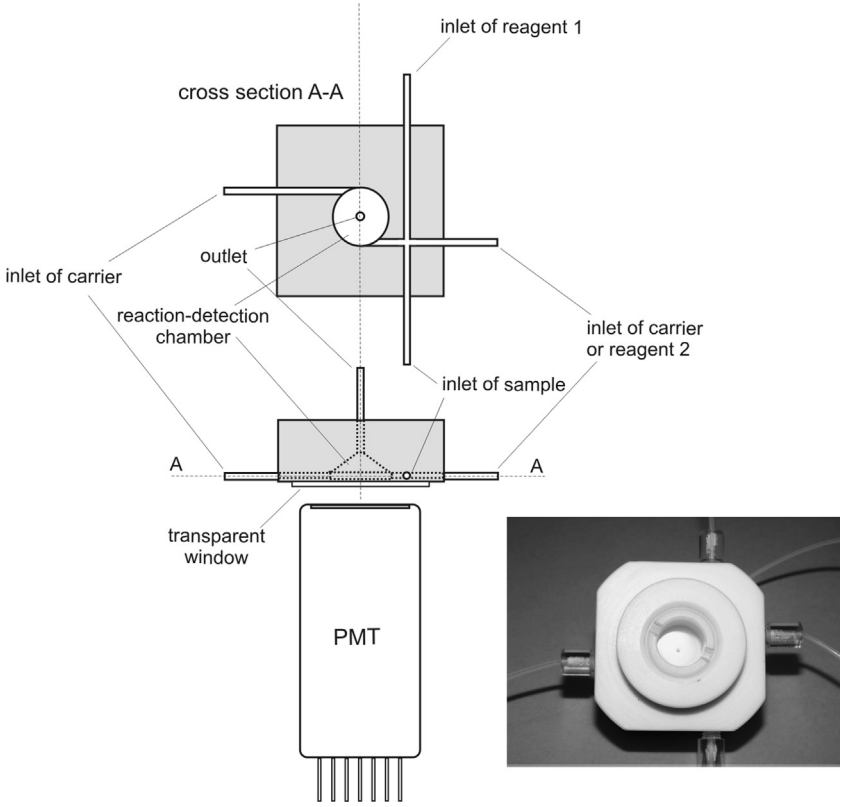

Fig. 2. Scheme and photograph of the direct-injection chemiluminescence detector.