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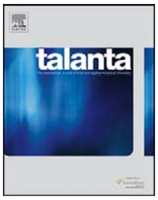

A novel flow-injection method for the determination of Pt(IV) in environmental samples based on chemiluminescence reaction of lucigenin and biosorption

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ABSTRACT

A new flow-injection chemiluminescence method (FI-CL) was developed for the determination of trace amounts of Pt(IV). The method is based on the quenching effect of the analyte on CL emission generated by lucigenin in alkaline solution. Application of a column filled with an algae *Chlorella vulgaris* immobilized on Cellex-T resin allowed to preconcentrate and separate the Pt(IV) ions from complex environmental samples, such as road dust. The developed method is simple and does not require sophisticated instrumentation. It is also characterized by a very low limit of detection (0.1 ng mL^{-1}), good sensitivity and precision (RSD < 3%). The accuracy of the presented method was confirmed by analysis of a certified reference material of tunnel dust (BCR-723). The content of Pt in road dust samples collected in Białystok (Poland) in 2009 determined by the evaluated method was 351.8 ± 54.6 ng g^{-1} and was higher than in samples collected in years 2000 and 2003.

1. Introduction

Production of vehicle exhaust catalysts is the most important application of platinum, palladium and rhodium. These metals are active components of car catalysts, which allow reducing the emission of carbon monoxide, nitrogen oxides and hydrocarbons. However, due to abrasion and deterioration of the catalyst surface during vehicle operation, platinum group metals are emitted with exhaust fumes into the environment. In consequence, elevated concentrations of platinum group metals in roadside environment (airborne particulate matter, road dust, tunnel dust, soil, vegetation, river water and sediments) have been observed [1–3]. Electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma mass spectrometry (ICP-MS) and adsorptive stripping voltammetry (AdSV) are the most frequently used detection techniques for the determination of platinum in environmental samples [4]. Due to low concentration levels of Pt (ng g^{-1}) and complicated composition of sample matrix, the preconcentration/separation step is often required prior to detection of the analyte. Procedures applied for the preconcentration/separation of platinum before its determination by spectrometric techniques have been reviewed [5].

Chemiluminescence (CL) is an analytical technique widely used for determination of traces of metals and organic compounds (ng mL^{-1}–pg mL^{-1}) in simple matrices [6,7]. High sensitivity and simplicity of instrumentation are the main advantages of this technique. The combination of CL detection with flow-injection analysis (FIA) provides high precision of measurements and possibility of automation [8,9]. The catalytic effect of platinum(IV) on chemiluminescence reaction of luminol oxidation in alkaline medium was employed for the quantification of this metal (limit of detection equals to 0.03 ng mL^{-1} Pt) [10]. The main problem limiting applicability of chemiluminescent method is its low selectivity, since lots of metal ions as well as organic compounds can affect the CL emission. The introduction of efficient procedure for separation of analyte from interfering matrix is necessary before its determination. A number of studies have proved that various microorganisms, such as algae, bacteria, fungi and yeast, due to its ability to metal binding, can be used as sorbents for preconcentration, separation and speciation studies of metal ions in analytical chemistry [11]. The mechanism of metal biosorption by microorganisms is complicated and dependent on the constitution of the cell wall (type of functional groups and their affinity for metal ions), metal solution chemistry and ambient conditions, such as pH, temperature and presence of other metal ions competing for binding sites. Metal binding mechanism can be combination of ion exchange, complexation, physical adsorption and microprecipitation. It was shown that unicellular green algae *Chlorella vulgaris* can be utilized for removal of metal ions, e.g. Cr(VI) [12], Pb(II) [13], Cu(II) [14] and Cd(II) [15] from aqueous solutions in a batch mode. Performing of biosorption process in a flow mode requires application of cells immobilized on/in natural or synthetic support, since they show better mechanical strength, rigidity, porosity and chemical stability in comparison with free cells. The algae *C. vulgaris* immobilized

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on silica were used for removal of paramagnetic ions of Mn(II) and Cr(III) from aqueous solutions [16]. Biosorption efficiency of metals was significantly improved (by about 30%) in the presence of an external magnetic field generated in a solenoid. Developed procedure was applied for the preconcentration/separation of manganese from river and snow water before its ETAAS detection. An enrichment factor of 21.2 and a limit of detection of 8 pg mL^{-1} Mn were attained. The algae *C. vulgaris* immobilized on silica gel were applied for mercury speciation in tap and seawater [17]. The uptake efficiency of CH_3Hg^+ and Hg^{2+} at pH 3 was higher than 97%. The separation of both species was performed by sequential elution with 0.03 and 1.5 mol L^{-1} HCl for CH_3Hg^+ and Hg^{2+}, respectively. The algae *C. vulgaris* immobilized on silica gel and cellulose resin Cellex-T were used for the separation of platinum and palladium from environmental samples prior to their determination by ETAAS [18,19]. Tested metal ions were quantitatively retained on the biosorbents in the pH range 1.5–1.8 and desorbed by 0.3 mol L^{-1} thiourea in 1.0 mol L^{-1} HCl solution. The detection limits of 0.2 and 0.4 ng mL^{-1} Pt, 0.096 and 0.8 ng mL^{-1} Pd were achieved by using Cellex-T-immobilized algae and silica-immobilized algae, respectively. The algae *C. vulgaris* immobilized on Cellex-T resin support were also applied for the preconcentration and separation of platinum before its determination by CL method based on catalytic effect of the analyte on the reaction of luminol oxidation in alkaline solution [20]. The developed method is characterized by good sensitivity and low limit of detection of the analyte (LOD = 0.06 ng mL^{-1}) and can be used for analysis of Pt in river water samples. However, the determination of this metal in more complex environmental samples (e.g. road dust) was impossible, due to strong matrix effect. Therefore, our further studies focused on developing more selective CL method of Pt(IV) determination. Literature survey shows that lucigenin (*N,N′*-dimethyl-9,9′-biacridinium dinitrate) is more selective CL reagent than luminol, since it was used for the determination of only three elements at trace levels: Co(II) [21,22], Cr(III) [23] and As(V) [24]. The developed methods were based on catalytic effect of analytes on the CL reaction between lucigenin and H_2O_2 (Co and As) or KIO_4 (Co and Cr) in alkaline solutions.

This paper describes a new flow-injection chemiluminescent method of Pt(IV) determination based on the quenching effect of the analyte on chemiluminescence generated by lucigenin in the alkaline medium. The introduction of an efficient procedure for the separation of interfering matrix and preconcentration of platinum before its CL detection provides an accurate determination of Pt in river water and road dust samples.

2. Experimental

2.1. Reagents and materials

A standard solution of platinum as hexachloroplatinic(IV) acid (30%) (POCh) was used. Stock solution of Pt(IV) (1000 μg g^{-1}) was prepared in 1 mol L^{-1} hydrochloric acid (Trace Select, Fluka). Working standard solutions were prepared daily by diluting the stock solution with HCl or NaCl solution.

Stock solution of lucigenin (*N,N′*-dimethyl-9,9′-biacridinium dinitrate) (purum p.a., Fluka) ($5.0 \cdot 10^{-3}$ mol L^{-1}) was prepared by dissolving an appropriate amount of the compound in Milli-Q water. It was stored in a refrigerator (at 4 °C). Working solutions were prepared before use by dilution of the stock solution with Milli-Q water. The analytical grade reagents: sodium hydroxide (POCh) and sodium chloride (Fluka) were used. The appropriate solutions of these reagents were prepared by dissolving the compounds in Milli-Q water.

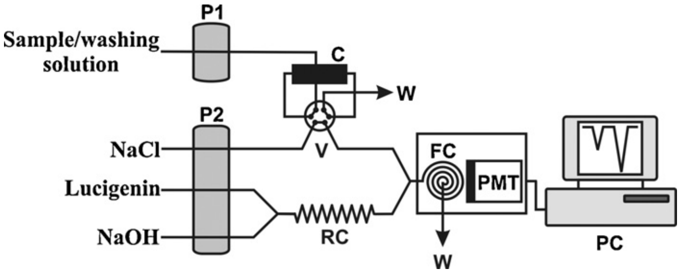

Fig. 1. Schematic diagram of FI-manifold for on-line preconcentration/separation of platinum on algae column followed by its CL determination; P1, P2—peristaltic pumps, V—injection valve, C—column filled with algae *C. vulgaris* immobilized on Cellex-T resin, RC—reaction coil, FC—flow cell, PMT—photomultiplier, PC—computer, W—waste.

Cellex-T anion-exchange resin, cellulose powder containing quaternary amine exchange groups—$C_2H_4N^+(C_2H_5)_3$ (Bio-Rad Laboratories, USA) was used as a support material for immobilization of algae *C. vulgaris*. Reversed-phase C_{18} bonded silica gel (LiChroprep RP-18, 25–40 μm particle size, Merck) was used.

BCR-723 (IRMM, Geel, Belgium)-certified reference material for platinum group elements (dust collected from the ceiling of road tunnel in Austria in 1998, particle fraction <90 μm) was used for quality control.

The environmental samples analyzed in this study were: road dust from Białystok (Poland) and water from the Biała and Supraśl rivers. The samples of road dust were collected in 2009 from the intersection with traffic lights (high traffic density) according to the procedure described in [25]. Only the fraction of particle size below 75 μm was analyzed.

2.2. Instrumentation

A FI-CL system used in this work is shown in Fig. 1. It was composed of two peristaltic pumps (Gilson Minipuls 3, France) delivering sample/washing solutions, eluent and reagents solutions, rotary injection valve (Model 5021 Rheodyne, Cotati, CA), glassy column (6 mm i.d. and 30 mm length) packed with immobilized microorganism and flow luminometer (KSP, Poland). The flow cell was a flat spiral of PTFE tubing (0.8 mm i.d., 150 cm length) positioned directly in front of the window of photomultiplier tube. The distance between the confluence point of all solutions and the flow cell was 15 cm. All flow lines were PTFE tubing (0.8 mm i.d.). The photomultiplier (Carls Zeiss, Jena, Germany) was located in a light-tight box and was operated at 1100 V. Detector response was recorded on a computer with KSP software. The emitted light was measured with no wavelength discrimination. During the optimization of chemical and hydrodynamic parameters of the used manifold, the algae column was replaced by an injection loop.

The CL spectra were recorded with a fluorescence spectrophotometer (F-2500 Hitachi, Japan) with the excitation source light being switched off.

For pH measurements, pHmeter CP-315M (Elmetron, Poland) was used.

A solid phase extraction unit Spe-12G (J.T. Baker, Germany), equipped with a glassy column filled with LiChroprep RP-18, was applied for removal of interfering matrix from environmental samples.

The digestion of samples was performed in microwave system ETHOS PLUS (Milestone, Italy).

2.3. Procedures

2.3.1. Preparation of biosorbent material

The green algae *C. vulgaris* cells were grown under controlled conditions described elsewhere [19]. After incubation, the cells were centrifuged for 10 min, washed with 0.12 mol L^{-1} HCl and next with Milli-Q water. Cellex-T resin was used as a support for biomass immobilization. The resin (0.9 g) was homogeneously mixed with 0.3 g of algae and with 5 mL of water. The resulting mixture was dried at 60 °C. The procedure (wetting with water, mixing and drying) was repeated twice in order to maximize the contact between the biomass and support surface.

2.3.2. Procedure of preconcentration/separation of Pt on biosorbent and its CL determination

The on-line preconcentration/separation and CL determination of Pt was performed in a flow manifold shown in Fig. 1. Before analysis, a column packed with 0.15 g of immobilized algae was preconditioned by passing 0.25 mol L^{-1} HCl solution for 5 min and next Milli-Q water for 2 min at a flow rate of 2.0 mL min^{-1}. The Pt(IV) standard or sample solution (10 mL) of pH 1.5–1.8 was loaded onto the column at a flow rate of 2.0 mL min^{-1} for the analyte retention and the effluent was directed to wastes. Next, the column was rinsed with 4 mL of Milli-Q water in order to remove any residual matrix ions. The injection valve was switched and the elution of retained platinum was carried out by passing 0.75 mol L^{-1} NaCl solution through the column at a flow rate of 2.7 mL min^{-1}. The eluent was merged with the mixed solutions of reagents ($8.0{\cdot}10^{-4}$ mol L^{-1} lucigenin and 1.5 mol L^{-1} NaOH) pumped at a flow rate of 2.7 mL min^{-1} and the resulting solution was directed to the CL flow cell. The decrease in the CL intensity relative to the baseline, corresponding to concentration of Pt(IV) ions, was measured with the CL detector as a negative peaks. The CL signal of analyte was calculated as the difference between background emission and emission in the presence of platinum ions. The average lifetime of the column was around 20 analytical cycles.

2.3.3. Pre-treatment of samples

Samples of river water (the Supraśl and the Biała rivers) were spiked with Pt (1.0; 2.0; 5.0 ng mL^{-1}). After 2-h equilibration, water samples were filtered through Iso-Disc Filters PTFE (25 mm × 0.45 μm, Supelco) and adjusted to the required pH with hydrochloric acid.

About 200 mg of dust was extracted with *aqua regia* in Teflon vessels in microwave system according to following heating program: 250 W for 5 min, 450 W for 10 min and 650 W for 15 min, repeated twice [26]. The obtained sample solutions were transferred to polyethylene vials and stored in a refrigerator (at 4 °C). Before analysis samples were evaporated almost to dryness in quartz crucibles. The residues were dissolved in 2 mL of concentrated HCl and heated almost to dryness. This procedure was repeated twice. The final residues were diluted with Milli-Q water to adequate volume (15 mL) and adjusted to pH 1.5–1.8.

The interfering compounds present in extracts from road and tunnel dust were retained on reversed-phase C_{18} column packed with 500 mg of LiChroprep RP-18. The used sorbent was conditioned by passing 5 mL of methanol and 5 mL of 0.01 mol L^{-1} hydrochloric acid. The 15 mL of sample was passed through the column at a flow rate of 1.0 mL min^{-1} and the effluent was collected.

3. Results and discussion

Chemiluminescence generated during reaction of lucigenin with hydroxide ions has been investigated by Maskiewicz et al. [27]. Our preliminary experiments showed that this CL emission can be inhibited by $PtCl_6{}^{2-}$ ions and the quenching effect was greatest in the absence of H_2O_2 or KIO_4. The registered CL spectra (Fig. 2) showed that maximum CL emission appeared at wavelength of 500 nm and the signal was much lower in the presence of Pt(IV) ions. According to literature data [28–31] the chemiluminescence observed in lucigenin systems is emitted by excited molecules of *N*-methylacridone (NMA*, λ_{max} = 454 nm), lucigenin (λ_{max} = 500–510 nm) and *N,N′*-dimethyl-9,9′-biacridylidene (DBA*, product of two-electron reduction of lucigenin, λ_{max} = 505 nm). Lucigenin and DBA are excited by energy transfer from NMA*. If the excited NMA, lucigenin and DBA return to their ground states simultaneously, emission of light is observed with maximum at wavelength between 450 and 510 nm. The shift of maximum of CL spectrum to longer wavelengths is rising with lucigenin concentration. This effect decreases with time as the lucigenin is consumed [28,29].

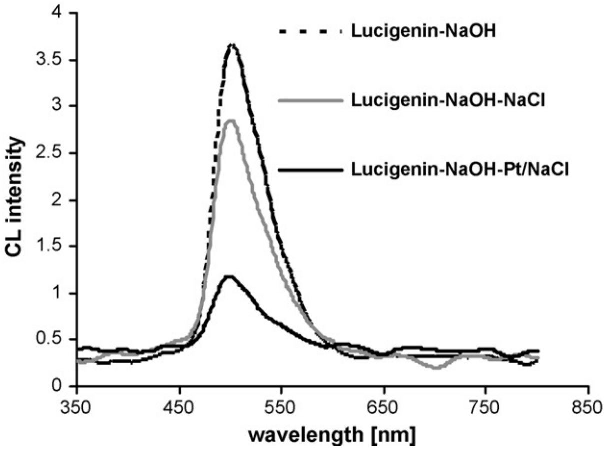

Fig. 2. Chemiluminescence spectra of: lucigenin-NaOH, lucigenin–NaOH–NaCl and lucigenin–NaOH–Pt/NaCl systems; measurement conditions: $1.7{\cdot}10^{-3}$ mol L^{-1} lucigenin, 0.5 mol L^{-1} NaOH, 0.25 mol L^{-1} NaCl, 0.3 μg mL^{-1} Pt(IV).

3.1. Optimization of FI-CL system

In order to obtain the highest sensitivity of measurements, optimization of the CL reaction conditions as well as hydrodynamic parameters of the FI-CL manifold (Fig. 1) was performed. Since chemiluminescence of lucigenin is generated in alkaline solutions, the influence of NaOH concentration on analytical signals of Pt(IV) was studied in the range of 0.5–2.5 mol L^{-1} (Fig. 3A). Significant increase in CL signal height was observed with increasing concentration up to 1.5 mol L^{-1}. As can be seen in Fig. 3B, the CL signal of platinum was rising with lucigenin concentration up to $8.0{\cdot}10^{-4}$ mol L^{-1}. It was noticed that with the increase of NaOH and lucigenin concentrations in the studied ranges, the background CL intensity was significantly rising. The NaOH solution of 1.5 mol L^{-1} and lucigenin solution of $8.0{\cdot}10^{-4}$ mol L^{-1} were chosen for further experiments. The optimal concentrations of reagents were selected considering the sensitivity of the measurements and stability of the baseline as it affected the precision. Our previous studies have proved that quantitative elution of Pt(IV) ions from the algae *C. vulgaris* immobilized on Cellex-T resin can be obtained with sodium chloride solution [20]. Therefore, NaCl solution was used as a carrier stream in the FI-CL manifold and the effect of its concentration (in the range 0–1.0 mol L^{-1}) on platinum signals was investigated. It was observed that with the increase of NaCl concentration in the studied range, the background CL intensity and the height of analyte signal decreased (Fig. 3C). The quenching effect of sodium chloride on lucigenin chemiluminescence was also evident from the CL spectra shown in Fig. 2. It has been reported in the literature that fluorescence of lucigenin (one of the emitting species) can be quenched by chloride ions [32]. To ensure quantitative elution of Pt(IV) from the biosorbent 0.75 mol L^{-1} NaCl was selected as an eluent/carrier stream in further experiments. Although at chosen concentration of NaCl signal of platinum was lower, the baseline stability and precision of the measurements were better (RSD

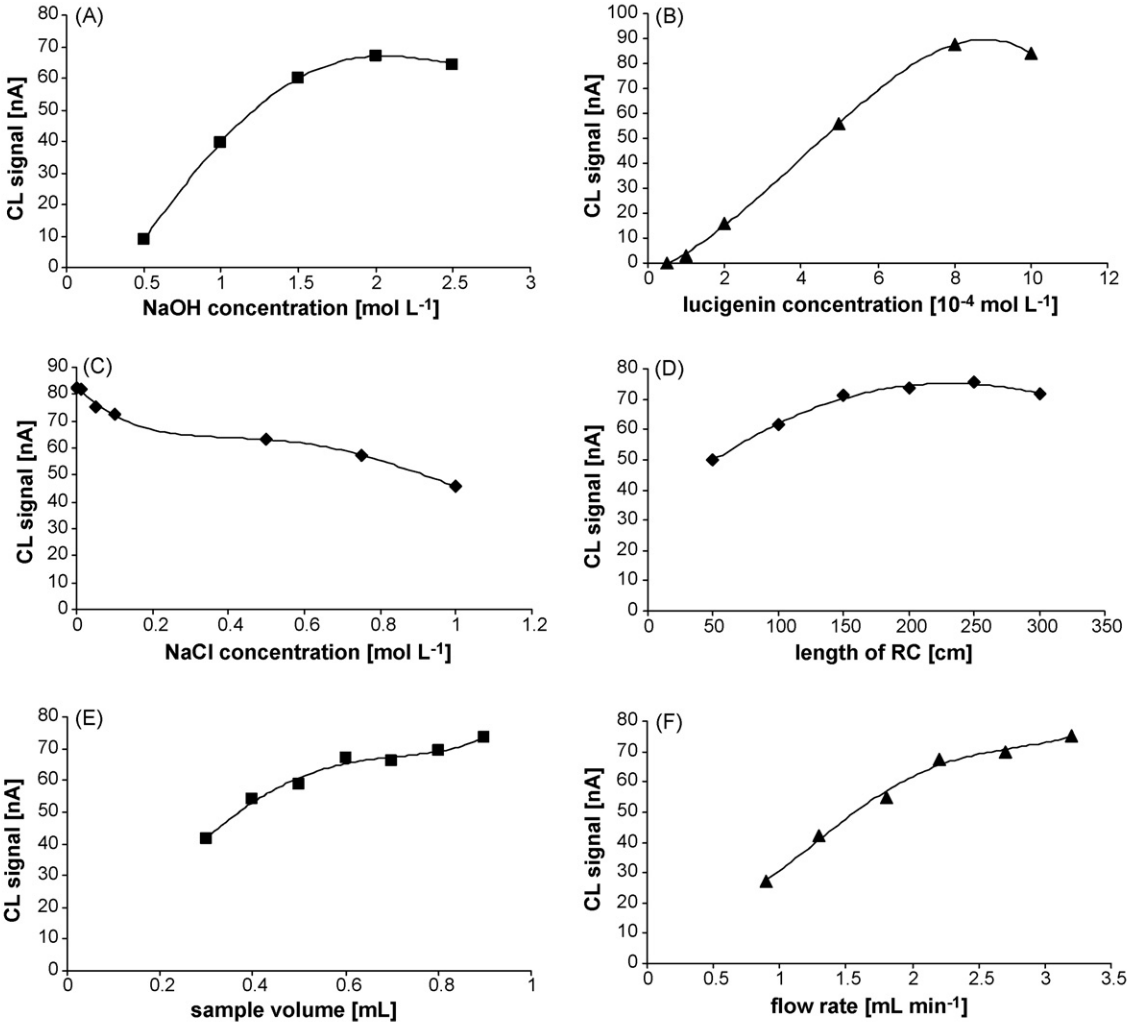

Fig. 3. Effect of conditions of CL reaction and hydrodynamic parameters of flow manifold on CL signal of Pt(IV) (10 ng mL^{-1}): (A) NaOH concentration (C_{Luc} = 5.0·10^{-4} mol L^{-1}, C_{NaCl} = 0.75 mol L^{-1}, RC = 250 cm, FR = 2.2 mL min^{-1}, SV = 0.7 mL); (B) lucigenin concentration (C_{NaOH} = 1.5 mol L^{-1}, C_{NaCl} = 0.75 mol L^{-1}, RC = 250 cm, FR = 2.2 mL min^{-1}, SV = 0.7 mL); (C) NaCl concentration (C_{NaOH} = 1.5 mol L^{-1}, C_{Luc} = 8.0·10^{-4} mol L^{-1}, RC = 250 cm, FR = 2.2 mL min^{-1}, SV = 0.7 mL); (D) length of reaction coil (C_{NaOH} = 1.5 mol L^{-1}, C_{Luc} = 8.0·10^{-4} mol L^{-1}, C_{NaCl} = 0.75 mol L^{-1}, FR = 2.2 mL min^{-1}, SV = 0.7 mL); (E) sample volume (C_{NaOH} = 1.5 mol L^{-1}, C_{Luc} = 8.0·10^{-4} mol L^{-1}, C_{NaCl} = 0.75 mol L^{-1}, RC = 250 cm, FR = 2.2 mL min^{-1}); (F) flow rate of carrier and reagents streams (C_{NaOH} = 1.5 mol L^{-1}, C_{Luc} = 8.0·10^{-4} mol L^{-1}, C_{NaCl} = 0.75 mol L^{-1}, RC = 250 cm, SV = 0.7 mL).

value of signal height was <3%). It is known that in some cases the CL emission generated by lucigenin can be greatly enhanced in the presence of organized surfactant assemblies (for example micelles) [33]. In addition, micellar medium allows avoiding precipitation of reaction products in the flow system. Thus, the effect of cationic (cetyltrimethylammonium bromide), anionic (sodium dodecyl sulfate) and non-ionic (Triton X-114) surfactants on chemiluminescence of lucigenin–NaOH–Pt(IV) system was examined in the range of concentration 0–2.0·10^{-3} mol L^{-1}. The results showed that studied surfactants reduce the CL signal of analyte by 6–76%, thus following experiments were performed in the absence of these compounds. In order to remove reaction products adsorbed on walls of tubing, the flow system was rinsed with diluted solution of wash-up liquid after experiments and with acidic solution of $KMnO_4$ once a week.

At the optimum concentrations of NaOH, lucigenin and NaCl solutions, the influence of hydrodynamic parameters of the flow manifold on the CL signal intensity was examined. In order to ensure efficient mixing between lucigenin and NaOH solutions the reaction coil (RC) was inserted in the flow manifold and its length was optimized. It was found that the CL signal of Pt(IV) increased with increasing length of RC from 50 to 200 cm and remained constant beyond this value (Fig. 3D). Reaction coil of 250 cm was chosen for further studies. As can be seen in Fig. 3E and F, increasing the sample volume (SV) in the range 0.3–0.9 mL and the flow rate (FR) of carrier and reagents streams in the range 0.9–3.2 mL min^{-1} resulted in an increase in analytical signals of platinum. As a compromise between sensitivity of measurements and time of analysis, the sample loop of 0.7 mL and the flow rate of 2.7 mL min^{-1} for each line were chosen. Other important parameter in FI-CL systems, namely the distance between the point of final mixing of all reagents and the flow cell was examined in the range from 5 to 55 cm. The maximum quenching effect of the analyte was obtained for the distance of 15 cm.

After optimization of CL detection step, column filled with green algae *C. vulgaris* immobilized on Cellex-T resin support was installed in a rotary injection valve of the flow manifold instead of a sample loop. The same optimal pH (1.5–1.8, adjusted with hydrochloric acid) and flow rate of a sample solution (2.0 mL min^{-1}) as obtained previously were applied [19,20]. Re-optimization of a flow rate of carrier/eluent stream in the flow system equipped with the algae column gave the same value of this parameter as in the absence of the column (2.7 mL min^{-1}). Elution efficiency obtained at this flow rate was 98.9 ± 2.8% (n = 5).

Table 1
Acceptable excess of interfering ions to analyte in determination of Pt(IV) by the FI-CL methods without and with separation step on algae column (relative error of determination ±5%).

Interfering ion	Acceptable concentration ratio of interferent to analyte	
	Without algae column (20 ng mL^{-1} Pt)	With algae column (2 ng mL^{-1} Pt)
Al(III)	5000	400,000
Zn(II)	5000	250,000
Ni(II)	2500	500,000
Cr(VI)	2500	25,000
Pb(II)	1000	250,000
Cr(III)	500	250,000
Pd(II)	250	5000
Fe(III)	100	10,000
Pt(II)	50	2500
Rh(III)	50	2500
Co(II)	1	500
Cu(II)	0.25	2500
Mn(II)	0.25	10,000

3.2. *Selectivity of the method*

The influence of other metal ions often found in environmental samples on the determination of platinum by the developed FI-CL method was studied. For this purpose, Pt(IV) solutions (2.0 ng mL^{-1}) were spiked with different concentrations of interfering ions (as listed in Table 1) and the separation and determination procedure was applied. For comparison, interfering study was also investigated in the flow manifold without a column. As can be seen in Table 1, application of the separation procedure on algae column caused considerable increase in the acceptable excess of foreign ions to analyte in comparison with direct CL determination. The most considerable effect was observed for Mn(II) and Cu(II) ions, as their acceptable excess after the separation step was 40,000 and 10,000 times higher compared to direct measurements, respectively. The Co(II)/Pt(IV) and Cr(III)/Pt(IV) concentration ratios increased by a factor of 500, whereas the Pb(II)/Pt(IV) concentration ratio by a factor of 250. The ions of Pt(II) and Rh(III) affect the determination of Pt(IV), if their concentrations are more than 2500 times that of analyte, whereas Pd(II) ions cause interference when Pd(II)/Pt(IV) concentration ratio is above 5000. It is worth mentioning that developed lucigenin-based CL method of Pt(IV) determination is considerably less susceptible to interferences caused by the presence of other metal ions in comparison with luminol-based CL method [20].

3.3. *Analytical characteristic*

The analytical characteristic of the developed FI-CL method of Pt(IV) determination after preconcentration of the analyte and matrix separation on algae column is presented in Table 2. The parameters obtained in the flow system without a column are showed for comparison. After the biosorption step, the sensitivity of CL measurements, expressed as a slope of the calibration graph, increased almost 4-fold and the limit of detection of Pt(IV) decreased 7-fold (to 0.1 ng mL^{-1}) compared to direct measurements. The calibration graph obtained for standard solutions of Pt submitted to biosorption procedure on algae column was linear in the concentration range 0.5–12 ng mL^{-1}. Reproducibility of the CL methods without and with separation step on algae column, expressed as a relative standard deviation of the slopes of the calibration graphs registered in following 4 days, is equal to 5.4% and 2.5%, respectively.

Table 2
Analytical characteristic of the FI-CL methods of determination of Pt(IV) (measurement conditions: $8.0\cdot10^{-4}$ mol L^{-1} lucigenin, 1.5 mol L^{-1} NaOH, 0.75 mol L^{-1} NaCl).

	Without algae column	With algae column
Determination range [ng mL^{-1}]	2–60	0.5–12
Slope of the calibration graph ± S.D. (n = 4)	5.6 ± 0.3	20.3 ± 0.5
Limit of detection [ng mL^{-1}]	0.7	0.1
Precision as RSD [%]	2.0[a]	2.9[b]
Sample frequency [h^{-1}]	63	4

[a] For 5.0 ng mL^{-1} of Pt(IV) (n = 10).
[b] For 1.0 ng mL^{-1} of Pt(IV) (n = 6).

Table 3
Results of determination of platinum by the FI-CL method in environmental samples after separation/preconcentration of the analyte on algae column.

Sample	Concentration of Pt(IV) [ng mL^{-1}]		Recovery of Pt ± S.D. [%] (n = 6)
	Added	Found ± S.D. (n = 6)	
Supraśl River	1.0	1.02 ± 0.01	102 ± 1
	2.0	2.08 ± 0.07	104 ± 4
Biała River	1.0	0.98 ± 0.03	98 ± 3
	2.0	1.99 ± 0.05	100 ± 2
	5.0	4.9 ± 0.1	98 ± 3
BCR-723[a]	–	76.3 ± 10.6 ng g^{-1}	93.8 ± 13.1[b]
Road dust 2009[a]	–	351.8 ± 54.6 ng g^{-1}	–

[a] After removal of matrix on RP-18 column.
[b] Against the reference value (81.3 ± 3.3 ng g^{-1}).

The accuracy of the developed FI-CL method was confirmed by analysis of the certified reference material BCR-723. In order to remove some undestroyed components of organic matrix, samples of dust extracts were passed through a column containing LiChroprep RP-18 sorbent before analysis. It was found that platinum ions were not retained on this sorbent, while compounds, which interfere with chemiluminescent determination of analyte were efficiently adsorbed. The Pt concentration in CRM determined by the modified method, including sample pre-cleaning step on RP-18 column followed by sorption of the analyte on algae column, was in close agreement with the reference value (Table 3).

3.4. *Determination of platinum in environmental samples*

The described above modified procedure of platinum determination was applied to the analysis of road dust collected in 2009 from the intersection with traffic lights (high traffic density) in Białystok, Poland. The determined content of Pt in dust samples was 351.8 ± 54.6 ng g^{-1} (Table 3) and was higher than content of this metal in road dust collected in the same city nine and six years ago (99.5 ± 19.6 and 265.6 ± 38.3 ng g^{-1}, respectively) [26]. Comparable concentrations of Pt were determined in road dust samples taken from the London Orbital motorway (in 1999) [34], roads in Perth (Western Australia, in 1999–2001) [35] and Sheffield (UK, in 2000–2006) [36] with maximum values of 356, 420 and 408 ng g^{-1}, respectively. There are a number of parameters which influence the content of platinum group metals on the roads. It was proved that highest platinum concentrations in road dust are found in urban areas of high traffic density, on roads in valley bottoms and at roundabouts or traffic lights with stop–start driving conditions [37].

For samples of river water, due to simpler composition of matrix, the separation step on RP-18 column can be omitted. The recoveries for the samples spiked with different concentrations of Pt(IV) were in the range 98–104% (Table 3).

4. Conclusions

A novel FI-CL method of Pt(IV) determination, based on the quenching effect of the analyte on chemiluminescence generated by lucigenin in alkaline solution, has been evaluated. To the best of our knowledge, it is the fist time when chemiluminescence of lucigenin–NaOH system was used for the determination of platinum. The application of a column filled with an algae *C. vulgaris* immobilized on Cellex-T resin significantly improved the selectivity of the method and the limit of detection (LOD = 0.1 ng mL^{-1} Pt(IV)) in comparison to direct determination. The lucigenin-based CL method is characterized by considerably better selectivity than luminol-based CL method [20] and can be applied for the determination of platinum in river water samples and, after sample pre-cleaning step, in road dust samples. It is worth to stress, that the majority of analytical methods of determination of metal ions based on chemiluminescence phenomenon, have been evaluated for analysis of samples containing relative simple matrices, such as waters. In our work the usability of the developed method for determination of platinum in complex environmental samples was confirmed by analysis of the certified reference material of tunnel dust (BCR-723). Considering the environmental aspect of our studies the significant increase of platinum content in road dust collected in Białystok (from 99.5 ± 19.6 to 351.8 ± 54.6 ng g^{-1}) was observed during the last decade.

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