



# Speciation of platinum by GFAAS using various possibilities of analytical signal enhancement



Rastislav Serbin<sup>a,\*</sup>, Yaroslav Bazel<sup>a</sup>, Silvia Ružičková<sup>b</sup>

<sup>a</sup> Department of Analytical Chemistry, Faculty of Science, Pavol Jozef Šafárik University, Šrobárova 2, 041 80 Košice, Slovak Republic

<sup>b</sup> Institute of Recycling Technologies, Faculty of Metallurgy, Technical University of Košice, Letná 9, 042 00 Košice, Slovak Republic

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## ABSTRACT

A novel method for determination of platinum species by application of graphite furnace atomic absorption spectrometry (GFAAS) was developed. The principle of determination is the formation of platinum ion associates (IA) with  $\text{SCN}^-$  and polymethine basic agent 1,3,3-trimethyl-2-[3-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)-propyl-1,3-dienyl]-3H-indolium chloride (TTDI), which can then be extracted by various organic solvents. Different options for analytical signal intensification (ultrasonic and microwave energy) were examined. The conditions found for ion associate formation and extraction have enabled the proposing of a new Pt(II) and Pt(IV) speciation process. These species can be reliably determined simultaneously at concentration ratios from 1:5 to 5:1. Moreover, the ion associates of platinum with TTDI can be extracted with toluene up to a volume ratio of aqueous and organic phases of  $V_{\text{aq}}:V_{\text{org}} = 50:1$ . This fact for Pt determination using GFAAS means decreasing the limit of detection (LOD) from  $7.1 \mu\text{g L}^{-1}$  to  $0.3 \mu\text{g L}^{-1}$ . The method was applied for Pt determination in a model and in spiked water samples.

## 1. Introduction

Platinum (Pt) belongs to the group of metals that exist on planet Earth in very low quantities. In particular, its concentration is about  $4 \text{ ng g}^{-1}$  in rocks and about  $1 \text{ ng g}^{-1}$  in soils [1]. The rarity of Pt along with its noble physical-chemical properties and the expense associated with its acquisition commonly contribute to its high price. Platinum, along with gold, silver, palladium, iridium, rhodium, osmium and ruthenium, have been classified under the common name of precious metals.

A number of instrumental procedures have been described for the determination of Pt; however, the very low Pt content in nearly all real samples and their complexity represents the major analytical challenge. For example, platinum naturally occurs with other metals having similar physical-chemical properties. Adsorption, coprecipitation, extraction and chlorination represent the most commonly used preconcentration techniques which are usually necessary prior to the determination of Pt; however, these techniques require complicated pretreatment procedures [2–9]. All these procedures can be used in combination with neutron activation analysis, chromatography and a number of spectroscopic methods, such as ICP-MS, ICP-OES and XRF, but they are also all associated with high instrumentation prices and operating costs. More importantly, there is little or no mention in the

literature of Pt speciation [Pt(II) and Pt(IV)] using these detection techniques. The most frequently used method for determining a Pt microamount is atomic absorption spectrometry. Modern spectrometers achieve high sensitivity of determination; even so this is not sufficient for reliable analysis of many natural and industrial samples. Due to the high atomization temperature of Pt and its low content in real samples, the most commonly used method for its determination is AAS with electrothermal atomization equipped with a graphite furnace. The platinum form which is most often determined is Pt (IV); only in a few cases is Pt (II) determined [10–12]. The speciation of Pt (II) and Pt (IV) forms is done only rarely [11,12]. In a boom time for GFAAS, some attempts have been made to determine Pt by using flame atomization (FAAS) [13,14]. However, compared to GFAAS, the achieved LODs are 100–1000 times higher, which is insufficient for real application.

It is known that Pt usually occurs in aqueous solutions in the form of anions, mostly the chloride acid complexes  $[\text{PtCl}_6]^{2-}$  and  $[\text{PtCl}_4]^{2-}$ , which differ in reaction activity. This allows the use of a polymethine agent in order to make such anions extractable as IA. Relevant IA are highly effective analytical tools for AAS speciation of microamounts of platinum.

The principles of the developed method for Pt speciation are the different conditions needed for the formation and extraction of Pt(IV) and Pt(II) ion associates with  $\text{SCN}^-$  and polymethine basic agent 1,3,3-

\* Corresponding author.

E-mail address: [rastislav.serbin@upjs.sk](mailto:rastislav.serbin@upjs.sk) (R. Serbin).

trimethyl-2-[3-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)-propyl-1,3-dienyl]-3H-indolium chloride (TTDI). This consists primarily in the use of different methods of intensification of the analytical signal (ultrasonic and microwave energy) followed by the semi-micro liquid-liquid extraction of platinum from aqueous-organic solutions.

## 2. Materials and methods

### 2.1. Chemicals and preparation of solutions

Bidistilled water was used for preparation of all aqueous solutions. All chemicals and solvents used were of analytical grade purity (unless stated otherwise).

The 0.01 mol L<sup>-1</sup> H<sub>2</sub>PtCl<sub>6</sub> stock solution was prepared by dissolving a small amount of platinum metal in the form of platinum wire of 99.99% Pt content (Medipharm, Slovakia) in 10 mL of concentrated aqua regia (HCl and HNO<sub>3</sub>, ITES, Slovakia). The solution was then evaporated to near dryness at the boiling point temperature. Then 5 mL of HCl (1:1) was added to the mixture and solution was evaporated again. This procedure was repeated three times to remove the nitrogen oxides. The residue was then added to bidistilled water to 100 mL. Solutions in concentrations between 10<sup>-5</sup> and 10<sup>-3</sup> mol L<sup>-1</sup> of Pt(IV) were prepared before measurement by dilution of a stock solution with bidistilled water.

The 0.01 mol L<sup>-1</sup> K<sub>2</sub>PtCl<sub>4</sub> (Merck, Germany) stock solution was prepared by dissolving a small amount of K<sub>2</sub>PtCl<sub>4</sub> in 100 mL of 1 mol L<sup>-1</sup> HCl. Solutions with a concentration between 10<sup>-5</sup> and 10<sup>-3</sup> mol L<sup>-1</sup> of Pt(II) were prepared before measurement by dilution of the stock solution with bidistilled water.

The 0.1 mol L<sup>-1</sup> NaSCN (ITES, Slovakia) stock solution was prepared by dissolving a small amount of NaSCN in 100 mL of bidistilled water. A solution with a concentration of 5 × 10<sup>-3</sup> mol L<sup>-1</sup> of NaSCN was prepared before measurement by dilution of the stock solution with bidistilled water.

The toluene, DMF and H<sub>2</sub>SO<sub>4</sub> were purchased from ITES, Slovakia.

The 10<sup>-3</sup> mol L<sup>-1</sup> TTDI (Jiacheng-Chem Enterprises Ltd., China) agent solution was prepared by dissolving 39.3 mg of TTDI in 1 mL of methanol (ITES, Slovakia) and then diluting with distilled water to 100 mL.

TTDI is an organic agent (Fig. 1) belonging to the organic basic dyes of the so-called group of 1,3,3-trimethyl-3H-indolium derivatives. The protonation and hydrolysis constants of TTDI are, respectively: pK<sub>pr</sub> = 1.80 ± 0.04 and pK<sub>h</sub> = 13.65 ± 0.11 [15].

### 2.2. Applied instruments

GFAAS determinations were performed using a PerkinElmer spectrometer, AAnalyst 600 model with an electrothermal atomizator in connection with an AS 800 autosampler. A hollow-cathode lamp 3QNY/Pt operating at 10 mA current was used for determination. The volume of analyte injected was 20 µL. Atomization was performed in an argon atmosphere. A basic wavelength of 265.9 nm with a 0.5 nm slit was selected. The optimized temperature program is given in Table 1.

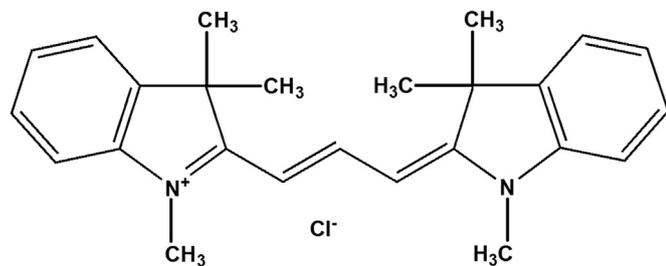


Fig. 1. Chemical structure of the TTDI polymethine agent used.

Table 1

AAS atomizator temperature program for Pt determination.

Order	Temperature, °C	Time for achieving temperature, s	Time remaining at temperature, s	Inert Ar gas flow, mL min <sup>-1</sup>
1	150	15	20	250
2	170	5	10	250
3	1300	10	20	250
4	2200	0	5	0
5	2450	1	3	250

Table 2

Optimized parameters for the formation and extraction of Pt IA.

Parameter	Optimal value
TTDI concentration	1.0 × 10 <sup>-4</sup> mol L <sup>-1</sup>
pH	1.0
SCN <sup>-</sup> concentration	5 × 10 <sup>-4</sup> mol L <sup>-1</sup>
Dispersive solvent dimethylformamide	16%
Extraction solvent	Toluene
Time of extraction	60 s
Time of centrifugation	5 min
RPM	3000 min <sup>-1</sup>
Preconcentration factor	50

The microwave exposure of samples was performed in a microwave reactor (CEM Discover, USA), in glass-septum closed cuvettes (10 mL), with the solution mixed during exposure. The temperature of the solution was monitored by an infrared sensor built-in directly under the cuvette.

Ultrasonic initiation was performed using an ultrasonic disintegrator (Person-Ultragen UZD500, Slovakia) equipped with a titanium probe with maximum a usable ultrasonic power generator of 500 W.

The pH values of the solutions were controlled by a digital OP-208/1 pH meter (Radelkis, Hungary) with glass electrode.

Centrifugation was performed using a CN-2060 centrifuge (MRC, Israel).

### 2.3. Experimental procedures

#### 2.3.1. Extraction GFAAS determination of Pt(IV)

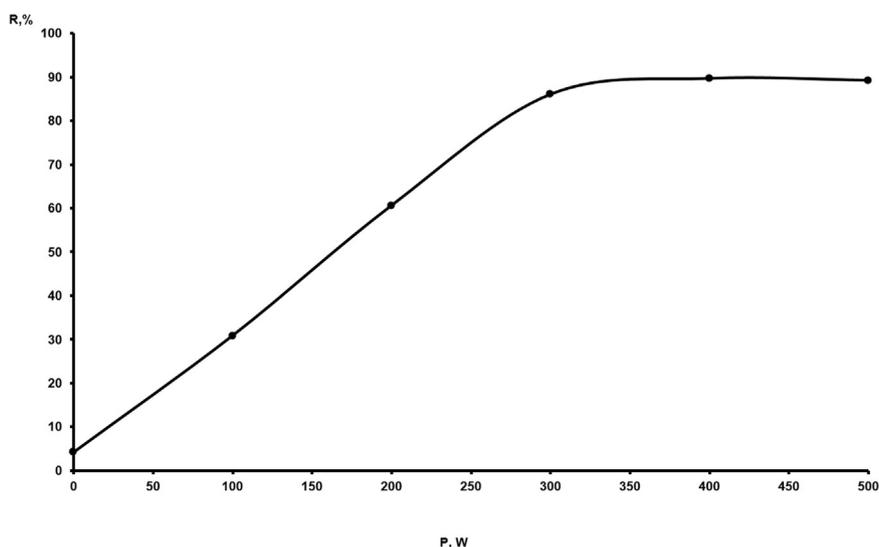
The following were added to the separating funnel: 0.2–1 mL Pt(IV) solution containing 0.2–1 µg Pt, 5 mL 5 × 10<sup>-3</sup> mol L<sup>-1</sup> NaSCN solution, 5 mL 1 × 10<sup>-3</sup> mol L<sup>-1</sup> TTDI solution, 5 mL 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 8 mL DMF, and the solution was filled to 50 mL with bidistilled water. After mixing, the ultrasonic probe at power of 400 W was immersed into the mixture. Exposure time was 5 min. After the mixture cooled to room temperature, 1 mL of toluene was added to the mixture and the mixture was extracted for 60 s. The extracts were separated and centrifuged, and the absorbance was measured at a wavelength of 265.9 nm.

The concentration of platinum was calculated from the equation of the calibration curve obtained under the same conditions of measurement.

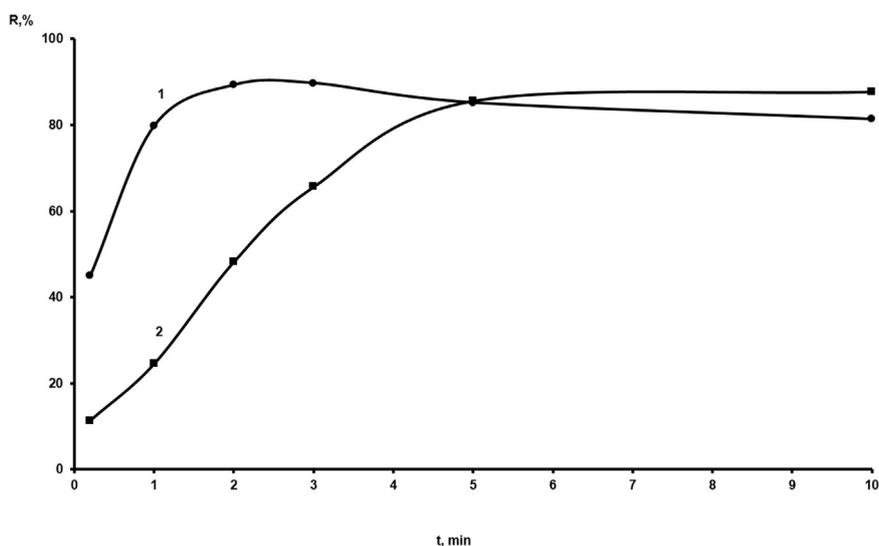
GFAAS measurements without extraction were carried out directly by measuring the prepared aqueous solution of the model samples. Platinum concentration was calculated from the calibration curve obtained using the aqueous calibration solutions of Pt(IV) standard.

#### 2.3.2. Extraction GFAAS determination of Pt(II)

The following were added to the separating funnel: 0.2–1 mL Pt(II) of the solution containing 0.2–1 µg Pt, 5 mL 5 × 10<sup>-3</sup> mol L<sup>-1</sup> NaSCN solution, 5 mL 1 × 10<sup>-3</sup> mol L<sup>-1</sup> TTDI solution, 5 mL 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 8 mL DMF, and the solution was filled to 50 mL with bidistilled water. Then 1 mL of toluene was added to the mixture, and the mixture was extracted for 60 s. The extracts were separated and centrifuged and



**Fig. 2.** Impact of ultrasonic generator power on the extraction of Pt ion associate with TTDI.  $t = 5$  min;  $1 \times 10^{-4}$  mol L<sup>-1</sup> TTDI; pH = 1;  $5 \times 10^{-4}$  mol L<sup>-1</sup> NaSCN;  $4 \times 10^{-8}$  mol L<sup>-1</sup> Pt(IV); 16% DMF,  $V_{\text{aq}}:V_{\text{org}} = 50:1$ .



**Fig. 3.** Impact of exposure time of ultrasound on the Pt IA extraction with TTDI.  $P = 400$  W;  $1 \times 10^{-4}$  mol L<sup>-1</sup> TTDI; pH = 1;  $5 \times 10^{-4}$  mol L<sup>-1</sup> NaSCN;  $4 \times 10^{-8}$  mol L<sup>-1</sup> Pt; 16% DMF;  $V_{\text{aq}}:V_{\text{org}} = 50:1$ ; (1) Pt(II); (2) Pt(IV).

the absorbance was measured at a wavelength of 265.9 nm. The concentration of platinum was calculated from the equation of the calibration curve obtained under the same conditions of measurement.

### 2.3.3. Extraction GFAAS determination of Pt(II) and Pt(IV) simultaneously

Determination of Pt(II) and Pt(IV) simultaneously was similar to the extraction GFAAS determination of Pt(II) and Pt(IV). The difference was in the use of both standards in the concentration ratios of 1:5 to 5:1. Determination of total platinum (II and IV) concentration was carried out analogously to the determination of Pt(IV). The concentration of the Pt(IV) was determined as the difference between the total concentration of Pt and the determined concentration of Pt(II).

### 2.3.4. Extraction GFAAS determination of platinum in spiked water samples

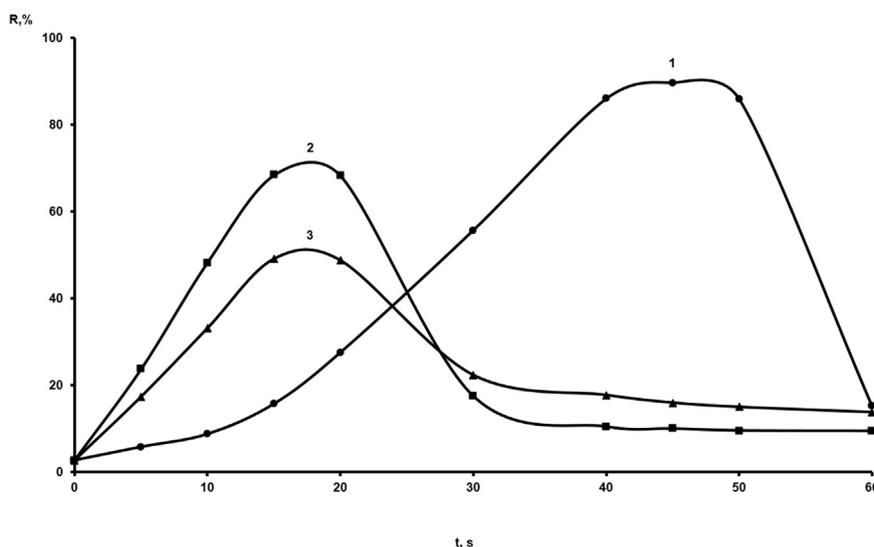
The following were added to a sample of river water (10–25 mL) in the separating funnel: 5 mL  $5 \times 10^{-3}$  mol L<sup>-1</sup> NaSCN solution, 5 mL  $1 \times 10^{-3}$  mol L<sup>-1</sup> TTDI solution, 5 mL 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 8 mL DMF, and the solution was filled to a volume of 50 mL with bidistilled water. The ultrasonic probe at power of 400 W was immersed into the mixture with exposure time of 5 min. After the mixture cooled to room

temperature, 1 mL of toluene was added and the mixture was extracted for 60 s. The extracts were separated and centrifuged and absorbance was measured at a wavelength of 265.9 nm.

## 3. Results and discussion

### 3.1. Conditions for formation and extraction of Pt(II) and Pt(IV)–TTDI ion associates

We see in this system the specific characteristics of platinum. This in particular is the kinetic inertness of some its complexes, associated with a low rate of balance formation due to the slow process of transformation of platinum complexes in aqueous phase [16,17]. It is known that mainly Pt(IV) complexes are inert [16] and are characterized by a low coefficient of distribution in a number of extraction systems. In our case, this is manifested by the protracted reaction with Pt(IV), SCN<sup>-</sup> and TTDI. The addition of the dispersant DMF increases the extraction efficiency [17]. Under optimal conditions we assume that a 1:2 ion associate is formed. The reaction mechanism of the formation and extraction of the ion associates can be described by Eqs. (1)–(7), where S is the extractant, (aq) stands for aqueous phase and (o) stands for organic phase.



**Fig. 4.** Impact of power and exposure time of microwave energy on the Pt(IV)IA extraction with TTDI.  $1 \times 10^{-4} \text{ mol L}^{-1}$  TTDI; pH = 1;  $5 \times 10^{-4} \text{ mol L}^{-1}$  NaSCN;  $2 \times 10^{-6} \text{ mol L}^{-1}$  Pt; 16% DMF;  $V_{\text{aq}}: V_{\text{org}} = 1: 1$ ; (1) P = 100 W; (2) P = 200 W; (3) P = 300 W.

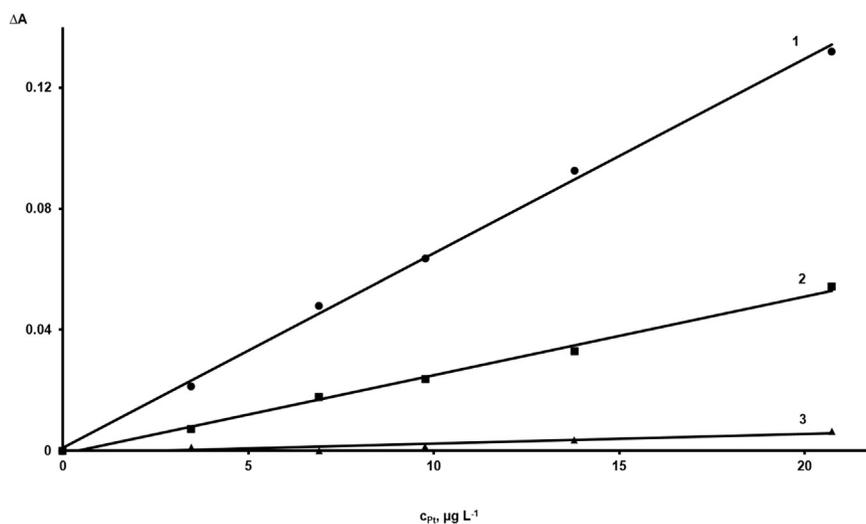
**Table 3**

Some metrological characteristics of platinum(IV) GFAAS determination.

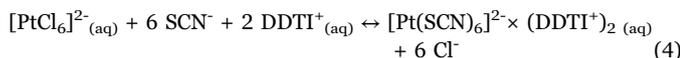
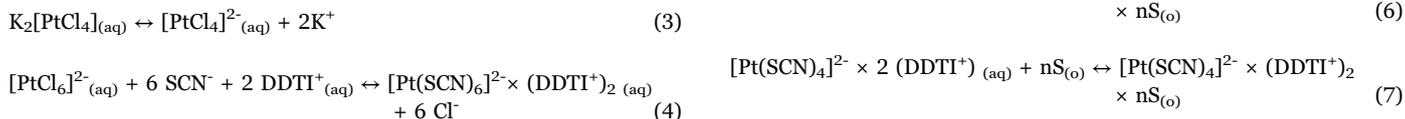
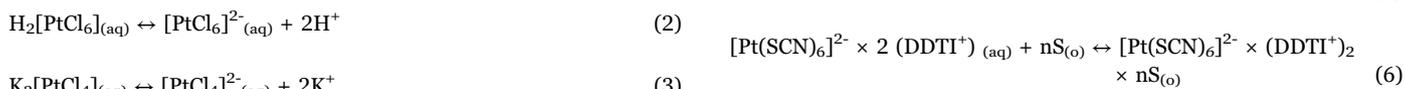
$V_{\text{aq}}: V_{\text{org}}$	Metrological characteristics, $A = a + b \times c \text{ (Pt), } \mu\text{g L}^{-1}$				$R^2$
	c (linearity region)	$a \pm \Delta a$	$b \pm \Delta b$	LOD**	
*	20–1000	$0.001 \pm 0.001$	$(0.235 \pm 0.006) \times 10^{-3}$	7.1	0.9998
2:1	12–500	$0.001 \pm 0.001$	$(0.458 \pm 0.007) \times 10^{-3}$	4.3	0.9998
10:1	3–120	$0.002 \pm 0.003$	$(2.06 \pm 0.01) \times 10^{-3}$	0.9	0.9996
50:1	1–22	$0.001 \pm 0.003$	$(6.40 \pm 0.08) \times 10^{-3}$	0.3	0.9978

\* direct AAS determination.

\*\* LOD calculated as  $3 s/b$  (s is the standard deviation of 10 blank tests, b is the slope of the calibration plot).



**Fig. 5.** Calibration dependences for Pt determination by the GFAAS method.  $1 \times 10^{-4} \text{ mol L}^{-1}$  TTDI; pH = 1;  $5 \times 10^{-4} \text{ mol L}^{-1}$  NaSCN; 16% DMF;  $V_{\text{aq}}: V_{\text{org}} = 50:1$ . (1) Pt(IV); (2) Pt(II) without energy supply; (3) Pt(IV) without energy supply.



**Table 4**

Extractive GFAAS platinum determination in the model samples (V(aq): V(org.) = 50:1; n = 5; P = 0.95).

Sample composition, µg	Determined Pt (IV), µg	Determined Pt (II), µg
0.30 Pt(II) <sup>a</sup>	–	< LOD
0.30 Pt(IV) <sup>a</sup>	< LOD	–
0.30 Pt(II) <sup>b</sup>	–	0.27 ± 0.04
0.30 Pt(IV) <sup>b</sup>	0.21 ± 0.11	–
0.30 Pt(II)	–	0.28 ± 0.06
0.30 Pt(IV)	0.33 ± 0.04	–
1.00 Pt(IV), 3.0 Pt(II)	0.99 ± 0.02	–
1.00 Pt(II), 1.00 Pt(IV)	1.03 ± 0.05	0.97 ± 0.04
0.20 Pt(II), 1.00 Pt(IV)	0.22 ± 0.04	0.98 ± 0.05
1.00 Pt(II), 0.20 Pt(IV)	1.01 ± 0.03	0.18 ± 0.03
0.20 Pt(IV), 30.0 Cu(II)	0.19 ± 0.02	–
1.00 Pt(IV), 15.0 Ag(I)	0.97 ± 0.06	–
1.00 Pt(IV), 7.0 Ru(IV),	1.06 ± 0.09	–
4.00 Rh(IV), 3.5 Ir(IV)	–	–
1.00 Pt(IV), 120 Ni(II),	1.05 ± 0.07	–
120 Co(II), 12 Zn(II)	–	–
VHG-LISAPT-100 <sup>c</sup>	10.05 ± 0.07	–

<sup>a</sup> direct determination without extraction in a sample volume of 25 mL.

<sup>b</sup> direct determination without extraction in a sample volume of 5 mL.

<sup>c</sup> 10 µg Pt declared.

**Table 5**

Determination of platinum in spiked water samples (n = 5; P = 0.95).

Sample	Added, µg	Found, µg	RSD (%)	R (%)
River water	–	Not found	–	–
River water	2.00 Pt(II)	2.09 ± 0.12	6.02	104.5
River water	1.00 Pt(IV)	0.97 ± 0.04	4.33	97.0
Tap water	–	Not found	–	–
Tap water	0.40 Pt(IV)	0.38 ± 0.03	8.28	95.0

To find the optimum conditions for formation and extraction of Pt with TTDI, various effects were investigated (acidity of the medium, TTDI concentration, the effect of various organic solvents non-miscible with water, the concentration of donoractive solvents, order of added reagents, the method of initiating the formation of Pt IA, effect of potential interfering ions, and others). The maximum absorbance value of IA extracts was considered to be optimal. Optimized parameters for the formation and extraction of Pt IA–SCN–TTDI are shown in Table 2.

### 3.1.1. Initiation of complex formation

To speed up the process of sample preparation and make more effective, we examined the possibility of using other forms of energy, such as ultrasonic and microwaves.

#### 3.1.1.1. Application of ultrasonic disintegrator with titanium probe.

Since the use of a conventional ultrasonic bath did not result in any significant results, an ultrasonic disintegrator with a titanium probe was applied for further experiments. Such probes can transmit ultrasonic energy directly into the sample. Comparing with the bath, because the probe is immersed directly into the sample, no potential energy can be absorbed by the medium in the bath and/or by the walls of the vessel containing the sample. The results showed that at the optimum power of 400 W (Fig. 2), the use of this approach reduced the time needed to achieve the maximum extraction efficiency of Pt(IV) IA to 5 min (Fig. 3).

In the case of Pt(II), utilization of the ultrasonic probe for short time (1 min) leads to significant enhancement of the analytical signal. In this case, the absolute values of the analytical signal after achieving balance in the both systems are practically identical. However, in contrast to Pt(IV), the Pt(II) is partially extracted with toluene from the aqueous organic medium at the optimum condition without energy being supplied (but much worse than with the energy added). These differences allow the Pt(II) and Pt(IV) forms to be determined simultaneously.

3.1.1.2. Application of microwave energy. Another way to speed-up the process of Pt(IV)–SCN–TTDI IA formation was to use microwave energy. The use of conventional microwave devices did not lead to any significant results. The reason could be the insufficient or non-homogeneous focus of the radiation power on the sample. Therefore, a CEM Discover microwave reactor with the transmission power focused on the sample, additive mixing, cooling and temperature and performance control was used for further research.

The results showed (Fig. 4) that a higher generated power of microwave energy achieves the absorbance maxima of extracted Pt(IV) IA with TTDI in a very short time (12–16 s), but the analytical signal is much lower than with lower power. The reason for this result may be the fact that the high energy of the microwave radiation causes decomposition of some components in the mixture. Significant prolongation of the optimal time at the lowest power could be caused by the exponential decline of temperature with decreasing power of the microwave energy.

### 3.1.2. Effect of order of added components

During the daily measurements in the Pt(II)–SCN–TTDI system without an energy supply, an occasional change of repeatability, and in case of change of the experimenter, reproducibility, was observed. Upon searching for the reasons for this, it became known that the reason was the order of addition of components to the reaction mixture. The maximum recovery is achieved by adding the components in the order H<sub>2</sub>O; H<sub>2</sub>SO<sub>4</sub>; Pt; NaSCN; TTDI and DMF.

### 3.1.3. Effect of interfering ions

The effect of interfering ions on the extraction of platinum expresses the factor of selectivity, i.e. the ratio of the concentration of an interfering ion to the concentration of platinum, in which the change in platinum signal does not exceed 5%. The selectivity of these extraction systems depends particularly on the concentration of rodanide ions. Platinum creates very stable rodanide complexes; therefore, maximum extraction occurs at a minimum abundance of rodanide ions. This could explain the high selectivity. The proposed procedure is not influenced by a number of elements which are able to form stable rodanide complexes (alkali metals, alkaline earth metals, Al, Mn, Ni, Co, Cr, Pb, In, Cu, etc.).

Under optimal conditions for the formation and extraction of ion associates the determination of platinum is not affected either by 10<sup>3</sup>–10<sup>4</sup>-times concentration of the alkali metals, alkaline earth metals, Al, Mn, Ni, Co, Cr and In; 250-times concentration of Cu and Pb; 100-times concentration of Cd and Zn; 60-times concentration of Ir; 30-times concentration of Ru; 20-times concentration of Ag; 10-times concentration of Rh; and 3-times concentration of Hg.

Pt(II) is extracted in the form of IA under optimum conditions without previous energy supply (microwave and ultrasound energy) and Pt(IV), because it is more inert than Pt(II), and it is extracted in the form of IA only after preliminary energy addition. On the basis of these differences, both forms of platinum may be determined simultaneously in concentration ratios 5:1 to 1:5.

## 3.2. Extraction preconcentration of platinum

The recovery of Pt IA with toluene is very high. This enables extraction preconcentration and a significant decrease in the limit of detection of Pt determination using the AAS method. The impact of the aqueous and organic phase ratio on the Pt IA extraction was studied. Experiments were performed such that the concentration of each component of the aqueous phase, except that of platinum, remains constant; only the total amount of the aqueous phase changes. It was found that increasing the aqueous phase volume in regard to the organic phase to a ratio of 50:1 the extraction separation and preconcentration of platinum may be connected in a single step, and the limits of detection for platinum determination by the AAS

**Table 6**  
Some AAS methods of determination of Pt with preconcentration.

Sample	Sample treatment	Detection	Analytical form of Pt	LOD, $\mu\text{g L}^{-1}$	Average analysis time (except of sample collection and/or digestion) (h)	Preconcentration factor	Ref.
catalyst, vegetation, soil, water samples	preconcentration on a column packed with silica gel functionalised with 1,5-bis(di-2-pyridyl)methylene thiocarbonylhydrazide	ETAAS	Pt(IV)	0.8	29	41.7	21
magmatic rocks; CRMs	preconcentration on modified activated carbon	GFAAS	Pt(IV)	0.96	> 6	50	22
salmetrol xinafoate and Ca-folinate	preconcentration after reduction by iodide or sulphite ions on oxime, sulphoxine and 2,2-diamino-diethylamine cellulose microcolumns	GFAAS, TXRF	Pt(II)	0.21; 0.18 and 0.30	> 6	20	10
spiked soil and water samples; CRMs	sequential extraction procedure, preconcentration using a vesicular coacervative CPE	GFAAS	PtCl <sub>6</sub> <sup>2-</sup> cisplatin, carboplatin	0.5 $\mu\text{g kg}^{-1}$	> 3	20	20
environ-mental samples	separation on a dithizone sorbent; elution with thiourea or nitric acid	GFAAS	Pt(IV) reduction to Pt (II)	1.0 $\mu\text{g kg}^{-1}$	> 18	not reported	23
motor vehicles exhaust fumes	fumes filtered through cellulose filter papers to collect suspended particles expelled along with the engine's escape fumes; dissolution	GFAAS	Pt(IV)	6.2	> 6	not reported	24
mine samples; CRMs	adsorption on the as-synthesized magnetic nanoparticles functionalized with 4'-aminobenzo-15-crown-5- ether packed into a micro-column	FI-column-GFAAS	Pt(IV)	1.01	> 3	17.8	25
swabs	CPE method in aqueous solution with diethyldithiocarbamate (DDTC) as chelating agent and Triton® X-114 as extraction medium	GFAAS	Pt(IV) or Pt(II)	0.2	> 4	29	19
spiked tap and waste water	selective accumulation of platinum on baker's yeast in batch mode; biosorption of platinum on algae <i>C. vulgaris</i> covalently immobilized on silica gel in flow mode;	GFAAS	Pt(IV)	0.4	> 3	not reported	26
road dust	biosorption of Pt(IV) on <i>Aspergillus</i> sp. immobilized on cellulose resin	ETAAS	Pt(IV)	0.02	> 24	9.7	27
plasma ultrafiltrate	Cellex-T sampling of a total volume of 150 $\mu\text{L}$ of plasma ultrafiltrate by 3 successive additions of 50 $\mu\text{L}$ separated by drying steps	GFAAS	Pt(IV)	5.0	> 1	4.29	28
plasma spiked tap and sea water; CRMs	in situ electrodeposition	ETAAS	Pt(IV)	2.54	< 1	not reported	29
spiked foods and beverages	SPE, hybrid adsorbent composed of cellulose fiber, activated carbon, and anion exchange resin Dowex 1x8	GFAAS	Pt(IV)	0.014	> 3	100	18
blood plasma and urine	on-line preconcentration on a column packed with silica gel functionalised with 1,5-bis(di-2-pyridyl)methylene thiocarbonylhydrazide	GFAAS	Pt(IV) and Pt(II)	2.3	< 1	25.7	11
pure copper and anodic slime samples	speciation of platinum by CPE in the presence of 4-(p-chlorophenyl)-1-(pyridin-2-yl)thiosemicarbazide (HCPTS) as chelating agent and Triton X-114 as a non-ionic surfactant	GFAAS	Pt(II) and Pt(IV)	0.08	> 1	42	12
Catalytic converters and natural water	halogeno complexes recovered using an Amberlite XAD-7 column	FAAS	Pt(II)	102.5	> 3	not reported	13
spiked river and tap water; model samples	SPE on Amberlite XAD-7 adsorption resin	FAAS	Pt(II)	103	> 3	not reported	14
	formation of Pt ion associates with SCN <sup>-</sup> and basic agent (TTDI), extraction by toluene	GFAAS	Pt(IV) and Pt(II)	0.3	< 1	50	this work

method are considerably reduced. Based on the constructed calibration curves, important parameters of extraction AAS determination of platinum were calculated (Table 3).

Extraction preconcentration of Pt IA with TTDI enables reliable AAS determination of trace amounts of platinum. The LOD achieves the value  $0.3 \mu\text{g L}^{-1}$  Pt, which is 24-times lower than the LOD of direct Pt AAS determination. Fig. 5. shows calibration plots for extractive Pt(IV) and Pt(II) determination by GFAAS. In comparison with Pt(IV), Pt(II) is particularly extracted without previous energy addition. These species can be reliably determined simultaneously in concentration ratios of 5:1 to 1:5.

### 3.3. Analytical application

As a supplementary confirmation of the applicability of the method, model samples containing various quantities of Pt(II) and Pt(IV) were prepared and tested. As can be seen in Table 4, the precision and accuracy of the technique is good. The method was applied for platinum determination in tap water and river water samples. The obtained results (Table 5) show that the determination has good reproducibility, with sufficient precision and accuracy.

## 4. Conclusions

Determination of Pt in real samples requires preconcentration and/or separation of Pt, such as by adsorption, coprecipitation and chlorination, which significantly complicates and prolongs the process of analysis (Table 6). Extraction techniques have been used for pretreatment in only a few articles, and these were predominantly solid phase extraction (SPE) [14,18] and cloud point extraction (CPE) [12,19,20]. CPE is a very efficient and powerful technique, but the price to pay for it is a complicated execution, its vulnerability to small temperature differences and the time demands of the process.

We herein suggest a novel analytical procedure for sensitive and rapid extractive GFAAS speciation of Pt(II) and Pt(IV) forms. This research showed fundamental differences in the Pt(II) and Pt(IV) extraction relating to the varying inertness of the relevant acid complexes. Pt(II) was extracted under standard conditions, and Pt(IV) only after the addition of energy. In both cases, it is possible to intensify the extraction as well as the platinum-related analytical signal by application of ultrasonic and microwave energy. At optimal ultrasonic generator power of 400 W, 5 min is needed to achieve maximum Pt(IV) IA extraction efficiency, whereby the efficiency of Pt(II) IA extraction is achieved in just 1 min. At microwave energy generator power of 200 W, the time for achieving maximum Pt(IV) IA extraction is reduced to 12–16 s, but the analytical signal is much lower than with lower power (100 W) and a longer extraction time. On the basis of the conditions for IA formation and extraction found, a new Pt(II) and Pt(IV) speciation procedure is proposed. These species can be reliably determined simultaneously in concentration ratios of 5:1 to 1:5. The proposed procedure was successfully applied for Pt determination in the model and in spiked water samples.

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