The HR-CS-GF-AAS determination and preconcentration of palladium in contaminated urban areas, especially in lichens ☆

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ABSTRACT

The increasing content of platinum group metal particles emitted into the environment by car traffic is gradually attracting the attention of the scientific community. However, the methods for the determination of platinum group metals in environmental matrices are either costly or suffer from low sensitivity. To facilitate the use of less sensitive, but significantly cheaper, devices, the preconcentration of platinum group metals is employed. For platinum, a multitude of preconcentration approaches have been published. On the contrary, the preconcentration approaches for palladium are still rare. In this work, the development, optimization, and testing of a new approach is described; it is based on a preconcentration of palladium on octadecyl modified silica gel together with the complexing agent dimethylglyoxime, and it is then analyzed with the high-resolution continuum-source atomic absorption spectrometry. For comparison, a newly developed sorbent, QuadraSil™ TA, with a high affinity for platinum group metals was also tested. The preconcentraiton approach was tested on the lichen *Hypogymnia physodes,* which served as a bioindicator of palladium emissions. The case study site was a mid-sized city in central Europe: Brno, Czech Republic. The dry "bag" monitoring technique was used to collect the palladium near roads with a large span of traffic density. The developed analytical approach confirmed an increasing concentration of palladium with increasing exposure time and intensity of the traffic. Consequently, a simple relationship between the amount of bioaccumulated palladium and traffic density was established.

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1. Introduction

Increasing concentrations of platinum group metals (PGMs), mainly platinum (Pt) and palladium (Pd), have been observed throughout the environment over the last twenty years. Naturally, Pd occurs together with other platinum metals in very low concentrations (0.015 mg kg^{-1} Pd and 0.010 mg kg^{-1} of platinum) (Reith, Campbell, Ball, Pring and Southam, 2014). Anthropogenic Pd have been reported in various environmental compartments such as airborne dust, aerosols, road and tunnel dust, soil, aquatic environments, sediments, plants, body fluids, and animal tissues (Ravindra, Bencs and Van Grieken, 2004). The sources of Pd include dentistry, the chemical industry, electronics, fuel cells, jewelry, and surgical tools (Garoufis, Hadjikakou and Hadjiliadis, 2009), with the largest source being the automotive industry in which Pd is one of the main components of road vehicle catalysts (Melber, Keller and Mangelsdorf, 2002); (Twigg, 2011). Together, Pt and Rh form an active catalytic layer that catalyzes the conversion reactions of toxic exhaust gases coming from the fuel combustion process into less toxic products. Globally, gasoline cars represent more than 85% of the total use of Pd in autocatalysis and its use is increasing ("Johnson Matthey", 2019); (Rosner, Coenen-Stass and König, 1991). The PGMs or their oxides are released from the catalysts in the form of elementary nanoparticles (Komendová, Žídek, Berka, Jemelková, Řezáčová, Conte and Kučerík, 2019) with a size below 0.3 μm; they are released into the environmental compartments nearby roads with high traffic due to the high temperature of flue gas, mechanical abrasion, the influence of a catalyst's poisons, the age of the catalyzer, and the riding style of car (Prichard and Fisher, 2012); (Goncalves, Domínguez and Alvarado, 2008). As a result, the most effected sites are urban agglomerations that have the highest car traffic (Komendova and Jezek, 2018); (Kosarova, Komendova and Skeril, 2015). The PGMs are already considered to be a global environmental pollution due to their easy transport upon

solubilization (Rauch, Hemond, Barbante, Owari, Morrison, Peucker-Ehrenbrink and Wass, 2005); (Ek, Morrison and Rauch, 2004). The solubilization is influenced by air turbulence caused by passing vehicles or from strong winds, as well as by other climatic conditions, the morphology of the local terrain, and the presence of barriers like higher plants (Goncalves, Domínguez and Alvarado, 2008). The occurrence of PGMs depends not only on the particular concentration but also on the form of the occurrence, the bioavailability, the solubility, and the mobility of metals. The concentration of platinum group metals released from automotive catalysts are in the magnitude of ng.km^{-1}, pg. m^{-3} in the air, road dust, soil, vegetation and in the animal body in ng.g^{-1} (Melber, Keller and Mangelsdorf, 2002), and the concentrations are steadily increasing (Ravindra, Bencs and Van Grieken, 2004). Unlike other metals, the toxicological information about Pd is not yet clear. Palladium and its compounds may cause medical complications such as allergic reactions, asthma, nausea, hair loss, skin and eye irritation, or other autoimmune disorders. Overall, clinical findings are not yet significant (Kielhorn, Melber, Keller and Mangelsdorf, 2002); (Faurschou, 2011).

An important group of monitored contaminated environmental components are plants. Both passive biomonitoring (e.g. grass or tree bark in the immediate vicinity of transport roads) and active biomonitoring (e.g. moss or lichen) are used to monitor the amount of PGMs. Pd is the most soluble of the PGMs, therefore it is also very mobile and has the greatest potential to be absorbed into living organisms. In plants, the largest amount of Pd was found in the root system. Palladium is transformed into biological materials through roots by binding to a sulfur-rich low-molecular substance (Wiseman and Zereini, 2009).

Biomonitoring is frequently used to determine the possibility of toxic metals entering biotic material. The most common bioindicators for the determination of environmental pollution by heavy metals are mosses, lichens (Pino, Alimonti, Conti and Bocca, 2010), ferns, grasses, tree bark, and needles (Szczepaniak and Biziuk, 2003); (Aničić, Tomašević, Tasić, Rajšić, Popović, Frontasyeva, Lierhagen and Steinnes, 2009).

Due to the relatively low concentration of PGMs in environmental matrices, their analysis requires either the use of costly techniques such as ICP-MS, or of the technique sample preconcentration, which enables the use of less expensive techniques such as AAS with flame atomization or atomization in a graphite cuvette. The next benefit of preconcentration is the separation of the matrix, which could interfere with the analyte detection. Up to now, the preconcentration has widely been used in the analysis of PGMs in environmental samples such as natural and waste water, soil, dust, atmospheric fallout, biological materials of plant and animal origin, and food. However, the preconcentration methods were developed mainly for platinum, and palladium was rather neglected.

For the separation of palladium, the most commonly used solid sorbents are modified polymer Amberlite resin (Kimuro, Gandhi, Kunda, Hamada and Yamada, 2017), polyurethane foam (Moawed, 2006), activated carbon (Sharifirad, Soleimani and Ashtiani, 2012), modified silica gel C18 (Komendova-Vlasankova and Sommer, 2002); (Tokalıoğlu, Oymak and Kartal, 2004); (Komendova, Nevrla, Kuta and Sommer, 2016) and a variety of newly developed sorbents, e.g. ion-imprinted polymer nanoparticles (Ghorbani-Kalhor, Behbahani and Abolhasani, 2015), magnetic metal-organic framework (MOF) (Bagheri, Taghizadeh, Behbahani, Akbar Asgharinezhad, Salarian, Dehghani, Ebrahimzadeh and Amini, 2012), nanoporous silica MCM-41 (Behbahani, Najafi, Amini, Sadeghi, Bagheri and Hassanlou, 2014a) and polypropylene amine dendrimers (POPAM)-grafted

multi-wallet carbon nanotubes (MWCNTs) (Behbahani, Gorji, Mahyari, Salarian, Bagheri and Shaabani, 2014b).

The aim of this work was 1) to develop a new preconcentration method for the determination of palladium in lichens, based on a C18 silica gel modified with dimethylglyoxime and including experimental conditions such as a selection of appropriate sorbents, solvents, and eluents with respect to the method of the final analysis, 2) to validate the method and compare it with selective sorption sorbent QuadraSil™ TA bound triamine (Nakajima, Ohno, Chikama, Seki and Oguma, 2009), 3) to use the newly developed approach to assess the actual contamination of air by palladium in a mid-sized city of central Europe (Brno, Czech Republic).

2. Materials and methods

2.1. Chemicals, reagents, sorbents, and reference material

For the optimization conditions of the AAS and preconcentration method was used certified reference material of calibration standard solution ASTASOL ® with concentration of Pd 1 ± 0.002 g l^{-1} in 5% HCl, Fe standard solution with 1 ± 0.002 g l^{-1} in 5% HCl and mixture ASTASOL-Mix ® consisted of Cd(II), Co(II), Cu(II), Cr(III), Mn(II), Ni(II), Pb(II), V(V), Zn(II) with concentration 100.0 ± 0.5 mg.L^{-1} in 5% HNO$_3$, all from Analytika Ltd., Czech Republic (http://www.analytika.net).

Dimethylglyoxime (diacetyldioxime) was purchased from Sigma-Aldrich (https://www.sigmaaldrich.com) and all used chemicals were of analytical reagent grade.

500 mg of silica gel C18 Bond Elut sorbent (Agilent Technologies) with average particle size 44−60 μm, specific surface area 460−520 m^2. g^{-1}and average pore diameter 60−87 Å were placed in 3 mL cartridges.

The 250 mg of selective sorbent QuadraSil™ Triamine TA (Sigma-Aldrich), with average particle size 20−100 μm, was filled into new empty 3 mL Bond Elut column Agilent Technologies (https://www.agilent.com) equipped with bottom and top frits.

The SILICA-cart column consists of a filled 1 mL polypropylene cartridge (Tatren PD 140) packed with 60 μm spherical silica TES-SEK (http://www.tessek.com) Separon SGX sorbent.

The Standard Reference Material of tunnel dust BCR-723 (JCR Joint Research Centre) with determined platinum metal content (Sutherland, 2007) was used to verify the entire analysis procedure: the sample decomposition, the preconcentration technique, and the final Pd determination by HR−CS−GF-AAS. Certified Pd concentration in BCR-723 was declared in the ratio 6.1 ± 2.5 ng g^{-1}. The measured values 5.770 ± 2.022 ng g^{-1} were in good agreement with the certified Pd content.

2.2. Lichen samples, sampling, and pre-treatment

In this work, the applied form of active biomonitoring was called dry "bag" monitoring, a technique that uses lichen (*Hypogymnia physodes*) as a bioindicator. Lichens are poikilohydric organisms that are able to withstand harsh environmental conditions and stress factors. They have root systems that breathe through their entire body surface, allowing for a large degree of absorption of hazardous elements (Pino, Alimonti, Conti and Bocca, 2010); (Huang, Xiang, Wang, RenJohnsonDavid, and Xu, 2019); (Kłos, Ziembik, Rajfur, Dołhańczuk-Śródka, Bochenek, Bjerke, Tømmervik, Zagajewski, Ziółkowski, Jerz, Zielińska, Krems, Godyń, Marciniak and Świsłowski, 2018); (Hoffman, Rattner, Burton, Jr. and Cairns, Jr., 2003). Most commonly, this method is used to capture dust and aerosols as well as to deposit metals or other pollutants in urban and industrial areas (Conti and Cecchetti,

2001); (Aničić, Tomašević, Tasić, Rajšić, Popović, Frontasyeva, Lierhagen and Steinnes, 2009).

Hypogymnia physodes was sampled from the bark of the tree *Pices abies* from the protected nature area Beskydy. The nearest third-class road is more than 5 km away. There was no inhabited area, roads or industry surrounding the sampling site. The Pd content in these samples was below the limit of detection. These organisms were then placed in mesh polyethylene bags (0.5 cm mesh size) and attached to road barriers beside nine roads with heavy traffic. The sampler consisted of three parts, the first of which was collected and analyzed after 90 days, the second part after 120 days, and the third after 150 days. These bags were located at different traffic-busy roads in the city of Brno. The sampling site locations for the placement of the "bags" were selected in consideration of the frequency of car traffic. These sites were all located in the city of Brno, Czech Republic. Details of the sampling sites are reported in Table 1.

Samplers were fixed using plastic tape to the road barrier. After exposure, the bags were dried at room temperature. Before the decomposition process, the content of the bag was deprived of the protective breathable nets, and the contents were quantitatively transferred into glass flasks. The decomposition of the lichen was performed by boiling it in *aqua regia*. The portion of the lichen sample (5–10 g) was quantitatively transferred into a round bottom flask and wetted with 15 mL of HNO3. The sample was left in a nitric acid until the next day, at which point 45 mL of HCl was added; the volume of the flask was then fed through a heating mantle to reach boiling temperature. After 2 h at reflux, 25 mL of water was added to the mixture, and the whole volume of the flask was boiled for 15 min. Followed by filtration, the mixture evaporated on a hot plate and the quantitative conversion decomposed the sample into a 50 mL volumetric flask.

2.3. Instrumentation

Optimization of the method and analysis of lichen samples was performed on the atomic absorption spectrometer contrAA® 800 D from Analytik Jena (Germany) with a continuous radiation source and high-resolution monochromator, with uses an Xe lamp across the entire spectrum with the possibility to use any atomic absorption line or molecular band for the determination of the elements. The spectrometer simultaneously solves background correction and stability by using Iterative Background Correction (IBC). The optical system consists of a high-resolution Echelle monochromator and a sensitive CCD detector. For the determination of Pd, the graphite cuvette atomization was chosen to provide lower detection limits.

For the determination of Pd, was selected primary line 244.791 nm with 100% relative sensitivity. Optimal measurement parameters of the temperature program were: drying 1 at 80 °C, drying 2 at 90 °C, drying 3 at 110 °C, pyrolysis 1 at 350 °C, pyrolysis 2 at 950 °C, atomization at 2200 °C, and cleaning at 2450 °C. Under these optimal conditions, the Limit of Detection (LOD) was 1.110 $\mu g.L^{-1}$ and the Limit of Quantification (LOQ) was 3.329 $\mu g\, l^{-1}$. The instrumental LOD and LOQ were calculated on the basis of the 3sigma definition (Shrivastava and Gupta, 2011) and were evaluated from 10 measurements of the blank solutions:

$$LOD/LOQ \ = \ FxSD/b$$

F: factor 3 or 10 for LOD and LOQ, respectively,
SD: standard deviation of the blank
b: slope of the regression line

All results obtained in this research are the average of three separate independent determinations and were each measured five times on the atomic absorption spectrometer.

For the preconcentration of Pd, the sorption apparatus was used, consisting of a pump 82.4 PCD with four cassettes ISMATEC ISO649 through which the solutions using silicone tubing were sorbed on the cartridges with the selected sorbent. These cartridges were connected to the vacuum system, J. T. Baker, SPE-12G.

2.4. Preconcentration procedures

2.4.1. Preconcentration on silica gel with dimethylglyoxime

Octadecyl modified silica gel C18 is the most widely used nonpolar sorbent. The sorption of metal ions requires modifying its surface by adsorption of an amphiphilic chelating agent which can easily interact with metal ions giving rise to the organo-metal complex. The chelating agent used in this work was dimethylglyoxime (DMG) which is among the most selective agents for transition metals such as Ni(II) and Pd(II). In the PGMs, only Pd in the presence of HCl is precipitated with DMG, giving a yellow Pd:DMG 1:2 complex. The complex is insoluble in water and dissolves in the presence of ammonia. This complex is formed even at a small amount of mineral acid and is the only form in which DMG stable precipitates in the medium with pH 1. X-ray analysis revealed a square-planar structure wherein two ligands are connected by the strong intramolecular hydrogen bond, stabilizings

Table 1
Characterization of sample collection places.

Sample number	Places of sampling	Traffic intensity (thousands of cars/24 h)[a]	GPS
1	D2 motorway	50	49°9′17.185″N, 16°37′47.436″E
2	Sportovní Street	45	49°13′1.656″N, 16°36′15.039″E
3	Tomkovo Square	40	49°12′47.963″N, 16°38′16.412″E
4	Hradecká Street [b]	35	49°13′47.300″N, 16°34′48.300″E
5	Otakara Ševcíka Street	35	49°11′27.825″N, 16°38′54.364″E
6	Hradecká Street [c]	25	49°13′47.759″N, 16°34′47.560″E
7	Koliště Street	20	49°11′35.136″N, 16°36′57.035″E
8	Poříčí Street	20	49°11′11.716″N, 16°35′44.651″E
9	Kotlářská Street	15	49°12′24.625″N, 16°36′3.952″E
10	Traffic free location	0	49°22′43.342″N, 16°66′75.894″E

[a] ("Road and Motorway Directorate of the Czech Republic. Traffic census.", n. d.).
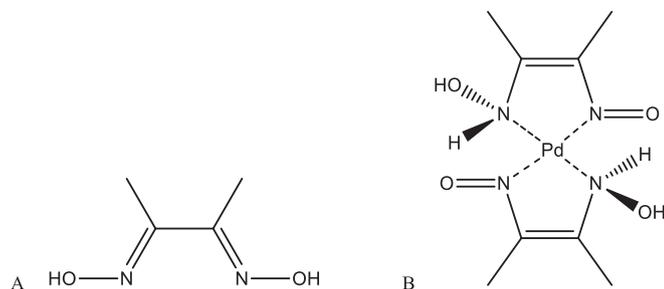[b] Downtown.
[c] From city.

Fig. 1. A dimethylglyoxime, B Bis(dimethylglyoxime)palladium.

the complex in a ratio of 1:2 metal:ligand (Fig. 1) (Panja, Bala, Pal and Ghosh, 1991). In addition, in the solid state, the complexes with nickel, palladium, platinum, and gold appeared to be stabilized by metal-metal interactions, with copper being the most complex stabilization by metal-oxygen bonds.

The separation of Pd based on the formation of the Pd(DMG)$_2$ complex was used in this work. The method was inspired by the results of (Tokalıoğlu, Oymak and Kartal, 2004) who used sorption dimethylglyoxime on bare silica sorbent, with only 40.80% sorption efficiency at pH 1.0. The available literature data sources showed that successful sorption should be carried out at pH = 4.0. However, under these conditions, in our work, we achieved the efficiency of only 65.40%. Therefore, instead of bare silica, silica gel modified with octadecyl C18 was chosen for this work because it was assumed to have a strong affinity to Pd(DMG)$_2$.

2.4.2. Preconcentration on QuadraSil™ TA sorbent

The newly developed approach based on the Pd(DMG)$_2$ complex was compared with the commercially available sorbent QuadraSil™, which is a registered trademark of the company Johnsons & Matthey. Chemically, it is a modified silica that, due to its steric properties, is highly selective for the reuptake of metal ions. QuadraSil™ is very robust, it is chemically, mechanically, and thermally resistant, spherically shaped and poorly swellable. Commonly, the particles have 54 μm. In this work, the QuadraSil™ TA triamine (Fig. 2) was used and the parameters of the preparation procedure were obtained from an article (Nakajima, Ohno, Chikama, Seki and Oguma, 2009).

3. Results and discussion

3.1. Development preconcentration method and testing of modified silica gel C18

The optimization of the parameters under conditions described in the chapter Materials and Methods for silica gel modified octadecyl chain showed a $100.30 \pm 1.5\%$ recovery of the Pd complex with dimethylglyoxime from the sorbed volume in the range of 10−1000 mL. As the final volume was 10 mL, the pre-concentration factor thus reaches 100. In addition, the factor can even be increased by evaporating the resulting eluate to lower volumes.

The mechanisms of sorption can be explained as follows: the free hydroxyl groups occurring on C18 are dissociated, hydrogen cation and a molecule complex of Pd(DMG)$_2$ are more easily
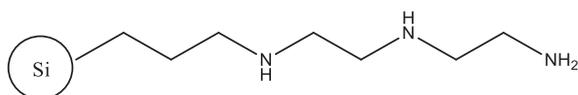
bonded. To ensure the formation of the Pd(DMG)$_2$ complex, a selective agent must always be present in excess in comparison to the Pd. In this work, it was found that the best sorption results were achieved when the Pd(DMG)$_2$ complex was already formed in the solution before it was adsorbed to the distilled water wetted sorbent. On the contrary, when the sorbent was conditioned by the DMG, and the pure Pd solution was sorbed, the sorption was not quantitative. This may be due to an insufficient amount of the sorbed agent or a flow rate that was too high during sorption.

During optimization, the elution procedure was tested following eight eluent solutions: 1 mol.L^{-1} HCl in absolute ethanol, absolute ethanol, 1 mol.L^{-1} HCl in ethanol (denatured), ethanol (denatured), 1 mol.L^{-1} HCl in acetone, acetone, 1 mol.L^{-1} HCl in acetonitrile and acetonitrile. The best results were achieved using 1 mol.L^{-1} HCl in absolute ethanol. When studying the effect of acidity on the sorption process, it was found that 0.1 mol.L^{-1} HCl is the optimal medium concentration.

For the assessment of interferences of the sorption, the influence of ions and metals was tested, the presence of which can be expected in a matrix of real samples or which can be sorbed on the lichen together with Pd from polluted environmental matrices. Solutions containing anions (NO$_3^-$, SO$_4^{2-}$), common cations (Al^{3+}, Ca^{2+}, NH$_4^+$, Mg^{2+}, K$^+$, Na$^+$, Mn^{2+}), and heavy metal cations (Cd(II), Co(II), Cu(II), Cr(III), Mn(II), Ni(II), Pb(II), V(V), Zn(II), Fe(II)) were prepared. The influence was tested for 100- and 1000-times excess of the concentration of these ions in comparison with Pd. It was found that the 100-fold higher concentration of anions containing sulfates and nitrates had no influence on the sorption of Pd. However, the same number of common cations and heavy metal cations caused a slightly positive interference, but the average value never exceeded 110% of the limit of the Pd sorption efficiency. In contrast, a 1000 times higher concentration of anions and cations caused slightly negative interferences, but the mean values did not fall below 90% of the efficiency of sorption. Therefore, the results showed a good reliability of sorption of Pd(DMG)$_2$ complex on C18 modified silica.

After optimization of the sorption process was completed, the sorption parameters in which 100% recovery for Pd was achieved were found to be: a flow rate of sorption of 1 mL min^{-1}, a rinsing sorbent 10 mL of distilled water, the sorption of the Pd solution with the addition of agents DMG at the concentration of 3.44 mmol.L^{-1} in 0.1 mol.L^{-1} HCl, rinsing 5 mL of distilled water prior to the elution, and finally an elution using 10 mL of 1 mol.L^{-1} HCl in absolute ethanol. The eluate was further processed as follows: it was transferred to a Teflon™ dish, evaporated to near dryness on a hot plate, and then the residue was dissolved in 0.1 mol.L^{-1} HCl, quantitatively transferred to a 10 mL volumetric flask, and filled to the mark by using 0.1 mol.L^{-1} HCl.

3.2. Comparison of developed method with preconcentration on QuadraSil™ TA

The preconcentration on QuadraSil™ TA was performed according to the article by (Nakajima, Ohno, Chikama, Seki and Oguma, 2009). The authors used 100 mg of sorbent in an on-line arrangement to the ICP-AES preconcentration method. Therefore, the method had to be optimized for the conditions used in this work and the efficiency of Pd sorption on the amount of QuadraSil™ TA was tested. It was found that the highest efficiency of Pd sorption $98.5 \pm 1.5\%$ was achieved for 250 mg of sorbent, while 100 mg achieved only $92.7 \pm 1.7\%$.

The mechanism of the sorption can be explained as follows: the amine functional group of diethylenetriamine shows a high selectivity for Pd in the presence of hydrochloric acid. The low pH maintains the Pd in solution in the form of chlorides or as a

Fig. 2. QuadraSil™ TA triamine.

complex which interacts with the amine.

In this work, the effect of HCl concentration on the efficiency of Pd sorption was assessed. The highest sorption efficiency was observed at 0.1 mol.L^{-1} HCl.

For the elution of Pd from the QuadraSil™ TA sorbent, the appropriate eluent is thiourea (Nakajima, Ohno, Chikama, Seki and Oguma, 2009), but its optimum concentration had to be tested. The elution was performed at five different thiourea concentrations. The best results were obtained for 0.05 mol.L^{-1} thiourea as an eluent.

For the assessment of interfering effects on the sorption efficiency by ions and metals, inorganic cations and anions were used in this work, which presumably occur in environmental samples. Thus, mixed solutions of anions, cations, and metals were prepared and tested. The results suggested that 100- and 1000-times excess of cations Al^{3+}, Ca^{2+}, NH$_4^+$, Mg^{2+}, K$^+$, Na$^+$ and Mn^{2+} have almost no effect on the Pd sorption. However, the same amount of anions such as SO$_4^{2-}$ and NO$_3^-$ have 100 times higher content of metal cations such as Cd(II), Co(II), Cu(II), Cr(III), Mn(II), Ni(II), Pb(II), V(V), Zn(II) and Fe(II) and caused a significantly negative interference. In other words, it appeared that the QuadraSil™ TA sorbent is also an effective sorbent for other metal ions.

Therefore, the sorbent QuadraSil™ TA is not applicable for the preconcentration of Pd in the case of environmental matrices containing heavy metal ions and some anions because they violate the selectivity of the sorbent to Pd. For this reason, all the analyses of real samples were carried out by sorption on C18 silica gel (see next chapter) with a higher sorption efficiency and lower influences of accompanying ions.

3.3. The determination of palladium in lichens exposed to air pollution in a mid-sized city of central Europe

As aforementioned, the method based on the formation of Pd(DMG)$_2$ complex sorbed on C18 modifed silica was used for the assessment of the Pd contamination in Brno, which is representative of a mid-sized city with moderate traffic in central Europe. In total, Pd was determined in 30 "bag" samples distributed all around the city. All samples were pre-treated using the above-described method and Pd was determined by using atomic absorption spectrometry.

All data measured by analyzing the Pd concentration in the lichen *Hypogymnia physodes* using this technique are reported in Table 2. For a better illustration, the data are also plotted in Fig. 3, where the density of the car traffic in the measured sites is also displayed.

The results confirmed the assumption that the amount of Pd will increase with the increasing sample exposure time in all localities. In addition, Fig. 3 indicates that the relative increase in Pd per traffic
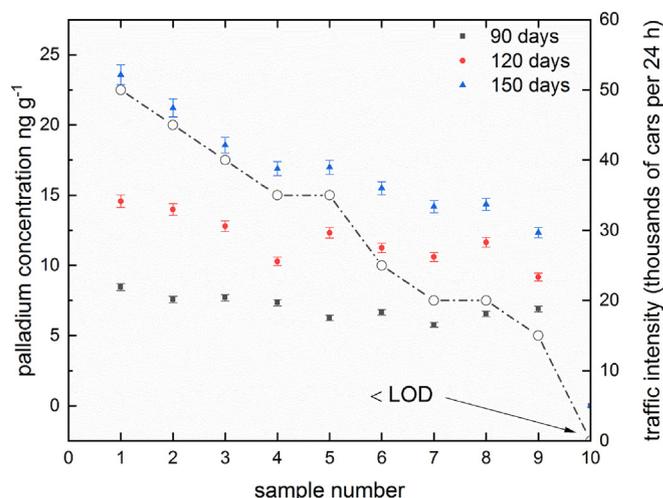
Table 2
Palladium content in lichen (ng.g^{-1}).

Sample	Exposure		
	90 days	120 days	150 days
1	8.456	14.57	23.58
2	7.561	13.99	21.22
3	7.689	12.80	18.56
4	7.337	10.29	16.89
5	6.258	12.33	16.99
6	6.654	11.25	15.50
7	5.775	10.60	14.19
8	6.550	11.64	14.35
9	6.890	9.160	12.34
10	< LOD	< LOD	< LOD

Fig. 3. Graphical representation of deposited Pd on lichens depending on exposure time and traffic intensity.

density increases with the length of exposition, which means that after 150 days the saturation of the lichen sorption capacity was still not reached. This is supported by Fig. 4, which reports the slopes of dependences of Pd concentration on exposition time for each sampling site with specific traffic car density. Accordingly, Fig. 4 represents a simple tool for prediction of Pd contamination in mid-sized cities. It is still questionable whether or not the data can be used in the prediction of Pd concentration in larger cities where the car traffic exceeds hundreds of thousands of cars per day.

Lichens are considered to be very good bioindicators of metal pollution. However, the outliers in Fig. 4 may be caused by the metabolic processes occurring in the lichen (Hoffman, Rattner, Burton, Jr. and Cairns, Jr., 2003). In addition, the lichen's condition depends largely on weather conditions and overall environmental pollution. For longer monitoring, the bag technology is not conducive to the dangerous transition of the lichen to the latency phase under unsuitable conditions. This can occur in the case of insufficient moisture and may also be due to excessive contamination of the surface of the lichen insole. The cause of this is mainly airborne dust, black carbon, exhaust emissions, and metals (Zhao,
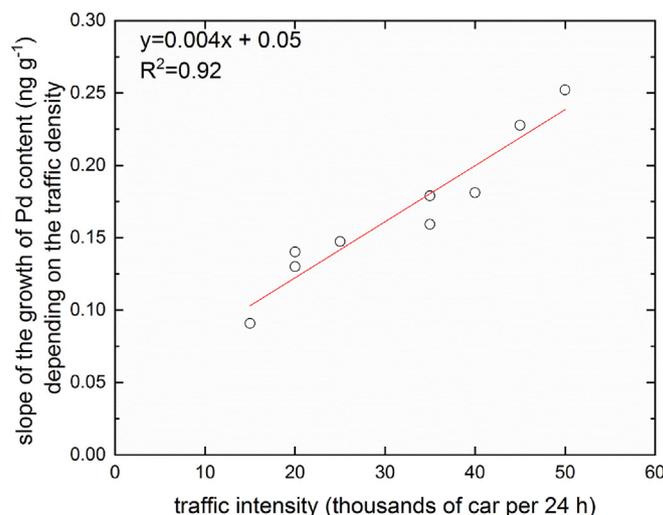

Fig. 4. Model curve for prediction of environmental load by palladium in dependence on density of automobile traffic.

Zhang, Jia, Liu, Chen, Li, Liu, Wu, Zhao and Liu, 2019). In addition, *Hypogymnia physodes* is the most widespread species of lichen in a temperate climate belt. It is one of the lichen species that is considered to be a nitrophobic organism. The nitrophobic species do not occur in nitrogen-enriched environments and avoid eutrophic sites. This fact may be another essential reason for the reduction of the metabolic functions of the exposed lichens because the exhaust gases to which the lichen became exposed to contain nitrogen oxides and nitrogen gas (Manninen, 2018).

4. Conclusions

A new preconcentration technique was developed for the determination of ultra-trace amounts of palladium in lichens. This preconcentration method has several advantages such as the height specificity and selectivity for Pd(II) sorption as a complex with dimethylglyoxime with a very high sorption efficiency (100%), a very low interference of matrix effect, a more affordable C18 silica gel sorbent, and the consumption of chemicals and organic solvents. In addition, the preconcentration efficacy of this method is good enough for the subsequent determination of Pd by using AAS or possibly other techniques with similar detection limits. Compared to commercially available sorbent QuadraSil™ TA, this approach appeared to be less prone to interferences with heavy metal ions and anions. For these reasons, the developed approach was used for determining Pd in lichens used as bioindicators of pollution caused by car traffic, which, as expected, increased with increasing exposition time and car traffic density.

The toxicity of Pd compounds has already been proven, but the environmental concentrations are still too low to draw conclusions on their direct effect on the health of humans living in areas with a high density of car traffic. For this reason, the amount of Pd and PGMs in various environmental objects should be continuously monitored. As a result of ever-increasing automotive traffic and exhaust emission requirements, the use of platinum-based catalysts will continue to be promoted and expanded. In the future, the palladium compound will be continuously emitted and thus endanger human health.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.113468.

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