



# The specialized twin-solution method for selective Pd(II) ions determination and methyl orange removal

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## ABSTRACT

The proper determination of Pd(II) ions in the presence of Pt(IV) ions in a waste solution is an intricate analytical issue. Having the knowledge about waste composition, we are able to properly design processes and their selective separation and recovery. Other important aspect is related to the dyes removal coming from textile industry, which is still not resolved. To solve these issues, in this work, we propose the twin solution, which describes a specialized method allowing for both selective Pd(II) ions determination and methyl orange removal. These processes take place in the range of tautomeric equilibrium of methyl orange (pH = 3 – 5). In order to follow the process of cyclopalladated compounds formation, UV-Vis spectra were registered at different conditions, i.e. pH, temperature as well as in the presence of different anions: Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> and cations: Na<sup>+</sup>, K<sup>+</sup>, Pt<sup>4+</sup>, Pt<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>. The developed method of Pd(II) ions determination is distinguished by high sensitivity and selectivity, even in the presence of Pt(IV) ions. Moreover, the palladium content can be determined using UV-Vis spectroscopy at two wavelengths, i.e. at 560 and 702 nm at 50°C. This extends the possibility of metal detection in the presence of cations having spectra in similar wavelength ranges. It is also concluded, that the process of removal of methyl orange is possible only in water: obtained product is unstable and forms an easy-filtratable blue/purple coloured precipitate.

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## 1. Introduction

### 1.1. Palladium(II) ions determination

The growing demands for precious metals and shrinking natural resources make the process of obtaining them from secondary sources an important economy aspect [1]. Especially metals from the platinum group, including platinum and palladium due to their broad use in catalysis are noteworthy. The recovery processes of these transition metals are necessarily accompanied by the need of the correct determination of the amount of elements presented in waste. Thus, one of the most interesting topics is a selective determination of trace amount of palladium(II) ions, especially in the presence of platinum (IV) as the accompanied ingredient. Generally, difficulties result from the nature of both metals which are related to their chemical properties. There are different techniques that are applied for their determination, and they were described

in details by Balcerzak [2,3]. Mostly, for palladium ions determination, spectrophotometry is applied due to its simplicity, low operating costs, accessibility and rapidity [4]. Using organic reagents which have been well described in the literature [5], it is possible a quantitative and/or qualitative Pd(II) ions determination. However, described procedures have some limitations, which are shortly mentioned here. Mostly, the literature described procedures including the extraction process as an intermediated stage during Pd(II) ions determination. The process of extraction was carried out in organic medium like o-dichlorobenzene [5], chloroform [6–8], dibenzoylmethane [9], n-butanol [10], benzene [11], carbon tetrachloride [12], etc. Thus, it forces the process to be multi-stage, in practice more expensive, and sometimes also time consuming. There are also some limitations related to pH of the solution. However, in the literature reagents can be found that can be applied for a broader range of pH (see Table 1).

Later on, more technologies were developed in which water or water base solutions were applied as medium for Pd(II) ions determination [19], but still they are subjected to some typical limitations.

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**Table 1**  
Spectrophotometric methods for palladium determination at different solvents and pH.

| REAGENT   | SOLVENT                       | pH      | Molar coefficient<br>$\lambda$ ( $\epsilon$ )                    | REF  |
|---|-------------------------------|---------|--|------|
| ethyl 3-phenyl-5-isoxazolone-4-carboxylate        | water                         | 1 – 6.5 | 350 M <sup>-1</sup> cm <sup>-1</sup> (370 nm)                    | [13] |
| ethyl 3-phenyl-5-isoxazolone-4-carboxylate        | 4-methylpentan-2-ol           | 1 – 6.5 | 370 M <sup>-1</sup> cm <sup>-1</sup> (370 nm)                    | [13] |
| 2,2'-diquinolyketone 2''-pyridylhydrazone (DQPH)  | chloroform                    | 1 – 6   | 19 500 M <sup>-1</sup> cm <sup>-1</sup> (634 nm)                 | [14] |
| 2-pyridyl-2-thienyl- $\beta$ -ketoxime            | chloroform                    | 0 – 7   | 920 M <sup>-1</sup> cm <sup>-1</sup> (433 nm)                    | [15] |
| pyridine-2-aldehyde-2'-pyridylhydrazone (PAPH)    | water                         | 12      | 1 400 M <sup>-1</sup> cm <sup>-1</sup> (520 nm)                  | [16] |
| Rhodamine 6G – Br <sup>-</sup>                    | dimethylformamide             | 2.5     | 30 · 10 <sup>4</sup> M <sup>-1</sup> cm <sup>-1</sup>            | [17] |
| thio-Michler's ketone                             | Isoamylalcohol                | 3       | 16 · 10 <sup>4</sup> M <sup>-1</sup> cm <sup>-1</sup> (520 nm)   | [20] |
| 5-phenylazo-8-aminoquinoline (PAQ)                | Methyl isobutyl ketone (MIBK) | 11–12   | 7.9 · 10 <sup>4</sup> M <sup>-1</sup> cm <sup>-1</sup> (620 nm)  | [21] |
| 3-(2'-thiacolyazo)-2,6-diaminotoluene (2,6-TADAT) | perchloric acid               | 0–12    | 5.35 · 10 <sup>4</sup> M <sup>-1</sup> cm <sup>-1</sup> (590 nm) | [18] |

### 1.2. Water treatment – Dyeing removal

The issue related with water treatment has special relevance to worldwide water demand. This fact is related to the increasing world population and a rising living standard. Awareness of the public about environmental protection and caring for natural resources has forced the industry to reach for new solutions that are aimed at waste-free production or giving environmentally friendly waste. This means that almost every sector tries to improve its technologies and to implement new solutions that will allow to achieve such a goal. Here we would like to highlight one of the aspects of purifying water waste from dyes. Dyes represent one of the most problematic groups of pollutants because they are not easily degradable [22] and often toxic [23]. Despite of this, dyes are commonly used in pharmaceutical, paper and textile industry. More than 50% of the dye produced in the world is based on azo compounds, which are the most important classes of dyes. Taking into account that textile industry produces many toxic waste [22] in the form of organic pollutants containing aromatic ring [24], the problem of their removal is serious. This kind of pollutants can be removed by biological treatment, catalytic oxidation, membrane filtration, sorption process, coagulation/flocculation, and other treatment methods, which were reviewed in details by Siew-Teng Ong et al. [25]. Bacterial decolorization and degradation of azo dyes under certain environmental conditions is also possible. This biological approach is inexpensive, eco-friendly and can be applied to wide range of dyes [26]. In this context, methyl orange as one of the most popular dye, which can be removed by several techniques. Among them adsorption process is mostly applied. For example, methyl orange can be removed from water by adsorption on coffee waste modified with cationic surfactants [27], by pumpkin seed powder [28], amidoxime [29], activated carbon [30], alkali – activated polypyrrole-based graphene oxide [31] or removed using magnetic adsorbents like  $\gamma$  - Fe<sub>2</sub>O<sub>3</sub>, magnetic carbon nanotubes [32], magnetic iron oxide/carbon nanocomposites [33]. This dye can be also neutralized using photo-catalyst containing silver nanoparticles attached to the surface of amidoxime fibers, during catalytic oxidation, membrane filtration, sorption process [25]. Another method was suggested by Liu et al. [34], who proposed the degradation of methyl orange by microwave-assisted catalysis of H<sub>2</sub>O<sub>2</sub> with chromium residue. Each of the methods described above, however, has its drawbacks and is not perfect. Therefore, new solutions are constantly searched for.

### 1.3. Motivation of this paper

Taking into account the potential applications, in this paper we underlined two aspects and we define two aims. The first aim of this study was to develop an innovative spectrophotometric method allowing the qualitative and quantitative determination of Pd(II) in the presence of Pt(II) and/or Pt(IV) ions in aqueous solutions. For this purpose, the metal ions and organic compound con-

taining an azobenzene group: methyl orange (MO), were used to create complex compound with characteristic UV-Vis spectrum. Thus, we studied the behavior of methyl orange (which is easily accessible) in the presence of different metal ions like Pd(II), Pt (II), Pt(IV) and also metals cations which can be found in industrial solutions, e.g. Na(I), K(I), Co(II), Cu(II), Ni(II), Zn(II). Taking into account the optical properties of metal ions and MO, the process of forming the organometallic complex could be monitored spectrophotometrically in time.

The second aim was to develop an innovative method for methyl orange removal from the aqueous solution. During experiments, it was observed, that using only water as a solvent and suitable conditions it was possible to efficiently remove the complex formed as the result of linking of Pd(II) ions with methyl orange. Moreover, the product of the reaction is unstable and forms a coarse blue/violet coloured precipitate, which can be easily removed using e.g. filtration.

## 2. Experimental

### 2.1. Materials and methods

#### 2.1.1. Chemicals

*Methyl orange* (p.a. Avantor Performance Materials Poland S.A.). The base solution was prepared by dissolving of 0.1 g of MO in 100 mL of deionized water. Next, proper volume of base solution was diluted in buffers (pH in the range 2.87 – 7.00), see Table 2.

*Pd(II) chloride complex ions.* The proper volume of base solution of Pd(II) ions with concentration 0.093 M, performed in accordance with our previous work [35], was diluted in buffers (pH in the range 2.87 – 7.00), see Table 2.

*Pt(IV) chloride complex ions.* The proper volume of base solution of Pt(IV) with concentration 0.076 M, performed in accordance with our previous work [36], was added to the solution containing Pd(II) ions.

*Solvents.* In order to keep constant value of pH, the Britton – Robinson (B–R) buffer was used. For this purpose 100 mL of acids mixture (0.04 M solutions of H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>BO<sub>3</sub> and CH<sub>3</sub>COOH and proper volume of 0.2 M solution of NaOH (in the volume range from 17.5 mL for pH 2.87 up to 52.5 mL for pH 7), was used. All reagents were pure analytic, Avantor Performance Materials Poland S.A.

*Anions.* In experiments sodium chloride (p.a., Avantor Performance Materials Poland S.A) and chlorate (p.a., Alfa Aesar GmbH & Co KG, Germany) were studied. For this purpose a proper mass of salts were dissolved in B–R solution containing Pd(II) ions (details in Table 2).

*Cations.* The source of cations was proper chlorate salts of such metals like Na, K, Co, Cu, Ni, Zn. All salts were analytical purity and delivered from Sigma Aldrich, Germany. In experiments 0.1 M solution of salts was used. For this purpose, a proper mass of salt

**Table 2**

The conditions of experiments. Conditions: initial concentration of reagents (Pd(II) ions and methyl orange) before mixing was equal ( $C_{0, Pd(II)} = C_{0, MO} = 5 \cdot 10^{-5}$  M). Total volume of reagents  $V = 4$  mL.

| Initial concentration of reagents  |                       | Volumetric ratio of MO to Pd(II) ions | T                    | pH                                   |
|--|-----------------------|---------------------------------------|----------------------|--------------------------------------|
| $C_{0, MO}$ , M  | $C_{0, Pd(II)}$ , M   | $V_{MO}:V_{Pd(II)}$ , mL/mL           | $^{\circ}C$          |                                      |
| <b>The stoichiometry</b>   |                       |                                       |                      |                                      |
| 0  | $5.000 \cdot 10^{-5}$ | 0.0 : 4.0                             | 20                   | 4.10                                 |
| $6.250 \cdot 10^{-6}$  | $4.375 \cdot 10^{-5}$ | 0.5 : 3.5                             |                      |                                      |
| $1.250 \cdot 10^{-5}$  | $3.750 \cdot 10^{-5}$ | 1.0 : 3.0                             |                      |                                      |
| $1.875 \cdot 10^{-5}$  | $3.125 \cdot 10^{-5}$ | 1.5 : 2.5                             |                      |                                      |
| $2.500 \cdot 10^{-5}$  | $2.500 \cdot 10^{-5}$ | 2.0 : 2.0                             |                      |                                      |
| $3.125 \cdot 10^{-5}$  | $1.875 \cdot 10^{-5}$ | 2.5 : 1.5                             |                      |                                      |
| $3.750 \cdot 10^{-5}$  | $1.250 \cdot 10^{-5}$ | 3.0 : 1.0                             |                      |                                      |
| $4.375 \cdot 10^{-5}$  | $6.250 \cdot 10^{-6}$ | 3.5 : 0.5                             |                      |                                      |
| $5.000 \cdot 10^{-5}$  | 0                     | 4.0 : 0.0                             |                      |                                      |
| <b>The influence of pH</b>   |                       |                                       |                      |                                      |
| $1.250 \cdot 10^{-5}$  | $3.750 \cdot 10^{-5}$ | 1.0 : 3.0                             | 20                   | 2.87<br>4.10<br>5.02<br>6.09<br>7.00 |
| The influence of temperature   |                       |                                       |                      |                                      |
| $1.250 \cdot 10^{-5}$  | $3.750 \cdot 10^{-5}$ | 1.0 : 3.0                             | 20<br>30<br>40<br>60 | 4.10                                 |
| The influence of other anions ( $Cl^{-}$ , $ClO_4^{-}$ )<br>(Concentration of anions in the sample was set as 0.075 M)   |                       |                                       |                      |                                      |
| $1.250 \cdot 10^{-5}$  | $3.750 \cdot 10^{-5}$ | 1.0 : 3.0                             | 20                   | 4.10                                 |
| The influence of other cations ( $Na^{+}$ , $K^{+}$ , $Pt^{2+}$ , $Co^{2+}$ , $Ni^{2+}$ , $Cu^{2+}$ , $Zn^{2+}$ ) in the presence of Pt(IV)<br>(Concentration of cations in the sample was set as 0.075 M) |                       |                                       |                      |                                      |
| $1.250 \cdot 10^{-5}$  | $3.750 \cdot 10^{-5}$ | 1.0 : 3.0                             | 50                   | 4.10                                 |
| The Pd(II) quantitative determination in the presence of Pt(IV)*   |                       |                                       |                      |                                      |
| $5 \cdot 10^{-6}$  | $5 \cdot 10^{-6}$     | 1.0:3.0                               | 50                   | 4.10                                 |
| $1 \cdot 10^{-5}$  | $1 \cdot 10^{-5}$     |                                       |                      |                                      |
| $5 \cdot 10^{-5}$  | $5 \cdot 10^{-5}$     |                                       |                      |                                      |
| $1 \cdot 10^{-4}$  | $1 \cdot 10^{-4}$     |                                       |                      |                                      |
| $2 \cdot 10^{-4}$  | $2 \cdot 10^{-4}$     |                                       |                      |                                      |

\* The values of initial concentration of reagents before reagents mixing.

was added to the flask (volume of 10 mL) containing Pd(II) and Pt (IV) ions in B-R buffer.

### 2.1.2. Methods of analysis

**Spectrophotometry UV-Vis.** The spectra of reagents were registered using spectrophotometer UV-Vis (Shimadzu, Japan), working in the wavelength range 190 – 900 nm. This device was equipped in reference and thermostatic cell. In all experiments, quartz cuvettes (Hellma) with optical path 1 cm were used. In standard procedure, a sample was collected immediately after mixing of two reacting solutions. Otherwise, the sample was collected and analyzed after 24 h, or at different time as it is indicated in the text. As a reference, an aqueous solution of proper solvent was used. All UV-Vis spectra and kinetic spectra were analyzed using Origin 2020 software.

**Nuclear Magnetic Resonance (NMR) spectroscopy.** The spectra were recorded at 300 K using a Bruker Avance III 600 MHz spectrometer. The  $^1H$ ,  $^{13}C$ , COSY, HSQC, and HMBC experiments were performed using standard procedures. In order to determine the structure of obtained compound, the sediment was collected, dried at room temperature and dissolved in DMSO  $d_6$  (dimethyl sulfoxide- $d_6$ , NMR purity).

**Fourier Transform Infrared Spectroscopy (FTIR).** The spectra were recorded on TENSOR II Bruker spectrophotometer, by ATR technique using the diamond crystal. During measurements, the spectra were 64 repeated over the wavenumber range  $350-4000$   $cm^{-1}$ , with resolution  $1$   $cm^{-1}$ .

**Density Functional Theory (DFT) calculation.** The structure of palladium complexes were optimized using DFT with the B3LYP hybrid functional, by using a basis set of LanL2DZ. Computations

have been performed using the Gaussian 09 program package and visualized with GausView5.0 [37].

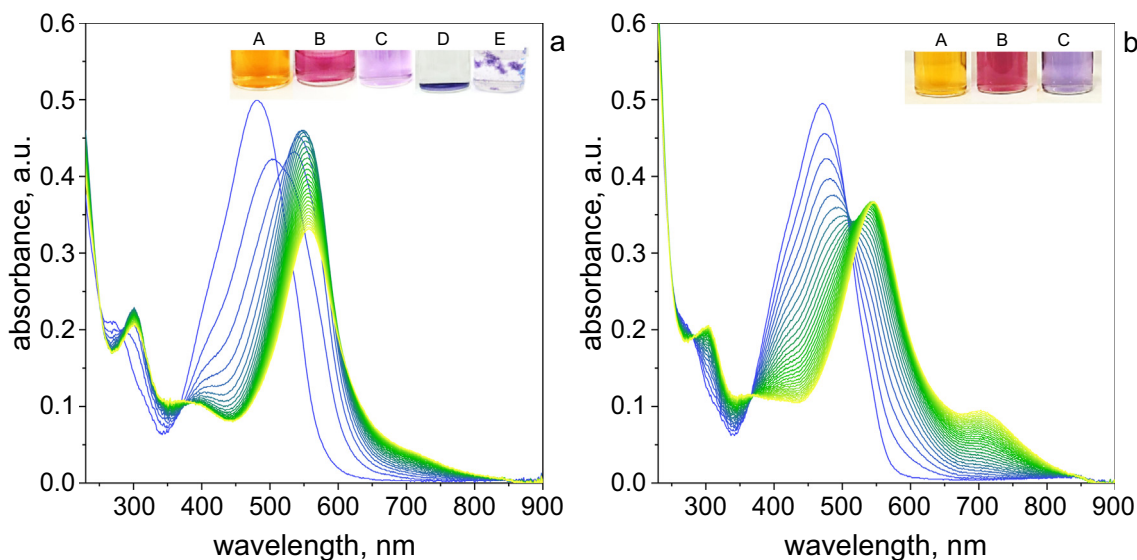
## 3. Results and discussion

### 3.1. Experimental conditions

The process of selective determination of Pd(II) ions was carried out under different conditions, which have been gathered in Table 2.

### 3.2. The process of complex formation between Pd(II) ions and methyl orange

The process of a complex formation between Pd(II) ions and methyl orange was carried out at different conditions, described in Experimental section (Table 2). Before experiments, reagents were characterized in details and obtained characteristic UV – Vis spectra, determined values of the molar coefficient for methyl orange (SI, Table S1) are shown in Fig. S1 – S3 and for Pd(II) ions in Fig. S4 – S6 (SI, paragraph 1.1). For a mixture of aqueous solutions of Pd(II) ions and methyl orange (the same concentration), in a volumetric ratio 3:1, we observed the change in colour from yellow-orange (coming from methyl orange, sample A, Fig. 1) via pink (sample B, Fig. 1) to violet (sample C, Fig. 1). These changes are also observed in the UV-Vis spectra and suggest the formation of a new structure. The colour of the final product depends on the solvents form: violet – blue deposit in water (Sample D-E, Fig. 1a) or violet solution in B - R buffer (Sample C, Fig. 1b).



**Fig. 1.** The spectra evolution as a result of reaction between methyl orange and Pd(II) ions in volumetric ratio (1:3), when as solvent H<sub>2</sub>O was used and the colour change (A-E) of mixture MO with Pd(II) ions. Conditions:  $C_{0,MO} = 6.25 \cdot 10^{-6}$  M (for sample E -  $C_{0,MO} = 1.25 \cdot 10^{-5}$  M),  $C_{0,Pd(II)} = 3.75 \cdot 10^{-5}$  M,  $T = 20$  °C (sample E,  $T = 50$  °C), deionized water as solvent (pH between 4 and 5) (a) or in B-R buffer solution (pH = 4.1) and the colour change (A-C) of mixture MO with Pd(II) ions in volumetric ratio (1:3). Conditions:  $C_{0,MO} = 1.25 \cdot 10^{-5}$  M,  $C_{0,Pd(II)} = 3.75 \cdot 10^{-5}$  M  $T = 20$  °C, pH = 4.1. (b). Scans were collected every 10 min for 290 min. Conditions (for spectra analysis):  $C_{0,MO} = 1.25 \cdot 10^{-5}$  M,  $C_{0,Pd(II)} = 3.75 \cdot 10^{-5}$  M  $T = 20$  °C.

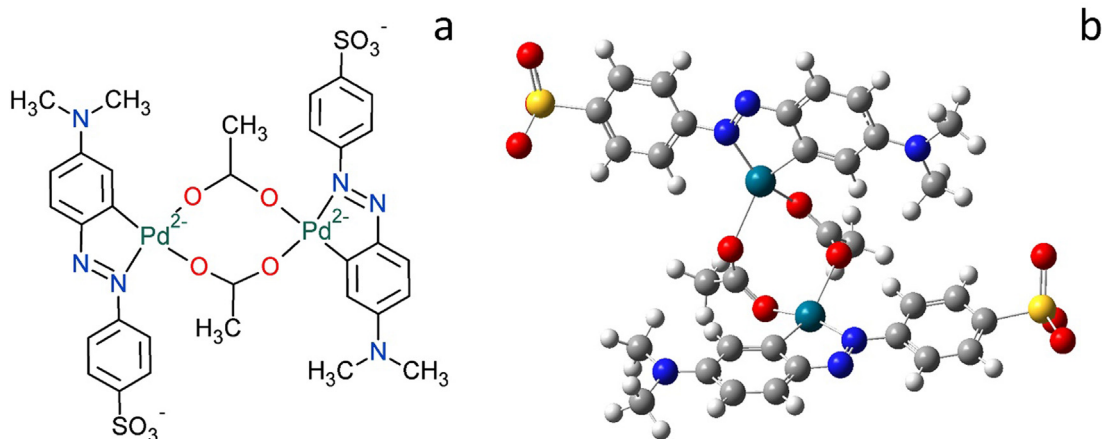
As it is shown in Fig. 1, the new spectra were formed with clear one (in water solution, AQ) or two maxima (in B-R buffer). The first one was located at 559 nm (AQ) whereas at this time scale in B-R solution the maximum was registered at 544 nm. The second peak appeared at 708 nm (Fig. 1b) with lower intensity. It is worth to note that maximum at 708 nm can be final, whereas further decreasing of maximum at lower wavelength and red shift take place with time (peak moving from 544 to 559 nm). The process after some time reaches an equilibrium and no further changes in this double peak were observed. The more detailed analysis of the spectral change (Fig. 1) suggests, that kinetics of the complex formation and its mechanism may differ depending on the used solvent. However, the characteristic points like peak location with maximum at 559 nm and colour change look similar (Fig. 1 A – C). The appearance of pink colour of the solution suggests also intermediated product(s) formation. To better understand the complex formation process between Pd(II) ions and methyl orange, the stoichiometry was studied. For this purpose, the stoichiometry of new complex in B-R buffer solution (pH = 4.1) was established using Job's plot (SI, Fig. S7 – S9, paragraph 1.2). Obtained results suggest that in the reacting system intermediate product appeared at stoichiometry 2:2, whereas the final product is at 1:3, as was shown in Fig. S9 (SI). The stoichiometry 2:2 is in accordance with literature, which describes similar family of azo - compounds. Ghedini et al. [38] show that in results of mixing equimolar reagents i.e. palladium (II) acetate with 4,4'-bis(hexyloxy)azoxybenzene [H(Azo-6)] in excess of acetic acid, the methathetical reaction takes place and dinuclear acetate bridge complex  $[(Azo-6)Pd(\mu-OAc)]_2$  was formed. It was also observed, that with time (2.5 h at 50 °C), the violet precipitate appeared. The dicyclopalladated product structure was proposed by Kulcsár and Čurić et al. [39]. In their work, solid palladium (II) acetate ( $Pd(OAc)_2$ ) and methyl orange were mixed by gentle grinding in an agate mortar. Then, the mixture was kept in closed vials saturated with vapours of such liquids as N,N-dimethylformamide (DMF), acetic acid (AcOH), or their mixture with water. Here also violet colour of the solution was observed, which has aged over time and form a more complex structure. The UV-Vis spectrum registered for complex formed at the beginning shows peak at 540 nm and a broad band in the range

of 600–800 nm. Kulcsár and Čurić et al. [39] concluded, that at first the dicyclopalladated product (1) is formed (Fig. 2), which in time forms a more complex structure.

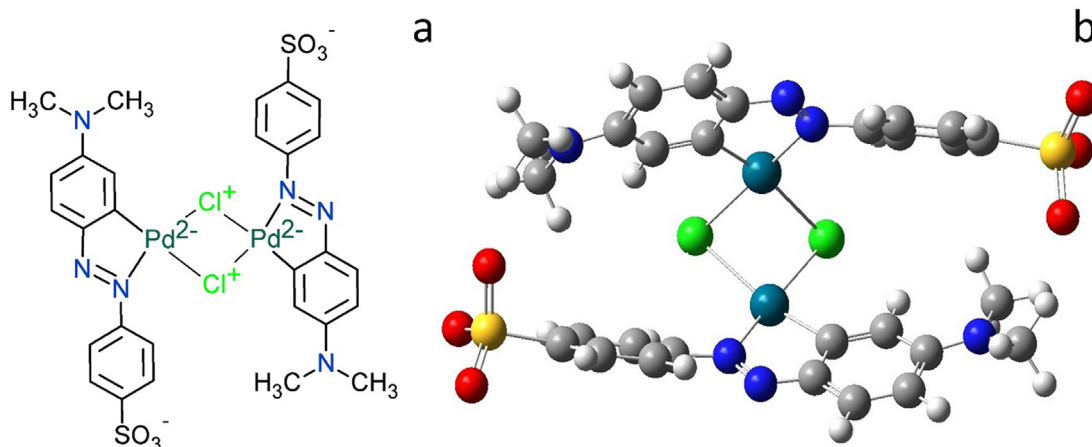
Comparing to our data, we also noticed a maximum in UV-Vis spectrum at 540 nm and broad peak between 600 and 800 nm after 150 min. since reagents were mixed (see SI, Fig. S10). These results are close to those obtained by Kulcsár and Čurić et al. [39] However, further peak shift is observed and a visible maximum at 708 nm was registered, which may be associated with the formation of further bridge according to that scheme proposed in the literature (Kulcsár and Čurić et al. [39]) or another process takes place. Dupont et al. [40], suggests possible mechanism of the bridge - splitting reaction of palladated N,N-dimethylaminophenethyl ligand with pyridine. This mechanism could explain the change in the complex structure, in which one of the non - active yet form of methyl orange substitutes to the formed complex. In essence, dinuclear acetate bridge complex is split into two complexes. However, at this stage, it is difficult to confirm such a supposition.

According to the literature, azobenzene compounds also form the H - shaped chloro - bridged dimer [41] (2), which contains a palladium - carbon  $\sigma$  - bond with the scheme given below (Fig. 3).

This product was probably obtained in an aqueous solution, in which formed complex has a characteristic peak at 559 nm and a broad peak between 600 and 800 nm. After aging, we observed precipitate. This precipitate was collected, dried at room temperature and it was directly analyzed on IR or dissolved in DMSO  $d_6$  for NMR analysis. The obtained FTIR spectra (more details are given in paragraph 1.3 in SI, Fig. S11), show the broad intensive band at  $504\text{ cm}^{-1}$  which is connected with several stretching modes of Pd-N and Pd-Cl vibrations. This peak confirms the presence of chloride bridge and formation of the structure 2. In this region, we could observe also S-O and C-C or C-H vibrations, but in the case of the Pd-MO complex, this band is more intensive than for pure methyl orange. At the same time, the bands at 570, 620, and  $695\text{ cm}^{-1}$  which are characteristic peaks for deformation vibration of C-C in the aromatic ring [42], have a smaller intensity which suggests stabilization of aromatic ring after connection C-Pd. Moreover, the bands at  $1117$  and  $1167\text{ cm}^{-1}$  revealed at methyl



**Fig. 2.** The structure of **1** (acetic bridge) (a) and optimized structure of **1** using DFT calculations (b). Red – oxygen; yellow – sulphur; green – palladium; grey – carbon; white – hydrogen; blue – nitrogen.



**Fig. 3.** The structure of **2** (chloride bridge) (a) and optimized structure of **2** using DFT calculations (b). Red – oxygen; yellow – sulphur; dark green – palladium; green – chloride; grey – carbon; white – hydrogen; blue – nitrogen.

orange spectrum, characteristic for C-N = N vibrations, and 1515 and 1601  $\text{cm}^{-1}$  characteristic for N = N vibrations, are shifted suggesting changes in the structure causing by bonding Pd to N = N. For NMR analysis the precipitate was dissolved in the solvent and the solution had a blue-green colour with a characteristic UV-Vis spectrum (see, paragraph 3.3.). This also suggests that the structure of the metalorganic complex has been reorganized due to the reaction of ligand replacement by solvent molecules [43]. According to Babić et al. [44]  $\{\text{PdCl}(\text{dms})\}_2(\mu\text{-azb})$  (**3**) is formed (scheme given in Fig. 4).

For the complex **3** the  $^1\text{H}$ ,  $^{13}\text{C}$  and 2D (COSY, HSQC, and HMBC) NMR spectra were recorded (Fig. 4, SI, Figs. S12–S16). In the proton spectrum, six non-equivalent signals were observed due to a loss of the ortho proton from each phenyl ring. Two broadened singlets, the most shifted downfield at  $\delta = 8.57$  and 8.27 ppm, come from H8 and H2 protons. In the higher temperature (344 K), these signals are split into two doublets with ortho coupling constants ca. 9 Hz (SI, Fig. S12). The observed downfield shift of H8 and H2 signals could be a consequence of intramolecular hydrogen bonds between hydrogen and oxygen atoms of DMSO, similar to the complexes, which was described by Babić et al. [44]. Based on the obtained NMR results, we postulate that complex like (**3**) is formed in DMSO solution. Additionally, in proton spectra the second set of signals of that complex is observed, indicating that ligands could be *trans* or *cis* oriented toward the Pd - C bond. The distribution

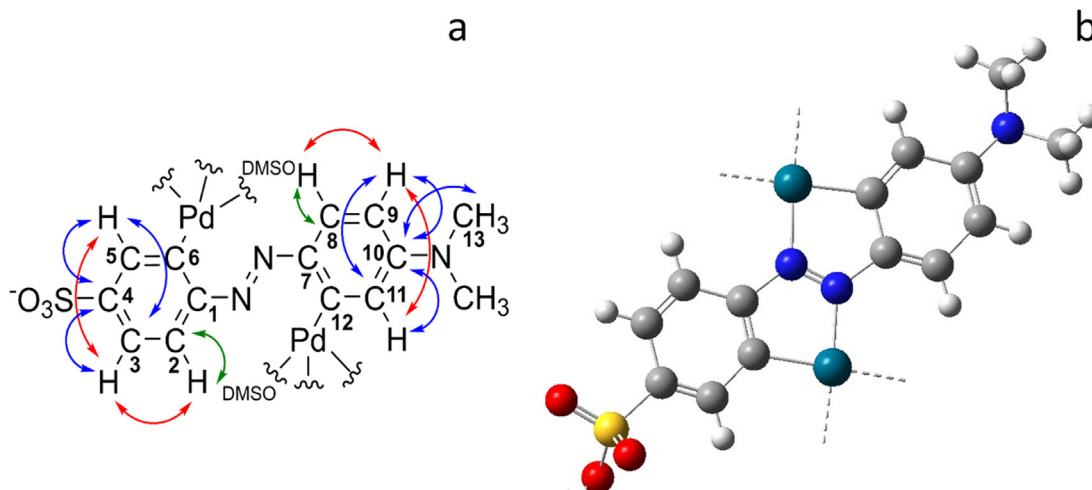
of the second minor isomer is much smaller than the upper study and equals approximately 20% (SI, Fig.S12).

### 3.3. The process of palladium determination without and in the presence of Pt(IV)

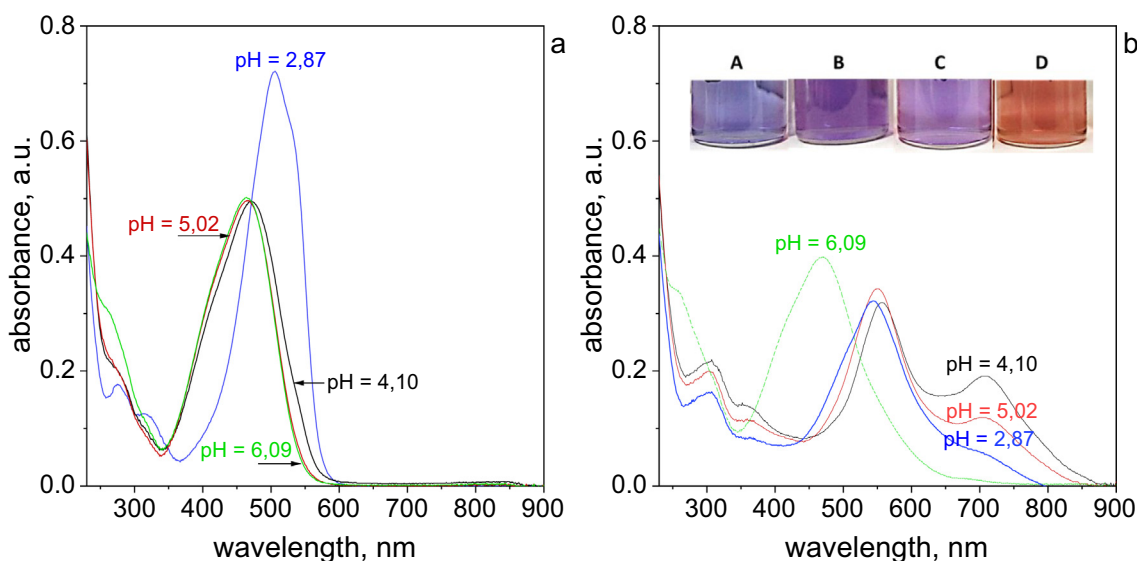
#### 3.3.1. The influence of pH

A very important aspect during Pd(II) ions detection is the sensitivity of the method to the pH of the solution. Thus, we used B-R buffer in the pH range 2.87 – 7.00. Tests were also performed for pH = 1 established using 0.1 M  $\text{HClO}_4$  (for pH 1 and 7 not data are given in the paper). After reagent mixing i.e. 1 mL of MO and 3 mL of Pd(II) ions (concentration before mixture:  $C_{0,\text{MO}} = C_{0,\text{Pd}}$  ( $\text{II}$ ) =  $5 \cdot 10^{-5}$  M), there were no changes in the initial colour of the obtained solution at pH = 1 (red), and small changes at  $\text{pH} \geq 6$  (yellow, with time turned to orange, Fig. 5b, sample D). The most interesting area for the process of complex formation between Pd(II) ions and MO was in the pH range from about 3 up to 5. The colour of obtained solutions in this pH range was shown in Fig. 5b. It is worth to note, that at pH = 2.87 the colour of the mixture of metal ions and methyl orange was red. For the obtained solutions, the UV-Vis spectra were recorded at the beginning (after reagents mixing) and after 24 h. Obtained spectra of **1** are shown in Fig. 5.

Depending on the pH of the solution, we obtained different spectra (t = 0 min., Fig. 5a), the character of which is mostly related



**Fig. 4.** Selected NMR correlation ( $^1\text{H}$ - $^1\text{H}$  COSY - red,  $^1\text{H}$ - $^{13}\text{C}$  HSQC - green, and  $^1\text{H}$ - $^{13}\text{C}$  HMBC - blue) for suggested complex **3** in DMSO solution (a). (See also SI, Fig. S14-16). Optimized structure of **3** using DFT calculations (b). Red - oxygen; yellow - sulphur; dark green - palladium; grey - carbon; white - hydrogen; blue - nitrogen.



**Fig. 5.** The spectra coming from solution containing the mixture of MO with Pd(II) at different pH at the beginning (a) and after 24 h (b). The colour of obtained solution mixed at different pH: A - 2.87; B - 4.1; C - 5.02; D - 6.09 after 24 h. MO mixed with Pd(II) ions in volumetric ratio (1:3) (c). Conditions:  $C_{0,\text{MO}} = 1.25 \cdot 10^{-5}$  M,  $C_{0,\text{Pd(II)}} = 3.75 \cdot 10^{-5}$  M (the value of concentration after reagents mixing),  $T = 20^\circ\text{C}$ .

to the original spectrum coming from methyl orange (see, SI, Fig. S8 a). The spectra registered at pH greater than 5 (Fig. 5a), in visible wavelength range seems to be similar. At pH = 4.1 we noticed a small red shift and maximum at 464 nm (pH = 6.09) was moved to 470 nm. It was also observed, that at pH = 6.09, the intensity of the spectrum in the range 250 – 300 nm is the highest. After 24 h, the solutions were again studied. In pH  $\leq 5.02$ , the double peak in visible range was observed with maximum at 708 nm and 544 nm (pH = 2.87) or 559 nm (pH = 4.01) or 550 nm (pH = 5.02), Fig. 5b. One peak (no visible maximum in the range 250 – 300 nm, Fig. 5a) splits into two peaks with maximum at 305 and about 360 nm (Fig. 5b). However, the intensity of these peaks are different but they can be correlated with the peak located at 708 nm. The spectrum obtained at the highest value of pH = 6.09 changed and also red shift of the maximum was observed (472 nm).

### 3.3.2. The influence of temperature

The process of complex formation (**1**) was also studied at constant values of pH and reagent concentration and different temperature, i.e. 20–60°C. For this purpose thermal bath was used. In all cases a purple colour of a mixture of Pd(II) ions and MO was observed. As it was expected, the time needed for this process was shortened up to half hour at 60°C with the spectrum intensity close to that obtained at 20°C. Results from the spectrophotometric study are presented in SI, Fig. S17.

The obtained spectra (Fig. S17) have different intensities but all of them show three distinct peaks located at  $\lambda_{1T}$ ,  $\lambda_{3T}$ ,  $\lambda_{4T}$  (detailed location was described in Table 3) and one “small” at  $\lambda_{2T}$ . Generally, the increasing temperature causes a decrease in maximum intensity at wavelengths  $\lambda_{1T}$ ,  $\lambda_{2T}$  and  $\lambda_{3T}$  and an increase at  $\lambda_{4T}$ . It is worth to note, that all peaks are moved towards shorter or longer wavelength and it is shown in Table 3.

**Table 3**

The change of wavelength at which the maximum on UV-Vis spectrum was observed. Conditions:  $C_{0,MO} = 1.25 \cdot 10^{-5}$  M,  $C_{0,Pd(II)} = 3.75 \cdot 10^{-5}$  M (the value of concentration after reagents mixing),  $T = 20\text{--}60^\circ\text{C}$ ,  $\text{pH} = 4.1$ .

| T, °C | $\lambda_{1T}$ , nm | $\lambda_{2T}$ , nm | $\lambda_{3T}$ , nm | $\lambda_{4T}$ , nm |
|-------|---------------------|---------------------|---------------------|---------------------|
| 20    | 305                 | 352                 | 559                 | 708                 |
| 30    | 308                 | 354                 | 560                 | 706                 |
| 40    | 308                 | 358                 | 561                 | 702                 |
| 60    | 312                 | 360                 | 567                 | 699                 |

As it can be expected, the process accelerated depending on the temperature and spectra changed faster.

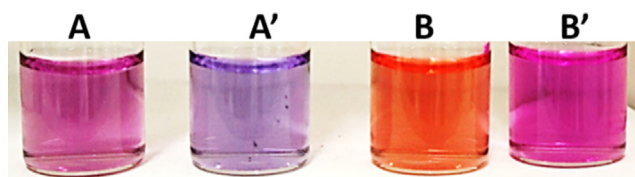
### 3.3.3. The influence of other anions on Pd(II) ions determination in the presence of Pt(IV) ions

Before checking how different cations influence the Pd(II) ions determination, we have examined first, which kind of salt we can use. Thus, we checked two types of anions like chloride and chlorate and we investigated their effect on the palladium detection. For this purpose, salts like sodium chloride and chlorate (their concentration before mixture with MO was set to 0.1 M) were mixed with a solution of Pd(II) and Pt(IV) and next with MO in volumetric ratio 3:1. Obtained results were gathered in Fig. 6. The process was carried out at two temperatures, i.e.  $20^\circ\text{C}$  and  $50^\circ\text{C}$  and the samples were photographed after 1 h.

As the result of mixing of metal ions, sodium perchlorate and MO, the change in colour from orange to pink (Fig. 6 A) and purple (Fig. 6 A'), was observed. As it can be expected the temperature accelerates the process and at  $50^\circ\text{C}$  purple colour appears in one hour and it is stable, whereas at  $20^\circ\text{C}$  it takes much longer time (one day later). In order to follow changes during the reaction between main components, i.e. Pd(II) ions and MO, the spectra were registered and shown in Fig. 7.

Fig. 7a shows the spectra change with time. Maximum located at 262 nm, which is associated with the presence of Pt(IV) ions in the solution, also decreases. However, this decrease can be related rather to hydrolysis process of Pt(IV), which at  $\text{pH} = 4.1$  may have following forms:  $[\text{PtCl}_6]^{2-}$  and  $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ . The hydrolyzed form has the same location of the maximum, i.e. at 230 and 262 nm [45].

On the UV-Vis spectra (Fig. 7a) the red shift can be observed. Location of the maximum change from 470 nm (see SI, Table S1) is characteristic for MO to 475 nm and then to about 540 nm (2 h later). Next, a small decrease of this spectrum is observed and the formation of new band with two maxima at 555, 704 nm ( $20^\circ\text{C}$ ) or 702 nm ( $50^\circ\text{C}$ ) occurs. As was mentioned before, increasing temperature causes process acceleration and the final product (**1**) appears within 1 h. It is also interesting that small changes can be seen between spectra obtained at  $50^\circ\text{C}$  and  $20^\circ\text{C}$  after 1 day. It suggests that the temperature changes value of the equilibrium constant, thus the obtained spectrum is a little bit more intense in comparison to that obtained in lower temperature. Obtained results confirm that the addition of sodium perchlorate does not



**Fig. 6.** The colour change (A-B) of mixture MO with Pd(II)/Pt(IV)/ $\text{ClO}_4^-$  (A, A')/ $\text{Cl}^-$  (B, B') ions in volumetric ratio (1:3). Conditions:  $C_{0,MO} = 1.25 \cdot 10^{-5}$  M,  $C_{0,Pd(II)/Pt(IV)} = 3.75 \cdot 10^{-5}$  M,  $C_{0,\text{anions}} = 0.075$  M,  $T = 20^\circ\text{C}$  (A, B),  $T = 50^\circ\text{C}$  (A', B'),  $\text{pH} = 4.1$ .

interfere with the determination of metal ions. In case of the sample with NaCl, the colour turned from orange to pink (Fig. 6 B, B'), after one hour depending on the temperature. It can be concluded that the addition of chlorides hinders the transition to purple colour as it happened in the case chlorate ions (Fig. 6 A'). This suggests that the process is somehow inhibited. Registered spectra show some changes. The first change at lower wavelength can be associated with Pt(IV) ions hydrolysis (decreasing maximum at 262 nm, which intensity is higher due to increasing amount of chloride ions in the solution and thus increasing stability of platinum complex and  $[\text{PtCl}_5(\text{H}_2\text{O})]^-$  form). The next change is related with the red shift of the peak at 472 nm. The further process is stopped and only pink colour (with maximum at 544 nm, Fig. 7 b) of the solution is obtained (Fig. 6 B'). It is worth mentioning that the addition of sodium in the form of perchlorate does not affect the detection of Pd(II) ions.

### 3.3.4. The influence of other cations on Pd(II) ions determination in the presence of Pt(IV)

Having found there is no interaction between perchlorate ions and the reaction of complex formation (**1**), we select for further study proper perchlorate salts of such metals like potassium, cobalt, nickel, copper, zinc. For this purpose, a proper amount of salt (concentration 0.1 M) was mixed with a solution containing Pd(II) and Pt(IV) ions (flask volume 10 mL). Next, 3 mL of such a solution was mixed with 1 mL of MO. The value of pH was kept constant at  $\text{pH} = 4.1$  using B-R buffer. The colour of obtained solutions was shown in Fig. 8.

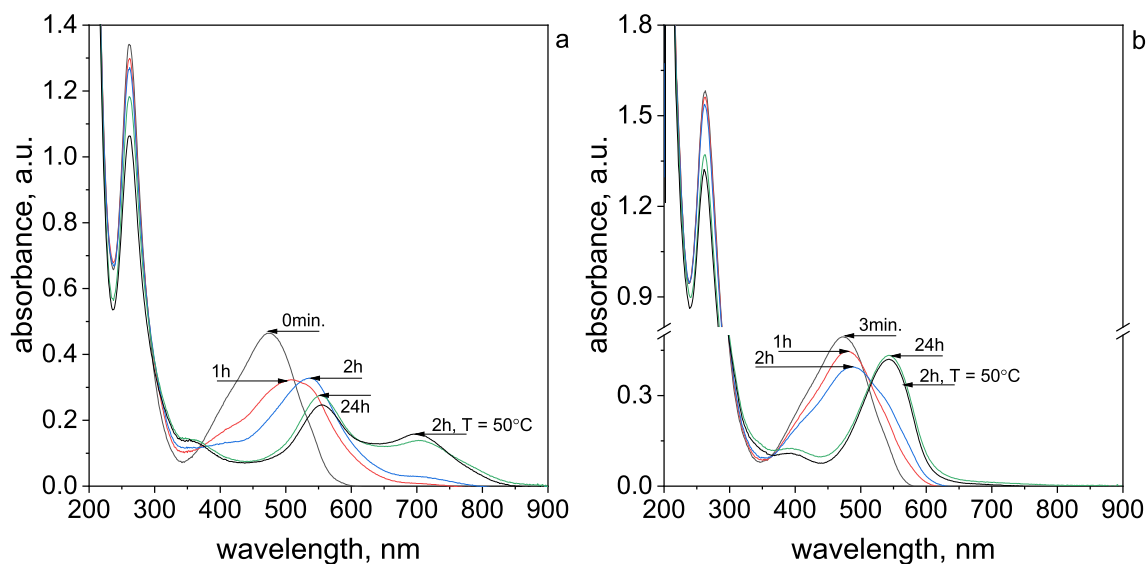
The colour of solutions is different depending on the used cations. It is not surprising, because we observe the imposition of colours derived from cations (green for Ni(II), pink for Co(II), blue for Cu(II), see Supporting Information, Fig. S18). It is worth to mention, that solutions containing potassium, nickel, cobalt, platinum were clear, while solution containing Cu(II) was not transparent and in the case of zinc ions after 10 min a white deposit on the vial bottom appears. However, for copper cations at temperature  $20^\circ\text{C}$  (Fig. 8) no visible change related with colour was observed and this suggests, that we can still qualitatively detect the presence of palladium.

The UV-Vis spectra of the obtained solutions containing different cations are shown in Fig. 9a. In the next Fig. 9b spectra obtained after mixing all components are shown, i.e. Pd(II), Pt(IV) and proper cations with MO. More spectra and their evolution details were included in SI (Fig. S19).

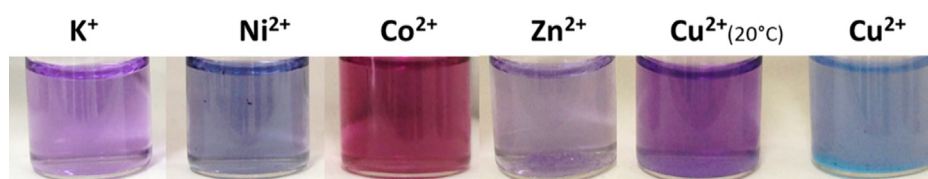
The registered spectra (Fig. 9a) indicate which cations may interfere with the spectrum of the final product. There are Ni(II) and Cu(II), which spectra have their peaks also in the interesting range, i.e. 470 – 800 nm (grey area in the image, Fig. 9b). After mixing all components, i.e.  $\text{Pd}^{2+}$ ,  $\text{Pt}^{4+}$ , cations and MO we obtained spectra, which showed that added cations like  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Pt}^{2+}$  do not interfere. Problematic seems to be  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  cations. In case of the first cation, the spectrum shown in Fig. 9b can be solved by subtracting the spectrum coming from the nickel ions themselves. The spectrum obtained for solution containing zinc and copper ions shows that they may be useful for Pd(II) determination but require a different approach. In case of Cu(II) ions it seems, that the amount of Pd(II) can be quantitatively determined at lower wavelength (plateau in the range 550–600 nm, SI, Fig. S19e).

### 3.3.5. The Pd(II) quantitative determination

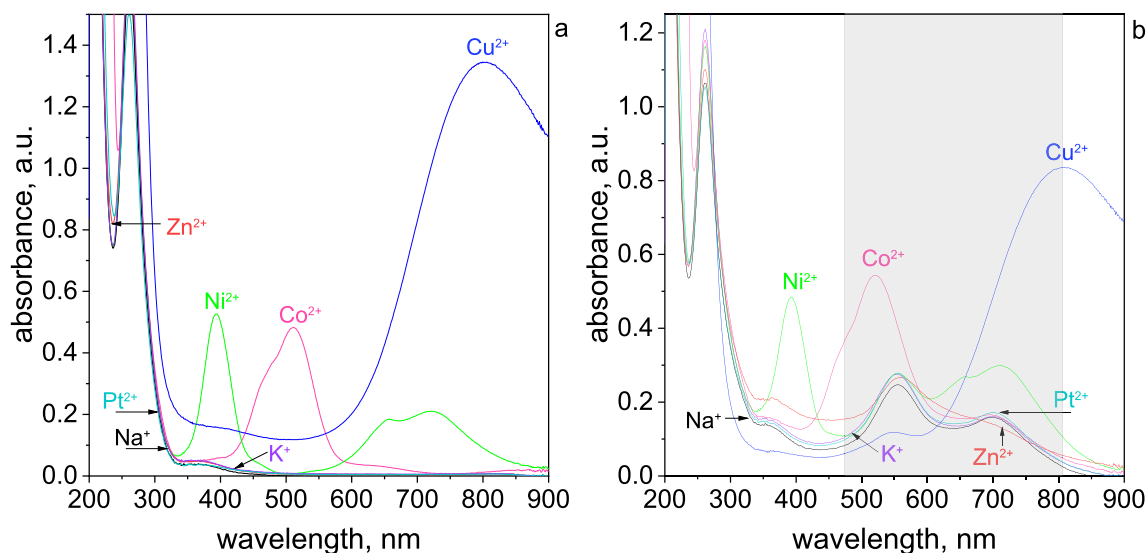
One of the important factors during selective Pd(II) ions determination is the sensitivity of the method to the initial metal concentration. For this purpose, we used a concentration of Pd(II) ions in the range  $5 \cdot 10^{-6}$  –  $2 \cdot 10^{-4}$  M. Next, 3 mL of Pd(II) solution was mixed with 1 mL of MO. The initial concentration of reagents



**Fig. 7.** The spectra coming from solution contains the mixture of MO with Pd(II)/Pt(IV) and  $\text{ClO}_4^-$  (a) or  $\text{Cl}^-$  (b). Conditions:  $C_{0,\text{MO}} = 1.25 \cdot 10^{-5}$  M,  $C_{0,\text{Pd(II)/Pt(IV)}} = 3.75 \cdot 10^{-5}$  M,  $C_{0,\text{anions}} = 0.075$  M,  $T = 20^\circ\text{C}$  or  $50^\circ\text{C}$ ,  $\text{pH} = 4.1$ .



**Fig. 8.** The colour change of **1** and different cations. Conditions:  $C_{0,\text{MO}} = 1.25 \cdot 10^{-5}$  M,  $C_{0,\text{Pd(II)/Pt(IV)}} = 3.75 \cdot 10^{-5}$  M,  $C_{0,\text{anions}} = 0.075$  M,  $T = 50^\circ\text{C}$ , 2 h later,  $\text{pH} = 4.1$ .



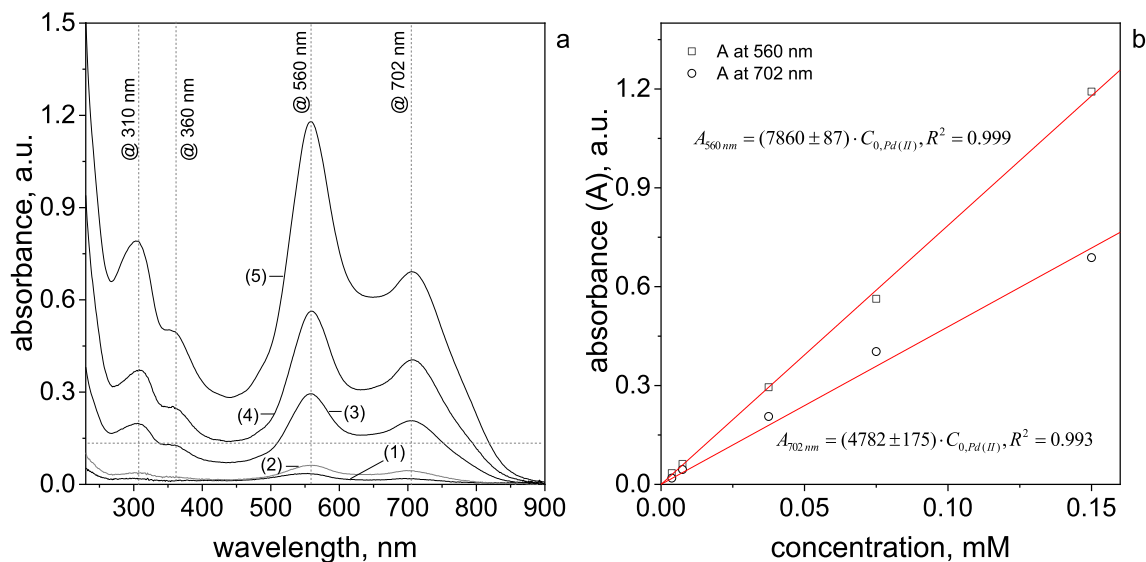
**Fig. 9.** The spectra of Pd(II)/Pt(IV) ( $C_{0,\text{Pd(II)}, \text{Pt(IV)}} = 5 \cdot 10^{-5}$  M) and cations ( $C_{0,\text{cations}} = 0.1$  M) in buffer ( $\text{pH} = 4.1$ ) (a); spectra coming from solution containing the mixture of MO with Pd(II)/Pt(IV) and different cations registered 2 h after their preparation at  $T = 50^\circ\text{C}$ ,  $\text{pH} = 4.1$  (b). Conditions:  $C_{0,\text{MO}} = 1.25 \cdot 10^{-5}$  M,  $C_{0,\text{Pd(II)/Pt(IV)}} = 3.75 \cdot 10^{-5}$  M,  $C_{0,\text{cations}} = 0.075$  M.

before mixing was the same. The process was carried out at constant  $\text{pH} = 4.1$  and temperature ( $50^\circ\text{C}$ ). The obtained spectra evolutions are shown in Supporting Information, Fig. S20a - c. In Fig. 10a the spectra obtained at different concentrations of reagents have been collected and compared.

As it can be expected, according to the Lambert-Beer law, the intensity of the spectrum increases with an increase of the concen-

tration of reagents. Based on obtained spectra, the graph of absorbance versus the initial concentration of metal ions was prepared as shown in Fig. 10b. The values of molar coefficient for two wavelengths (560 and 702 nm at  $50^\circ\text{C}$ ) were determined from the slope of the fitted curves to the experimental points. The relation between concentration of metal ions and absorbance can be expressed as follow:





**Fig. 10.** The spectra of the solution containing **1** at different initial concentration of reagents after 96 h (a). The dependency of absorbance vs. initial Pd(II) concentration (b). Conditions: the value of concentration before reagents mixing  $C_{0,MO} = C_{0,Pd(II)} = 5 \cdot 10^{-6}$  M (1);  $C_{0,MO} = C_{0,Pd(II)} = 1 \cdot 10^{-5}$  M (2);  $C_{0,MO} = C_{0,Pd(II)} = 5 \cdot 10^{-5}$  M (3),  $C_{0,MO} = C_{0,Pd(II)} = 1 \cdot 10^{-4}$  M (4);  $C_{0,MO} = C_{0,Pd(II)} = 2 \cdot 10^{-4}$  M (5),  $T = 50^\circ\text{C}$ ,  $\text{pH} = 4.1$ .

$$A_{560\text{nm}} = 7860 \cdot C_{0,Pd(II)} \quad (9)$$

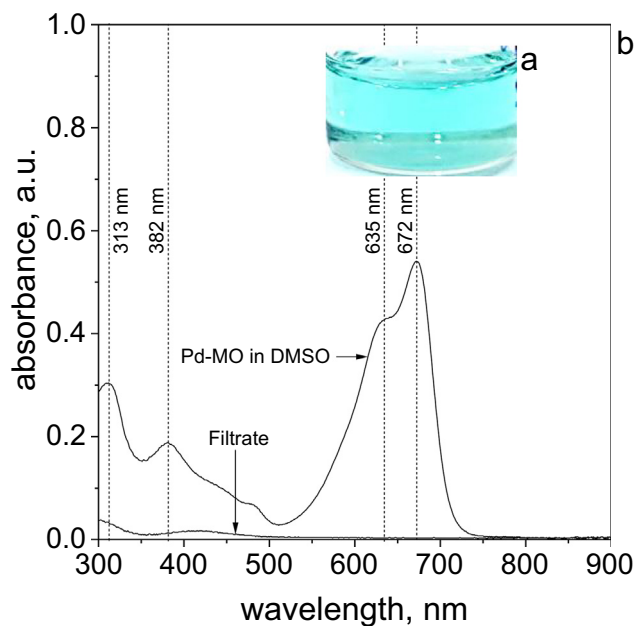
$$A_{702\text{nm}} = 4782 \cdot C_{0,Pd(II)} \quad (10)$$

These equations allow for determination of Pd(II) concentration. Moreover, we have the possibility to determine Pd(II) ions concentration at two wavelengths, i.e. 560 and 702 nm at  $50^\circ\text{C}$ . This is particularly helpful if there are other metal cations in the tested solution (see paragraph 3.3.4). It is worth to mention, that for a lower concentration of Pd(II) it is better to collect a sample after about 96 h, whereas for higher amount of metal ions 110 min. is enough. The values of absorbance at this time are higher, thus sensitivities of the applied method also increase and molar coefficient equal  $\lambda_{560\text{nm}}(\epsilon) = 8429 \pm 235 \text{ mol}\cdot\text{dm}^{-3} \cdot \text{cm}^{-1}$  and  $\lambda_{702\text{nm}}(\epsilon) = 4956 \pm 64 \text{ mol}\cdot\text{dm}^{-3} \cdot \text{cm}^{-1}$  (see SI, Fig. 20d).

### 3.4. The process of methyl orange removal from water solution

The obtained results showed, that after reagents mixing (in volumetric ratio 1:3) i.e. methyl orange and Pd(II) ions in aqueous solution (only water as solvent), the efficient removal of methyl orange in form of complex was possible. The product of the reaction was unstable and forms a coarse blue/purple coloured precipitate, easy to filtrate (Fig. 1E). The precipitate and filtrate were separated and examined after 1 h since reagents were mixed (at  $50^\circ\text{C}$ ). For this purpose, the syringe filter (RC membrane filter,  $0.2 \mu\text{m}$ ) was used. Next, the precipitate in the filter was rinsed with less polar solvent i.e. 2 mL of DMSO (relative polarity 0.444 whereas for water it is 1.0). As it can be expected the solid complex was easily dissolved and the blue-green solution was obtained (Fig. 11a). Then, the solution was analyzed spectrophotometrically and obtained result was shown in Fig. 11b.

The UV-Vis spectrum in considered wavelength showed peaks localized at 313, 382 and peak at 672 with shoulder at 635 nm. Falcão et al. [46] analyzed dimethyl sulfoxide and indicated that DMSO has no absorption band in the region between 300 and 600 nm, and they registered only a small absorption at the wavelength of 532 nm. Thus, the whole signal is coming from the complex. Moreover, the spectrum of the complex is similar to that given by Babić et al. [44] and suggests formation of **3** in DMSO. The obtained filtrate (colourless) was also examined. The UV-Vis



**Fig. 11.** The colour (a) and spectrum of the solution containing the complex formed between MO and Pd(II) dissolved in DMSO and spectrum of filtrate (b). Conditions: the value of concentration before reagents mixing  $C_{0,Pd(II)} = C_{0,MO} = 5 \cdot 10^{-5}$  M,  $T = 20^\circ\text{C}$ .

spectrum (Fig. 11b) of the filtrate solution confirms, that there is no methyl orange in the solution.

## 4. Conclusions

The novel spectrophotometric method of Pd(II) ions determination, based on a metalorganic complex formation, is proposed. This method is cheap and easy to conduct. Moreover, it allows for determination of very low amount of metal i.e. 0.4 mg/L, even in the presence of Pt(II), Pt(IV). It is shown that this technique can be applied both for solutions containing chlorate and chloride ions (concentration below 0.01 M) and cations like sodium, potassium,

cobalt and nickel. It is also concluded, that the presence of copper and zinc as well as higher amount of chloride requires additional treatment in order to allow proper Pd(II) ions determination. Most relevant innovation is the developed “twin solution” which, depending on the used solvent, may be applied for palladium determination (in B–R buffer) or methyl orange removal (AQ) from waste solution. Moreover, this second technique is also promising for Pd(II) determination. It was shown that after precipitate dissolution in more polar solvent like DMSO, there is another possibility for palladium determination. This was confirmed by obtained UV–Vis spectrum shown in Fig. 11. This work will be continued as the data obtained suggest that it will be possible to determine really low quantity of metal, of the order of 10 µg/L.

### CRedit authorship contribution statement

**Magdalena Luty-Błocho:** Conceptualization, Formal analysis, Investigation, Methodology, Writing - original draft. **Agnieszka Podborska:** Investigation, Formal analysis, Writing - original draft. **Bogdan Musielak:** Investigation, Formal analysis, Writing - original draft. **Volker Hessel:** Writing - review & editing.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2021.116884>.

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