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

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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

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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

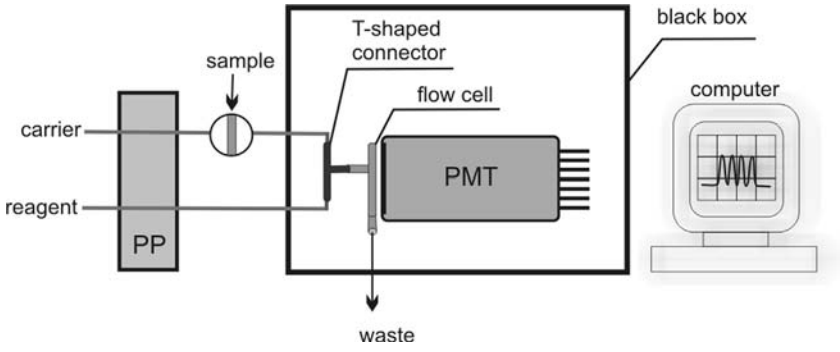

Fig. 1. Schematic diagram of a typical FIA system used in combination with chemiluminescence detection. PP—peristaltic pump; PMT—photomultiplier tube.

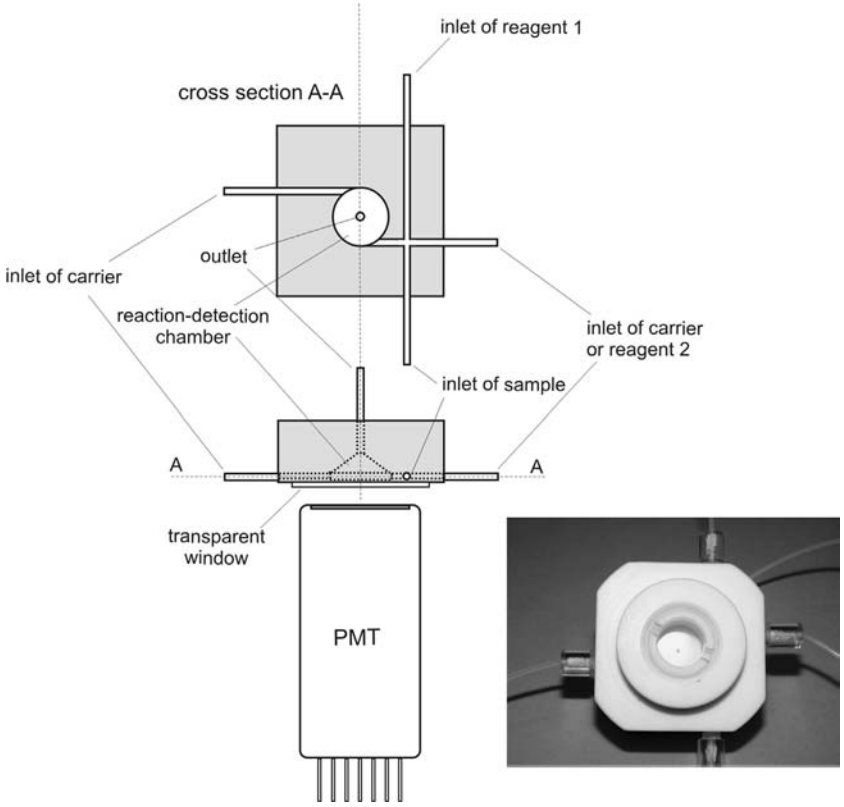

Fig. 2. Scheme and photograph of the direct-injection chemiluminescence detector.

not been previously described. Creating a new flow cell integrated with merging point and detection zone is constantly being researched [7–9].

In this paper we present an innovative methodology that allows for a CL-based mixing module to be combined with a flow detection cell. In this system, a sample and a reagent are injected in countercurrent directly into the cone-shaped detection cell situated in front of the photomultiplier window. The mixing and detection processes take place in the flow cell, "in-situ". The detection cell is integrated with the system of solenoid micro-pumps. The pumps allow for precise dosage and fast mixing of the reagents involving in the CL reaction. The idea of applying the solenoid micro-pumps in direct-injection detectors has been developed in our group for several years and was previously proposed for photometric detection [20,21].

2. Experimental methods

2.1. Reagents

All the solutions were prepared with analytical-grade chemicals and with deionized water obtained from the Milli-Q water purification system (Millipore, resistivity > 18.2 MΩ cm). Potassium permanganate was obtained from Sigma-Aldrich (Steinheim, Germany). Luminol was obtained from Fluka (Buchs, Switzerland). Concentrated (30%) H_2O_2, solid Na_2CO_3 and $NaHCO_3$ were obtained from StanLab (Lublin, Poland). The cation solutions (Fe (III), Cu(II), Co(II)) were prepared by appropriate dilution of the standards for ASA. The Cr(III) solution was prepared by dissolving the solid chromium(III) nitrate nanohydrate (Sigma-Aldrich, Steinheim, Germany) in deionized water. As a carrier, a buffer Na_2CO_3/$NaHCO_3$ solution (pH = 10.5) was used. This buffer was also applied for preparing all the luminol solutions. H_2O_2 and luminol solutions were prepared daily.

2.2. Direct-injection chemiluminescence detector

The direct-injection chemiluminescence (DID-CL) detector was constructed using one block of Teflon (Fig. 2). Inside the block, a cone-shaped reaction-detection chamber with a total volume of 280 μL was drilled. The detector chamber was closed with a transparent glass window. The diameter of the base of the cone was 1 cm, which gives an active light-transparent surface in front of the photomultiplier window about 0.785 cm^2.

There are two inlets to the detector chamber drilled at its bottom, close to the transparent window and the photomultiplier tube. The inlets are oriented tangentially to the wall of the chamber. The diameter of these inlet channels is 1 mm. The outlet is positioned at the top of the chamber. One of the inlets is used for injecting the sample and reagents, the second one is for cleaning the chamber using a carrier solution.

The inlets of the sample and reagents are designed in such a way that enables efficient mixing. They form a cross junction. The sample and the reagent no. 1 are injected simultaneously, from opposite directions, in countercurrent. However, there is some blind volume, the distance between the confluence point and the inlet to the detector chamber. This space is occupied by the mixture of the sample and reagent 1, which need to be moved to the detector chamber. Otherwise, the repeatability of the determination process could be unsettled. The volume of this "blind space" was estimated as 3.9 μL. A single injection of the carrier can be used to transport the solution from that space to the detector chamber. Every injections should be time-synchronized. The sample and the reagent 1 should be injected first, and the carrier afterwards. Alternatively, the second reagent (Fig. 2, reagent 2) can be used instead of the carrier solution. Each solution was injected into the detector using an independent solenoid pulse micro-pump of an appropriate nominal volume.

2.3. Flow manifold

The multi-pumping flow system (MPFS) (Fig. 3) was constructed from the solenoid-operated micro-pumps (Cole-Parmer (USA)) of a nominal volume of 20 μL (product no. P/N 73120-10) and 50 μL (product no. P/N 73120-22), and flow lines made with a PTFE tube (ID = 0.8 mm, Bio-chemValve Inc, Boonton, USA). The pumps with smaller volume are recommended for injecting the sample and reagent solutions, the bigger ones for the propelling the carrier. For taking pictures of the detector interior, an ordinary web camera was applied instead of the photomultiplier. The camera and the photomultiplier were vertically oriented. The outlet of the detector was oriented at the top to enable an easier escape for air bubbles, which can potentially appear in the system.

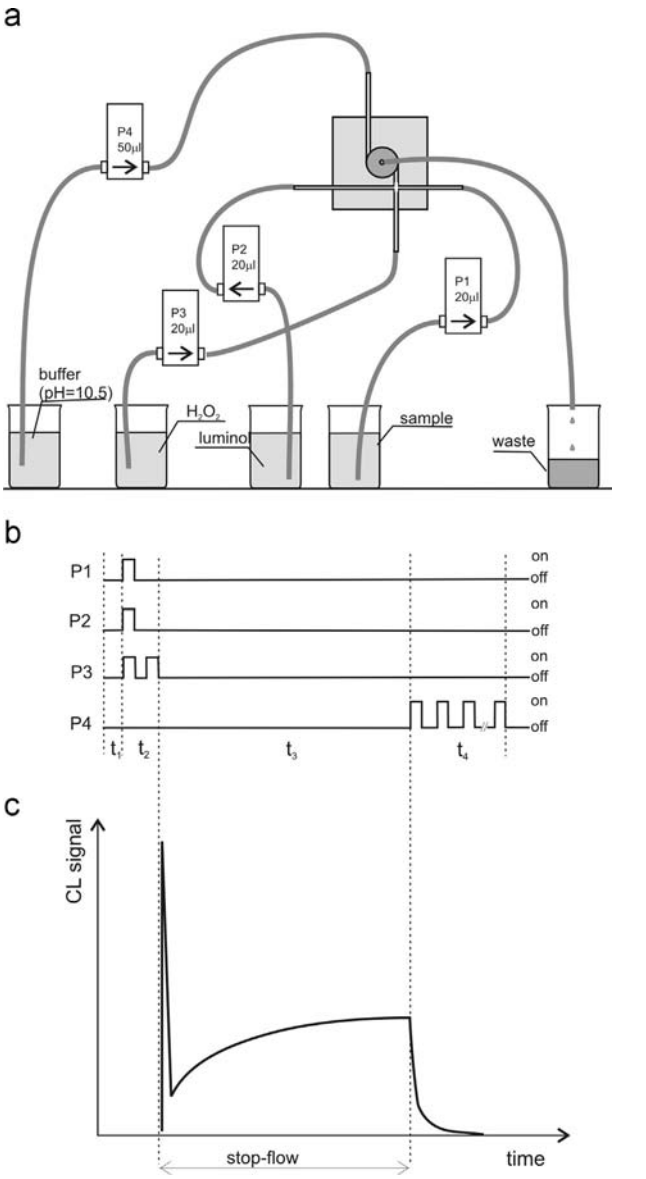

Fig. 3. Flow diagram of the multi-pumping flow system (a), the switching sequence of the pumps (b) and an example of the CL signal (c).The time intervals mean: t_1—stop-flow for the baseline recording, t_2—time for sample and reagents injection into the detector, t_3—stop-flow for recording the CL signal, t_4—time for cleaning the reaction-detection chamber.

The solution contained respectively: selected heavy metal ions (as a sample) and luminol (as a reagent), which were injected into the detector chamber using the solenoid micro-pumps P1 and P2 (Fig. 3, time t_2). At the same time the second reagent, hydrogen peroxide, was injected using the pump P3. Next, the analytical signal was developed and recorded under the stop flow conditions (Fig. 3, time t_3). To wash the detector chamber before the next cycle, several repetitions of the carrier injection using the pump P4 were carried out (Fig. 3, time t_4). The timing program of the pumps was optimized from the point of view of the highest and the most repeatable analytical signals (details in next paragraphs).

The micro-pumps and photomultiplier were PC-controlled by the measurement system of our construction [22]. The software was developed in the Delphi programming language. The main window of the program used is presented in Fig. 4.

3. Results and discussion

3.1. Reagent mixing and reaction-detection chamber cleaning

In preliminary investigations, the following two processes were tested: mixing the reagents and cleaning the reaction-detection chamber. For that purpose, the experiments with injection of potassium permanganate were performed. A web camera was used for observation. The solutions were injected using 20 μL solenoid micro-pumps. The pumps aspirate and inject the solutions very rapidly, in a violent manner. In typical flow analysis, such a nature of solution transport is considered an inconvenience. It allows, however, for rapid and precise mixing of the liquids [23].

To check if the mixing of a sample and a reagent is adequate and efficient, potassium permanganate was injected in countercurrent with water. As is shown in Fig. 5b, the solution obtained in this experiment was uniform in color after less than 1 s, which proves the effective and fast homogenization of the solution. By comparison, in a flow-batch CL system the homogenization process using magnetic stirrer takes a few seconds (up to 2 s [18] or 4 s [19] depending on the mixing conditions). Before the homogenization, the mixing chamber need to be filled with all the reagents. This step takes additional time (about 6 s when calculated according to the data presented in reference [18]), which means the analytical signal in flow-batch analysis is recorded after almost 8–10 s.

The cleaning process of the reaction-detection chamber was also checked using a potassium permanganate solution. This time it was injected instead a carrier (Fig. 5c). The swirling motion of $KMnO_4$ solution was observed. After entering the chamber, potassium permanganate solution slipped and washed the chamber wall. Finally, it escaped the detector through the outlet oriented at the top of the cone-shaped chamber. It was noted that it is recommended for effective cleaning to use the pump of nominal volume 20 μL in over a dozen repeated injections.

At the end, the procedure of cleaning the reaction-detection chamber for CL detection was elaborated on. As the luminol reagent is insoluble in water but well soluble in alkaline solutions, the buffer alkaline solution (pH = 10.5) was applied as a cleaning medium. It was checked that for achieving baseline of CL signal close to zero, about 30 repeated injections using the 50 μL pump are necessary. This means that about 1.5 mL of buffer solution is necessary for effectively washing the detector chamber between analytical cycles. The washing procedure took about 16 s. It would be possible to shorten this time by applying the pump of higher nominal volume (e.g. 100 μL).

3.2. Chemiluminescence detection of Co(II), Cu(II), Cr(III) and Fe(III)

In order to check the properties and the operating characteristic of the direct-injection CL detector, the Fenton-like reaction was selected. This is a well-known fast reaction, which has been applied by many researchers in combination with a variety of flow analytical systems [1,4,12,16]. In the Fenton-like reaction, ferric ions or other transition metal ions (e.g. Co^{2+}, Cu^{2+}, Cr^{3+}) are combined with H_2O_2 to produce free radicals. The highly reactive free radicals are involved in the process of luminol oxidation. The highest intensity of CL signals are usually observed at pH in the range from about 10 to 11 [12,24–26].

It was observed, that the time-dependent CL characteristics strongly depend on the type of ions used (Fig. 6). At the beginning of each cycle, immediately after mixing, a strong CL signal was always observed (Figs. 4 and 6). This strong and short illumination (light-flash) appeared about 1 s after injection of the sample and

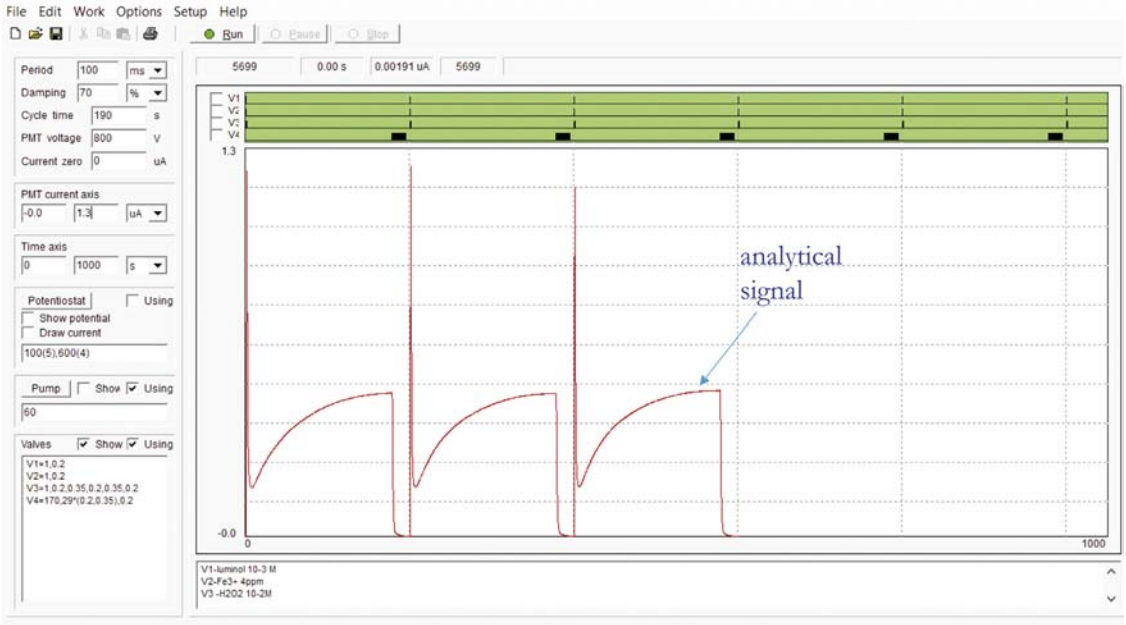

Fig. 4. The main window of the computer program used for controlling the work of the photomultiplier and the MPFS system with the recorded analytical signal obtained for Fe(III) detection.

reagent. The maximum of the CL emission for this part of the curve was several times higher than those registered later, in the following part of kinetic curves.

Comparing the long-time characteristics (Fig. 6b and d), where 30 min. stop-flow was applied, we find that the kinetics curves for Co(II) and Cu(II) ions were different during about 180 s. Then, the CL intensity was increasing in similar way to the end of the investigated interval. Using Cr(III) ions as a catalyst, a relatively fast decreasing CL signal was observed within a few seconds. Next, the signal was dropping more slowly and stabilized after about 400 s at the low level of about 0.01 μA (the background level was 0.002 μA). For the iron(III) ions, the gradual increase in signal was observed within about 180 s, then the chemiluminescence slowly decreased and stabilized at a relatively high level.

Presented kinetic curves can be used for selecting the cycle time appropriate for quantitative analysis. For example, for fast iron(III) determination the short light-flash at the beginning of the reaction can be taken into account and consequently a very short stop flow time (about 5 s) can be recommended. As the second solution, non-equilibrium signal can be taken into account and about 50 s of the stop flow. The third solution is to use a relatively stable and high signal, which appeared after about 180 s of the stop-flow. There is some compromise between the magnitude of the analytical signal and the time/cost of the analysis.

We hope the curves presented in Fig. 6 are helpful in more detailed investigations of the kinetics and mechanisms of chemiluminescence reactions. For example, the kinetic information derived from the whole curve profile (rise and fall rates) can be

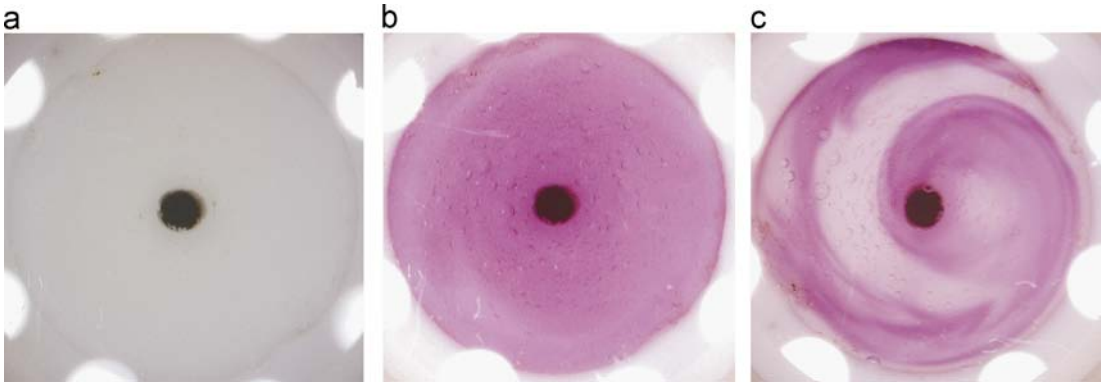

Fig. 5. A view of the detector interior: (a) filled with water; (b) water and potassium permanganate injected in countercurrent; (c) only potassium permanganate solution injected as a carrier. Pictures taken less than 1 s after injection.

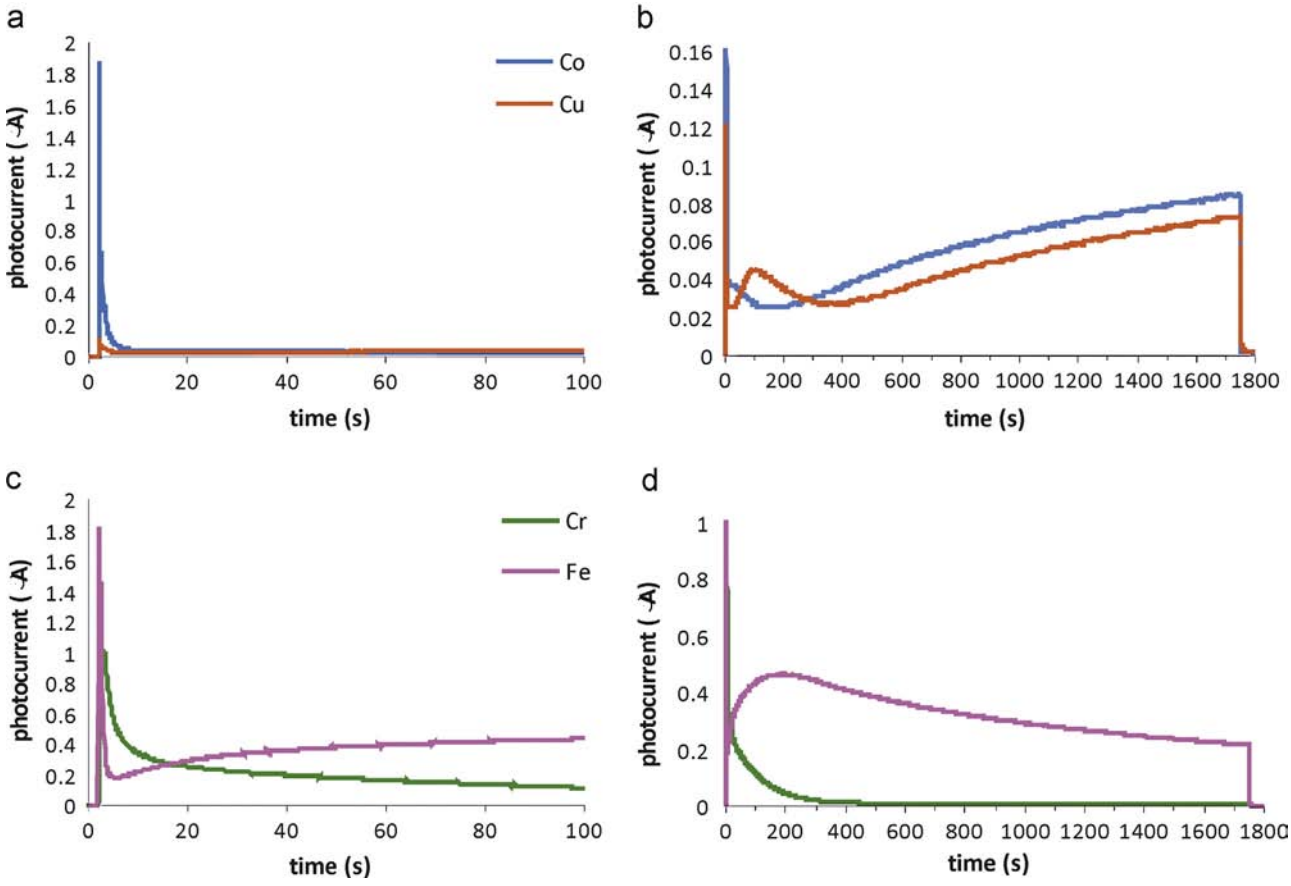

Fig. 6. The influence of different metal ions on the shape of time-dependent CL characteristics. The concentration of Co(III) was 30 μg L^{-1}, Cu(II) and Cr(III) 1 mg L^{-1}, Fe(III) 4 mg L^{-1}.

related to the analyte concentration. This relationship can be more selective and precise than those provided by the height or area under the emission-time curve [27].

For the next investigations, only iron(III) ions were applied as the catalyst.

3.3. Influence of oxidant volume

When evaluating the influence of oxidant volume, the maximum of the CL signal occurring within 180 s of stop flow was taken into consideration. The injection of oxidant was repeated several times. By assaying 1–6 injections of H_2O_2 using pump P3 (corresponding to 20–120 μL) it was observed that the CL increased with the number of injections (Fig. 7). For 140 μL of injected oxidant, a slight decrease in photocurrent was observed. The number of injections was then selected to be 6, corresponding to 120 μL of H_2O_2.

3.4. Influence of a sample and reagent volume

After defining the optimum volume of oxidant, the subsequent task was to choose an appropriate volume of the sample (Fe^{3+}) and reagent (luminol). It was observed that the volume of sample and reagent influence the shape of time dependent CL signals (Fig. 8). The slop of the curves, both the rising and decaying parts, was changed with the volume of Fe^{3+} and luminol injected into the reaction-detection chamber. The maximum photocurrent, for all the curves, was achieved within about 180 s. Therefore, the time of 200 s was chosen as a cycle time for our next experiments.

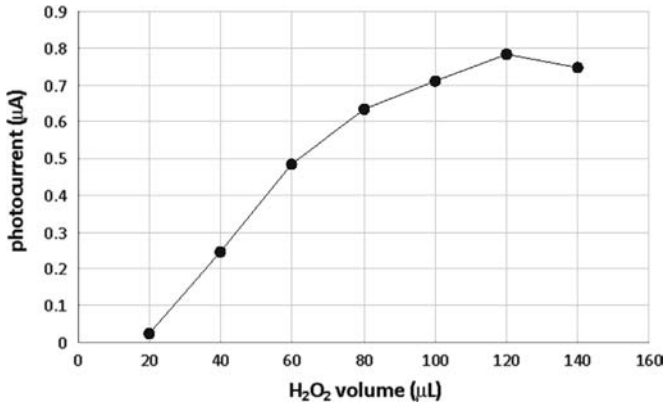

Fig. 7. The influence of the oxidant volume on the CL signal. A single injection of sample and reagent in countercurrent was applied. Each point represents the mean of four consecutive measurements ± S.D.

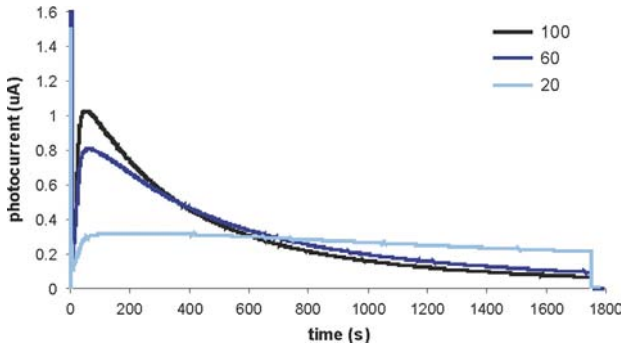

Fig. 8. Influence of the sample and reagent volume on the time-dependent CL characteristics. 20 μL—single, synchronized injection of the sample and reagent; 60 or 100 μL—3 and 5 injections continuously repeated at the beginning of cycle.

It was sufficient to reach the maximum analytical signal and to have time to clean the entire flow system.

The influence of the sample and reagent volume on the CL photocurrent is presented in Fig. 9. The volume of 80 μL was chosen as optimal (four injections using the 20 μL pump). The higher volume produced a higher signal, but the repeatability was worse. The total volume of the reaction-detection chamber was 280 μL. Taking 80 μL of sample, 80 μL of reagent and 120 μL of oxidant, the reaction-detection chamber was filled by the reactants. Increasing the number of injections beyond four resulted in some molecules involved in analytical process escaping out of the detector.

3.5. Analytical characteristics

After optimizing the detector work, all the flow system was tested by preparing the calibration graph (Fig. 10). We decided to compare the maximum CL signal occurring immediately after mixing the reagents (short light-flash signal, 5 s of the stop-flow), with the signal maximum achieved within 180 s of the stop-flow. Both the graphs obtained were linear, the first up to 5 mg L^{-1}, the second up to 10 mg L^{-1}. The theoretical limit of detection calculated as $3s_b/S$, where s_b is the standard deviation for 10 measurements of the blank and S is the slope of the calibration graph, were 0.2 and 0.025 mg L^{-1} respectively. This is correlated with a better repeatability of the signals achieved within 180 s of the stop-flow. The repeatability (R.S.D.) calculated for 10 injections

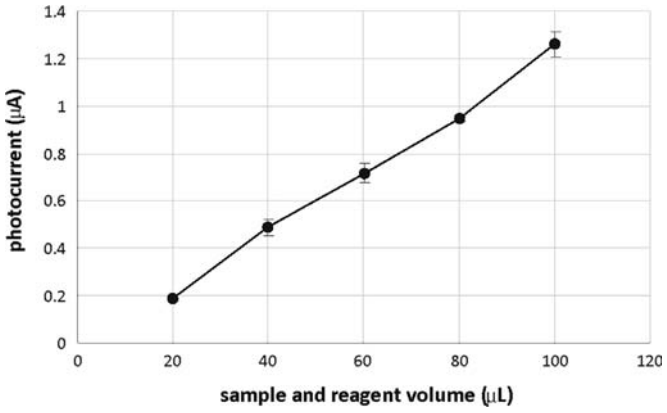

Fig. 9. Influence of the sample and luminol injected volume on the peak high (Fig. 8). Sample: Fe^{3+} 4 mg L^{-1}; reagent: luminol 10^{-3} ml L^{-1}. Each point represents the mean of four consecutive measurements ± S.D.

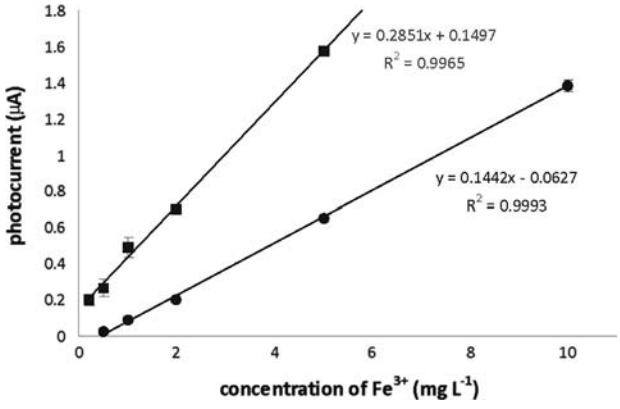

Fig. 10. Calibration graph for chemiluminescence determination of Fe(III), based on luminol oxidation reaction. (■)—signal read immediately after injection (light-flash); (●)—signal read within 180 s of stop flow. Each point represents an average of at least four consecutive measurements ± S.D.

Table 1
Comparison of the analytical features achieved by the proposed direct-injection CL detector and othertypical flow configurations.

Parameter	Direct-injection detector and MPFS	Spiral-type detector and FIA [28,29]	Fountain-type detector and SIA [30]
Reaction coil	Does not exist	Exists (length 190 cm, volume 1.5 mL)	Exists (length 35 cm, volume 0.15 mL)
Detection limit ($\mu g\ L^{-1}$)	25[a]	0.0012[b]	6[c]
Working range	0.5–10 mg L^{-1} (9×10^{-6}–2×10^{-4} M)	0.05–2 nM	10^{-5} M
Regression coefficient, R^2	0.9993	0.996	0.9884
Repeatability[d] (%)	2–5	1.2–5	No data
Injection throughput (injections h^{-1})	144	~5	72
Sample consumption (μL)	80	1800	200
Reagents Consumption (μL):			
Luminol	80	No data	150
H_2O_2	120	No data	150

[a] Detection limit calculated as $3s_b/S$, where s_b is the standard deviation for 10 measurements of the blank and S is the slope of the calibration graph.
[b] Detection limit as a concentration of Fe(III) equivalent to the blank.
[c] Detection limit corresponding to the signal-to-noise ratio of three ($S/N=3$).
[d] R.S.D.—relative standard deviation.

of the standard 2 mg L^{-1} was equal to about 5% for 5 s of the stop-flow, 2% for the 180 s of the stop-flow. Therefore, if the stable repeatable signal and low detection limit are more preferred than the short analysis time, the stop-flow time of 180 s seems to be an appropriate choice for Fe(III) determination. Taking into account the light-flash signal, we can obtain better sensitivity and a much higher sampling rate, because the time of analysis can be shortened to 25 s (injection throughput—144 analyzes per hour).

3.6. Comparison of DID-CL–MPFS system with other flow systems

A critical comparison of the results obtained using the proposed direct-injection detector with the already existing flow systems was carried out. All the systems compared were based on the reaction with luminol used for the Fe(III) determination. A typical FIA system equipped with the spiral Teflon tube detector [28,29] and a sequential injection (SIA) system with fountain type detector [30] were taken into account. The results are summarized in Table 1.

The detection limit for the DID-CL–MPFS system was the highest. However, it should be emphasized that the method of its calculation was different for every system compared. Detection limit for our system was calculated as $3s_b/S$, where s_b is the standard deviation for 10 measurements of the blank and S is the slope of the calibration graph. This method takes into account the influence of the calibration step on the detection limit. Obata et al. [28] employed only the concentration of Fe(III) equivalent to the blank as a detection limit. Takayanagi et al. [30] estimated the detection limit as a concentration of Fe(III) corresponding to the signal-to-noise ratio of three ($S/N=3$). Moreover, the lowest detection limit for the systems described by Obata's [28] and Jong's [29] groups is the result of the preconcentration step applied in this method. Therefore, the detection limit achieved using our method is comparable with those described previously. The working range for our method corresponds with the range achieved for the fountain type detector.

DID-CL–MPFS system is characterized by a very good linearity in the tested range of Fe(III) concentration and a satisfactory repeatability. The consumption of the reagents and sample is much lower, the injection throughput very high compared to other systems.

The main advantage of the DID-CL–MPFS system is the possibility for rapid measurements of the chemiluminescence and the kinetic study. Furthermore, the system described is very simple, easy to optimize and operate. It is portable since it does not employ a peristaltic pump—the most expensive, energy consuming an heavy part of flow systems.

4. Conclusions

The proposed novel construction of a chemiluminescence detector is a promising alternative to the commonly used coiled tubing flow cells. The injection of the reagents directly into the detector chamber enables us to register the CL signal immediately after the moment of mixing. The detection process takes place under the stop flow conditions and the kinetic investigations of fast CL reactions are possible. The reaction kinetics is the main factor determining the time of analysis. The detector can be applied for quantitative analysis yielding satisfactory analytical parameters.

Implementing this detector in a precise, fully automated multi-pumping flow system creates compact equipment with profitable parameters: (1) portability owing to small weight and size, (2) high precision in volume propulsion and high repeatability of the method, (3) low consumption of reagents and energy.

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