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Short communication

A novel direct-injection photometric detector integrated with solenoid pulse-pump flow system

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ABSTRACT

A novel flow photometric detector based on paired emitter-detector diodes (PEDD), coupled with solenoid pulse micro-pumps is presented. The photometric detection chamber also plays a role of the reaction chamber. Both solutions, a sample and a reagent, are injected by solenoid micro-pumps directly and simultaneously into the chamber in countercurrent. This method ensures fast and effective mixing of the injected solutions. A good accuracy and precision of the injected volumes assure the pulse micro-pumps. This method, in comparison with other flow methods, does not require the application of the reaction coil. Thanks to this, the dispersion of the sample is minimized.

The presented flow network is easy to control, miniaturize and exhibits a very low consumption of reagents and the sample. Two chemical systems were chosen and presented as models of photometric reactions: the first – Fe(III) with thiocyanate, and the second – Cr(VI) with 1,5-diphenylcarbazide. To obtain the highest repeatability, the total volume of the solutions should be smaller than the volume of the reaction-detection chamber. In this case, the whole coloured product remains in the chamber. The use of the proposed direct-injection PEDD detector considerably simplifies analytical procedures. The shape of analytical signals and their potential applications have been discussed.

1. Introduction

Optical detection is one of the most popular and the most active areas of research in analytical chemistry. This is largely due to the increasing availability of inexpensive, high-intensity light emitters such as light emitting diodes (LEDs). Apart from their price, these devices have other advantages, for example they are a very efficient source of nearly monochromatic light. As a result, they can be useful in reducing the complexity of photometric devices by eliminating the necessity for using wavelength selectors as diffraction gratings. LEDs are small and require low supply power, so they are ideal for miniaturization of analytical devices [1,2].

LEDs were first used for chemical analysis about thirty years ago [3]. Since then they have been improved and a variety of LED-based optical sensors has been developed. Nowadays, they are applied in commercial analytical systems and specialized detectors. Usually, LEDs systems are designed for determination of specific analytes that absorb or are excited at the wavelength emitted by the applied LED.

In typical applications LEDs are used only as a light source combined with photodiodes which measure the light intensity after its passage through the sample [4–7]. Recently, the analytical utility of LEDs as light detectors has been investigated [8–10]. In this configuration usually two identical LEDs are employed [11]: one is used as a light source and the second as a light detector. It is possible to use two properly chosen different LEDs [8,12]. There are examples of applications of such paired emission-detection diodes (PEDD) devices in chromatography [12] and in static conditions [13]. Some of PEDD detectors are implemented in flow analysis, mainly flow injection analysis (FIA) [8,9,11] and in multi-pumping flow systems (MPFS) based on the use of solenoid pulse micro-pumps [1,14].

Solenoid micro-pumps are an interesting alternative to peristaltic pumps, typical propulsion devices in conventional flow systems like FIA [15–17]. Peristaltic pumps weigh typically 1.5–5 kg and work with supply power of 125 V or 220–240 V. It is considered [1] that micro-pumps offer excellent opportunities to reduce supply power to 12 V and to miniaturize the propulsion system.

The solenoid micro-pumps in some publications are called pulse-pumps because of the aspiration-injection nature of pulses. Pulse nature of the flow can be used to mix solutions more effective to the point where the confluence of fluids occurs. It is emphasized that the confluence point, which had the shape of the letter “Y” or “X”, only improves mixing conditions. Mixing of the liquids occurs here in a rapid and precise way [17]. Although, the role of reaction coils as promoters of mixing between the sample and reagents is less significant than in the other flow systems. Until now reaction coils were necessary and always applied in the MPFS systems.

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The aim of this work is to propose a new construction of photometric PEDD-detector integrated with solenoid pulse micro-pump system. In this system a sample and an appropriate reagent are injected directly into the detection chamber. The entire mixture remains on the optical pathway of the detector and an additional reaction coil is not necessary. Utilization of the elaborated flow system as a compact, economical analytical tool is emphasized.

2. Experimental

2.1. Reagents

All solutions were prepared with analytical-grade chemicals and with deionised water obtained from the Milli-Q (Millipore) water purification system (resistivity > 18.2 MΩ cm). Potassium thiocyanate and nitric acid were obtained from POCh (Gliwice, Poland). Carrier solutions: 0.1 mol L^{-1} HNO_3 and 0.05 mol L^{-1} H_2SO_4 were prepared through appropriate dilution of concentrated nitric acid (Merck, Germany) and sulfuric acid (POCh, Gliwice, Poland). Carmine solution was prepared through dissolving solid Carmine (Fluka, Switzerland) in water.

A 10 μg mL^{-1} stock standard solution of Fe(III) was prepared through dilution of the AAS standard (WZORMAT, Poland). Working solutions were prepared through appropriate dilution of stock solution with water and HNO_3 to obtain the final concentration of Fe^{3+} ions and H^+ ions just as in the carrier. A 5% (w/v) solution of KSCN was prepared through dissolving of crystalline KSCN in water.

A 1 mg mL^{-1} stock standard solution of Cr(VI) was prepared through dissolving of 0.3735 g of K_2CrO_4 in 100 mL of 0.005 mol L^{-1} H_2SO_4. Working solutions were prepared through appropriate dilution of stock solution with water and H_2SO_4. A 0.25% stock solution of 1,5-diphenylcarbazide (DFK) was prepared by dissolving of 0.125 g of reagent in 50 mL of acetone with addition of 0.5 mL of 5 mol L^{-1} H_2SO_4. Working solutions (0.005% DFK) were prepared through appropriate dilution of stock solution with water and H_2SO_4.

2.2. Apparatus

The solenoid-operated pulse-micropumps were purchased from Bio-chemValve Inc. (Boonton, USA) and have an internal volume of 10 μL (product no. 120SP1210-4TE) or 50 μL (product no. 120SP1250-4EE). The flow lines were made of a PTFE tube (ID 0.8 mm) obtained from Bio-chemValve (product no. 008T16-080-20).

The LEDs were purchased in a local electronic parts shop. For the investigations of the complex Fe(III)-thiocyanate (λ_{max} = 470 nm [18,19]): as an emitter diode, a blue LED (Kingbright L-7113PBC-A, λ_{max} = 470 nm) was chosen. As a detection diode – a green LED with λ_{max} = 520 nm was used, which can detect light of wavelength below this point [12]. For the investigations of the red dye Carmine the same pair of LED was used.

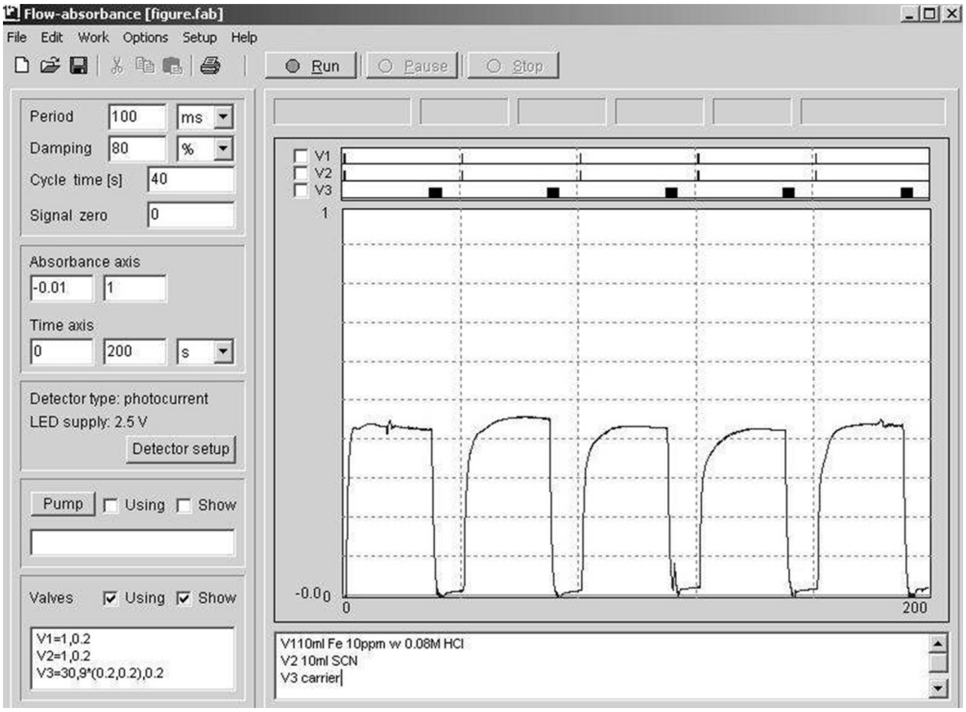
For the investigations of the Cr(VI)-DFK (λ_{max} = 540 nm [18]): as the emitter diode a green LED (Huey Jann Electronic HB5D-433AGCA-D, λ_{max} = 525 nm) was chosen and as a detection diode – a yellow-green diode (λ_{max} = 560 nm).

The pulse-micropumps and PEDD detector were PC-controlled by the measurement system of our construction. The software was developed in Delphi programming language. This program enables the user to select the LED voltage or current and to record photocurrent or photopotential of an LED diode. Other tasks of that computer program were to control the work of solenoid micropumps and to calibrate the signal of absorbance. Fig. 1 presents the main window of the program controlling the manifold. An example of a recorded analytical signal is presented in the window.

3. Results and discussion

3.1. The construction of PEDD direct-injection detector

The PEDD detector was fabricated using one block of Teflon. Inside the detector body there was a tube-shaped reaction chamber (Fig. 2). The reaction chamber also works as a photometric



Period 100 ms
Damping 80 %
Cycle time [s] 40
Signal zero 0

Absorbance axis -0.01 1

Time axis 0 200 s

Detector type: photocurrent
LED supply: 2.5 V

☐ Using ☐ Show

Valves ☑ Using ☑ Show

```
V1=1,0.2
V2=1,0.2
V3=30,9*(0.2,0.2),0.2
```

```
V110ml Fe 10ppm w 0.08M HCl
V2 10ml SCN
V3 carrier
```

Fig. 1. The main window of the computer program used for controlling the micro-pumps and measuring of absorbance by PEDD detector. Left-bottom corner – edit window for programming the pulse-micropumps; at the top – diagram of the micropumps state.

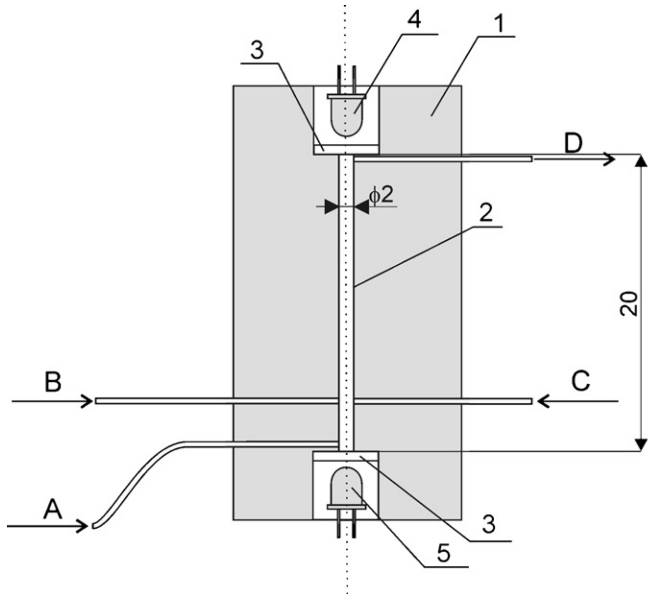


Fig. 2. Schematic diagram of the direct-injection PEDD detector. 1 – body of the detector; 2 – reaction-detection chamber; 3 – transparent windows; 4 and 5 – emission and detection LEDs. Inlet of the carrier solution (A), sample (B), reagent (C) and outlet of the waste (D).

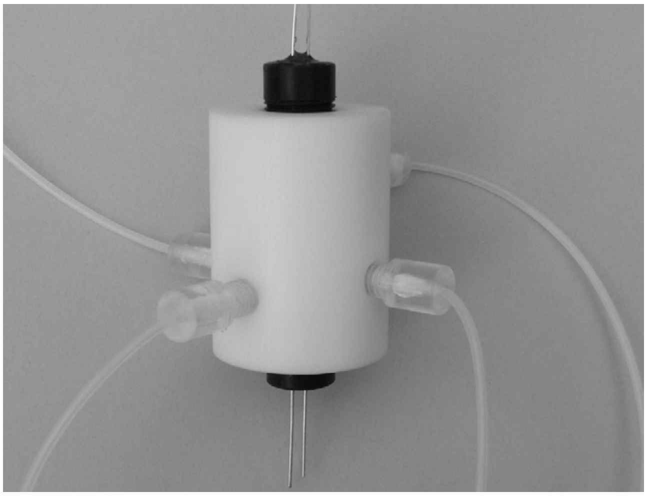


Fig. 3. Photo of the direct-injection PEDD detector.

detection channel. At both ends of this channel, two paired LEDs were placed. One LED is used as a light source and second one as a light detector. The LED that is used as the light source can of course be combined with an appropriate photodiode (an LED-PD pair). However, the use of carefully paired emitter-detector diodes (PEDD) can provide, depending on the application and/or analytical technique, higher selectivity of analysis and can lower overall cost of the device. Nevertheless, the PEDD detection imposes preparation of an appropriate pair of LEDs dedicated for proper analysis (pairing of LEDs).

The chamber wall was white in colour and not transparent. This property should minimize the distortion of analytical signal caused by the Schlieren effect. Such an effect may exist because of differences in the refraction indices of the mixed solutions and is commonly associated with insufficient mixture between the sample, reagent and carrier.

The light that reaches the detector LED has a relatively high intensity due to the absence of optical components (e.g. mirrors, lenses), which can partly absorb or disperse the emitted radiation. As the result, it is possible to use a cell with a longer light-path. The described reaction-detection chamber had a length of 20 mm and a diameter of 2 mm (the total volume of about 60 μL). The chamber was separated from both LEDs with transparent glass windows. The windows were made of typical optical glass, because our current studies deal with visible light. For measuring the intensity of the UV-light the application of the quartz glass windows is essential. The photo of the detector is presented in Fig. 3.

The inlets of carrier solution (Fig. 2A), reagents and sample (Fig. 2B and C) were situated perpendicularly to the axis of the reaction-detection chamber. To achieve effective mixing conditions, the inlet of the reagent and the inlet of the sample were placed opposite each other. The liquid outflow from the detector followed thought the path situated on the opposite side of the reaction-detection chamber (Fig. 2D). It was essential that the inlets of reagents and the sample were closer to the outlet than the inlet of the carrier solution. Thus, it was possible after the detection process to remove the whole volume of the reagent mixture from the chamber and clean it before the next injection.

The volume of the reaction-detection chamber had to be larger than the total volume of both the solutions – the sample and reagent. That way, all the solution involved in the chemical reaction remained on the optical pathway inside the detector. Therefore, it was important to use suitable micro-pumps. For volume of the chamber of 60 μL – two micro-pumps with nominal volume of 10 μL per pulse can be recommended. In order to effectively clean the reaction-detection chamber, it is advisable to use a pump, for example 20 or 50 μL per pulse.

To use LEDs in proposed PEDD-flow system, they were first placed in special holders (Fig. 3). The holders with LEDs were screwed into the detector body.

3.2. Flow manifold

The design of the flow manifold exploiting the PEDD direct-injection detector was very simple: every solution used was aspirated and then injected into the system by independent micro-pumps. The pumps were responsible for injecting solution, controlling the inserted volume, managing the time and sequence of insertion, transporting in and out of the detection chamber. The schematic diagram of the applying flow network used in this work is shown in Fig. 4.

Before the analytical cycle began, the chamber of detector was filled up with the carrier stream (HNO_3) by using the pump 3. The measuring cycle started by establishing the baseline. Next, in countercurrent, simultaneously, injection of sample (Fe^{3+}) and reagent (SCN^-) using the pump 1 and 2 was done. At that moment, the chemical reaction began and the measurement of absorbance was performed in a stop-flow condition. Such a method of introducing reagents ensures effective mixing. What is more, the inner volume of detector was 60 μL and the injected volume was 10 μL per stoke for both pumps. As the result, all the inserted solution remained on the optical pathway of the detector.

Finally, after the proper time of stop-flow taken to measure the absorbance, the pump 3 was activated for injection of the carrier solution again in order to clean the chamber. To be sure the removal of reagents solution from the detector chamber was thorough, several strokes of pump 3 had to be used. Because the pump 3 allowed for insertion of 50 μL per stroke, the total volume of 500 μL was pumped through.

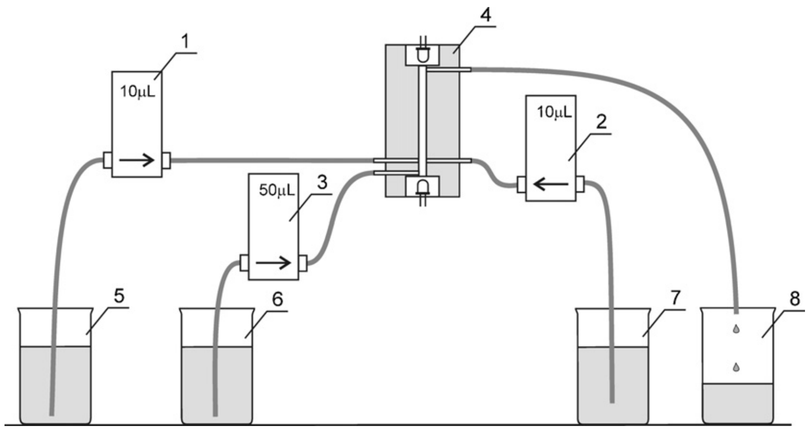


Fig. 4. The manifold used for Fe(III) determination. 1, 2 and 3 – pulse-pumps; 4 – PEDD direct-injection detector; 5 – sample (Fe^{3+}); 6 – carrier (HNO_3); 7 – reagent (SCN^-); 8 – waste.

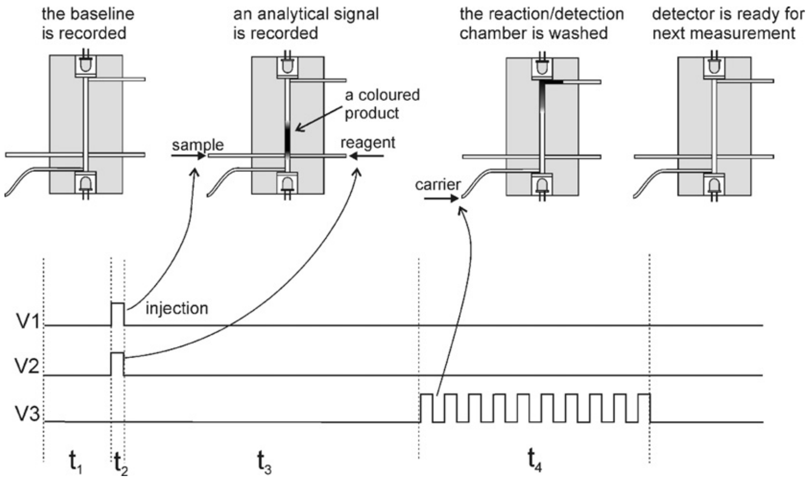


Fig. 5. The diagram of the typical micro-pumps switching sequence. V1, V2, V3 – timing course for switching micro-pumps 1, 2 and 3; t_1 – stop-flow (all the pumps were OFF) for baseline recording, t_2 – time of the solenoid activation inside the pumps 1 and 2, t_3 – flow-stop for measuring the analytical signal, t_4 – time of cleaning the reaction-detection chamber using the pump 3.

3.3. Programming the micro-pumps switching sequence

Experiments were carried out with diaphragm micro-pumps operated by a solenoid. The diaphragm was maintained in a stable position with an inner spring mechanism. When voltage was applied, the solenoid coil was activated and the diaphragm was pulled back creating a partial vacuum in the pump body. This pulled the liquid into the pump chamber. The drop of applied voltage resulted in de-energizing of the solenoid and the spring forced the diaphragm back into the stable position. As a result, the solution was pressed out by the pump. The solenoid micro-pumps were operated individually and allowed the selective introduction of reagents into the chamber of the detector. That way, the precise injection of sample and reagent was established and the synchronization of the reagent addition was possible. The example of the programs applied to control the work of solenoid pumps is shown in Fig. 5.

3.4. Kinetics study

Measured absorbance is proportional to the number of molecules, which absorb the light (the Lambert–Beer law). While the number of light absorbing molecules is constant, we should not observe any changes in the absorbance. In preliminary kinetics investigations we checked whether this law is fulfilled in our conditions. For this experiment we used dye Carmine. If the volume of the detection chamber (60 μL) is larger than the total injected volume (10 μL of Carmine + 10 μL of water), the probability that some light absorbing molecules escape out of the detection chamber is low. In this experiment stop flow for the absorbance measuring was prolonged to 500 s (Fig. 6). During this time the absorbance signal was stable. Dilution over time and incomplete homogenisation should not influence the absorbance signal.

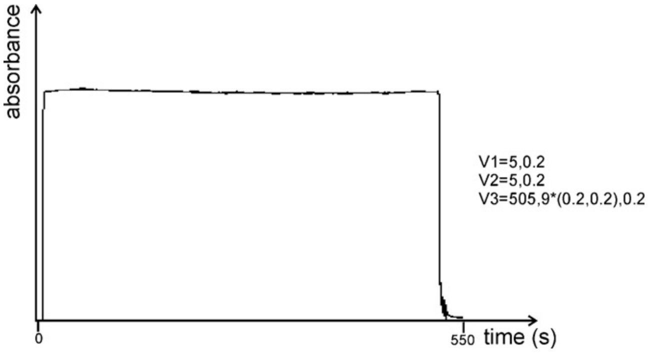


Fig. 6. Kinetic study of the dye Carmine. The pumps program is indicated on the right. Stop flow: 500 s. Cycle time: 550 s.

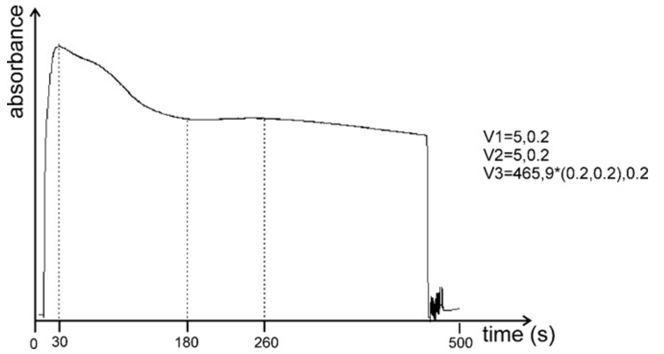


Fig. 7. Kinetic study of the complex Fe(III)-SCN formation and corresponding pumps program. Concentration: sample (Fe^{3+}) – 5 μg mL^{-1}; reagent (SCN^-) – 5% (w/v); carrier solution (HNO_3) – 0.1 mol L^{-1}. Stop flow: 460 s. Cycle time: 500 s.

In kinetics study, complexation of thiocyanate ions with iron(III), a reaction well-known in spectrophotometry, has been chosen as a model reaction. Thiocyanate reacts with iron(III) to form a series of complexes which can be presented with a following formula: $[Fe(SCN)_n]^{+3-n}$, where $n = 1–6$. The number of thiocyanate ions that coordinate around each iron(III) ion is determined by the concentration of both reagents and pH. At a relatively low thiocyanate concentration and iron(III) concentration in the range of μg mL^{-1}, the coloured products consist mainly of the $[Fe(SCN)]^{2+}$ ions. The optimum wavelength for monitoring this red colour complex has been reported in the literature and λ_{max} is typically within the range of 470–480 nm [18,19]. This reaction is considered fast and is used extensively for the determination of both iron(III) and thiocyanate.

Unfortunately, the colour of the Fe(III)-SCN complexes is not stable. It was noticed that the intensity of the colour decreased by up to several percent after 30 min and up to a half of its initial value after 6 h [18]. It can be explained by the reducing action of thiocyanate on the Fe(III). The development of the colour intensity was monitored with the elaborated PEDD direct-injection detector (Fig. 7). The stop-flow and measuring of the absorbance was conducted over the time of 460 s. The colour development occurred rapidly, approximately within the time of 25–30 s. After that, the absorbance started to decrease relatively fast. After 180 s, we observed short stabilization of the absorbance and a reduction in the pace of decrease followed. At the end of a measuring cycle, the signal decreased by about 25% of the highest value. If we use this system for quantitative determination of Fe(III) or SCN^-, the best moment for measuring the absorbance is at about 25–30 s after reagents mix together. These results seem to be the most useful for analysis, because the calibration graphs are expected to have the highest slope (the best sensitivity). The obtained results suggest that a detector based on the concept presented in this paper can be used to design an analytical quantitative procedure and for some kinetic investigations, e.g. using procedures such as initial rate or two point procedures.

3.5. The shape of analytical signal

Because of instability of the colour of the ion complex $[Fe(SCN)]^{2+}$ it is recommended to measure the absorbance as soon as possible. Therefore, analysis in flow conditions with direct injection of the sample and reagent into the detection chamber is desirable. This way, errors caused by changes in the analytical signal can be avoided and the sensitivity of the method improved. The shape of the analytically useful signal depends mainly on the kinetics of an observed chemical reaction. The characteristic signal that is recommended for determination of Fe(III) using the thiocyanate method is presented in Fig. 8.

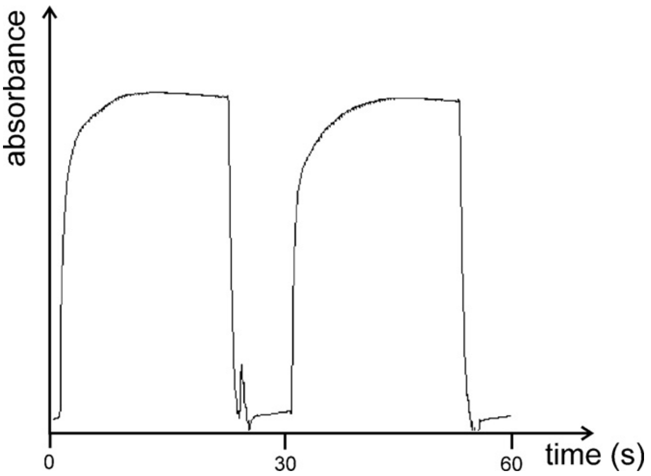


Fig. 8. The analytical signal obtained for Fe(III) or thiocyanate ions determination. Concentration: carrier solution (HNO_3) – 0.1 mol L^{-1}; sample (Fe(III)) – 5 μg mL^{-1}; reagent (SCN^-) – 5% (w/v). Stop flow: 20 s, cycle time: 30 s. The pumps program compatible to this described in Fig. 5.

Proposed method can have promising applications in determination of some colourful products that have long time of formation. Usually, especially in bath condition methods, it is necessary to wait a long time for the moment the reaction is finished and the signal of absorbance is constant. Fig. 9 presents an analytical signal obtained during the development of the reaction of Cr(VI) with 1,5-diphenylcarbazide (DFK).

When incorporating a method of direct observation of colour developing, it is easy to estimate the time sufficient to obtain an acceptable analytical signal. For the reaction of Cr(VI) with DFK, the colour formation increased asymptotically. From the analytical point of view, the most useful part of the curve is when the absorbance is constant in time. Considering the precision of micro-pumps and therefore repeatability of the analytical signal, it is possible to measure the absorbance in any selected time, assuming it is more than 110 s. Obviously in this situation, the longer time the better sensitivity. But the choice is a matter of finding the right balance between the sensitivity and time of analysis.

3.6. Sample and reagent volume

It is worth mentioning that the detector presented in this paper, combined with pulse micro-pumps system, enables users not only to save the time of analysis but also reduce the amount of reagents and sample used. This amount is very low, determined by the pumps. In our preliminary experiments we used pumps working with the volume of 10 μL, so such was the consumption. It is possible, of course, to use pumps of smaller or larger nominal volume,

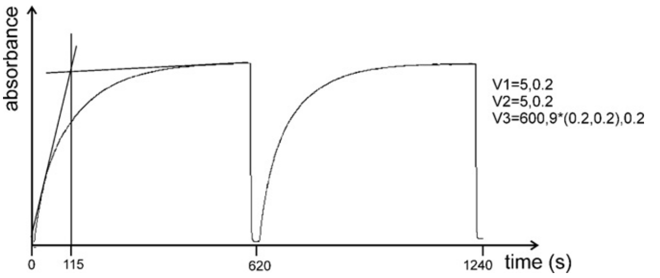


Fig. 9. The analytical signal obtained for Cr(VI) determination. Carrier solution: H_2SO_4 0.05 mol L^{-1}; sample: Cr(VI) 1 μg mL^{-1}; reagent: DFK 0.005% in 0.05 mol L^{-1} H_2SO_4. Stop flow: 595 s. Cycle time: 620 s. The pump's program is presented on the right.

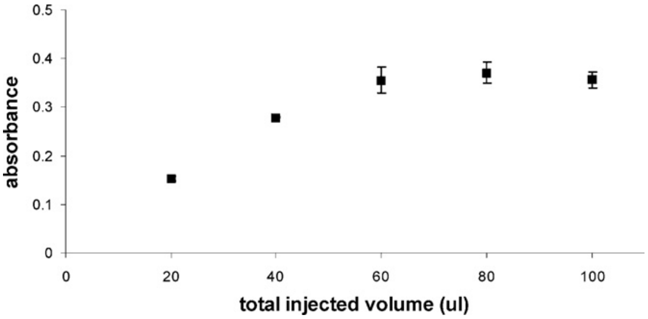


Fig. 10. Influence of the total injected volume (sum of the sample volume and reagent volumes) on the absorbance intensity. Pumps used for propelling sample (dye Carmine) and reagent (water): both 10 μL. Each point represents the average of five consecutive measurements, bars indicate the standard deviation of the value obtained.

depending on the volume of reaction-detection chamber used. It is only recommended that the total volume of the sample and reagent be smaller than the volume of the reaction-detection chamber used (see Section 3.4).

This is also some compromise between the cost of analysis and the magnitude of the analytical signal. To check how the total volume of injected sample and reagent influences the signal we performed injection of dye (Carmine) and water. The obtained results are shown in Fig. 10

First point in Fig. 10 represents only single, simultaneous injection of dye and water in countercurrent. The second point concerns the repetition of such injection twice, the third point – repetition of injection tree times and so on. We can find that in the beginning magnitude of the signal increased with increasing of the injected volume. Measured absorbance depends on the number of molecules which are able to absorb the light. We can also recognize that repeatability for first two points is very high. From the point when the volume of the dye and water equalled the volume of the reaction-detection chamber (60 μL), we obtained a series of signals of lower repeatability. Therefore, for this configuration, when using 10 μL pumps, the recommended total injected volume is below 60 μL, i.e. 40 μL.

4. Conclusions

In our opinion, the preliminary experiments performed with direct-injection PEDD detector lead to the important conclusion:

1. Because the applied detector plays a role of the reaction chamber as well, it is possible not to use additional mixing elements, like a reaction coil or a mixing chamber. The proposed detector acts as a confluence point, too. That way the sample and reagent are mixed together in a precise and rapid method.
2. The application of the reaction-detection chamber allows us to avoid unnecessary dilution of the sample and reagents, which is typical for every flow systems because of the dispersion process.
3. When applied, this system enables us to lower the reagent consumption (only 10 or 20 μL of sample and reagent or less – depending on the pumps used). This results in a considerable reduction in the cost of an analysis and lowers the volume of generated wastes.
4. This method imposes the work in stop-flow conditions and creates good conditions for study of reaction kinetics.
5. The increment of sample throughput has been achieved. Solutions do not have to be transported to the detector. The time of analysis should depend mainly on the reaction kinetics.
6. Proposed flow system is very compact and small in size, requires no more than 12 V in supply voltage. This creates an opportunity for application in mobile laboratories.

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