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Platinum uptake by mustard (*Sinapis alba* L.) and maize (*Zea mays* L.) plants

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Abstract The ability of platinum uptake by hydroponically cultivated plants – Indian mustard (*Sinapis alba* L.) and Anawa maize (*Zea mays* L.) – was investigated. The efficiency of the transport of platinum compounds from the roots to above ground organs was estimated. For platinum determination in plant samples, digested in closed system with microwave energy, very sensitive analytical methods were applied – adsorptive stripping voltammetry (AdSV) and mass spectrometry with inductively coupled plasma (ICP-MS). For validation of the obtained results the recovery of platinum was examined. The accumulation factors (AF) of platinum: more then 800 and 400 for roots of Indian mustard and Anawa maize, respectively and about 90 and 30 for above ground organs of both species were found.

Key words platinum • plant samples • voltammetry • mass spectrometry with inductively coupled plasma (ICP-MS)

Introduction

The interest in studying platinum group metals biocycles in the environment is just a consequence of introducing modern cars equipped with catalytic converters, that reduce conventional air pollution up to 90%, simultaneously releasing nobel metals: platinum (Pt), palladium (Pd) and rhodium (Rh). It is estimated that between 0.5–0.8 μg of Pt can be emitted by one car per 1 km of the road, most of which is found in a distance of 1 to 3 m from the road [3]. Highest amount of these elements was found in the soil but due to atmospheric dispersion they are trapped by plant hairs and glutinous leaf surface. Increased deposition of platinum on the flora surrounding streets and highways brought out some concern about this accumulation at possible toxic levels – especially platinum oxide – but data on the bio-circulation of nobel metals are scare.

Uptake of elements from platinum group is documented for grasses and cucumbers [8] therefore, it can be assumed that, similarly to heavy metals, there are plant species that possess ability to accumulate nobel metals.

The aim of this work was to evaluate the ability of mustard plants and maize for platinum uptake and translocation to above ground organs.

As platinum concentration in the environmental samples is rather low for the determination of this element a very sensitive analytical methods should be applied. For this purpose mainly mass spectrometry with inductively coupled plasma (ICP-MS) [4, 6, 7, 9] and voltammetry [1, 5, 9] are used. Both these methods let to determine platinum at ng and sub-ng level.

During the presented studies platinum determinations were carried out by ICP-MS. Adsorptive stripping voltammetry (AdSV) was applied as a reference method. Plants were digested in closed system with microwave energy.

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Experimental methods

Reagents

- HNO_3 (d = 1.40 g mL^{-1}), HCl (d = 1.15 g mL^{-1}), H_2SO_4 (d = 1.84 g mL^{-1});
- $HClO_4$ (d = 1.67 g mL^{-1}), Suprapur (Merck);
- standard solution of Pt(II) containing 1 mg mL^{-1} was prepared from ampoules AAS standard (Merck); formaldehyde, hydrazine sulphate (POCh Gliwice, Poland).

All solutions were prepared using deionized water from Milli-Q-Water-System, Millipore (USA).

Apparatus

- Polarographic analyzer μAUTOLAB (The Netherlands) and an electrode system: HMDE as a working electrode, saturated Ag/AgCl as a reference electrode and glassy-carbon as an auxiliary electrode. Determinations were carried out in a quartz voltammetric vessel.
- Inductively Coupled Plasma Mass Spectrometer SCIEX "Elan 6100 DRC" Perkin Elmer (USA).
- Domestic microwave oven Sharp, R-5A51 (850 W) (Japan).
- Hg-lamp 125 W (Poland).
- Low-pressure vessels type P/N 323000, CEM (USA) (max. pressure 13.8 bar).
- Laboratory mill, Fritsch (Germany).

Plant cultivation

The seedlings were grown in greenhouse in terms: 16 h light and 8 h night by relative humidity of air 50%. Seeds of mustard and maize were sown into artificial medium (glass balls) and seedlings at cotyledon stage were placed in containers with nutrient solution [2]:

$Ca(NO_3)_2$ – 1003 mg L^{-1}, KNO_3 – 583 mg L^{-1}, $MgSO_4$ – 513 mg L^{-1}, KH_2PO_4 – 263 mg L^{-1}, NH_4NO_3 – 488 mg L^{-1}, $MnSO_4$ – 6.1 mg L^{-1}, H_3BO_3 – 1.7 mg L^{-1}, $Na_2MnO_4 \cdot 2H_2O$ – 0.37 mg L^{-1}, FeNa EDTA – 79.0 mg L^{-1}, $CuCl_2 \cdot 2H_2O$ – 0.39 mg L^{-1}, $ZnSO_4$ – 0.44 mg L^{-1}.

To the nutrient solution platinum, in a form of $[Pt(NH_3)_4](NO_3)_2$, was added in amount 500 mg L^{-1}. All the time the solutions in the containers were aerated.

Samples pretreatment

When the hydroponic cultivation was finished plants were collected and roots were washed three times with deionized water. Then the plants were divided into roots, leaves and stems. Plant material was oven dried at 105°C for 3 h followed by 24 h at 75°C. Thus the obtained dry material was ground in an agate mill. Homogenized samples were stored in 50 mL PE bottles.

Microwave decomposition of the samples

About 250 mg of sample was weighed into CEM Teflon vessel and a mixture of 1 mL HNO_3, 1 mL $HClO_4$ and 0.5 mL HCl was added. The vessel was screwed up tightly and placed in the microwave oven. Heating of the sample was carried out in several cycles increasing time and power of microwave energy with 2 min waiting time between the cycles (3 min 255 W, 4 min 425 W, 5 min 595 W, 6 min 850 W). After cooling down it was quantitatively transferred into volumetric flask (25 mL) and diluted to the mark with deionized water. Before voltammetric determination the sample solution was placed in quartz tube, 50 μL H_2O_2 (30%) was added, and the UV irradiation was done for 6 hours.

Voltammetric determination

In the quartz crucible 10 mL deionized water, 200 μL conc. H_2SO_4, 100 μL HCHO (2 mol L^{-1}), 100 μL $N_2H_2 \cdot H_2SO_4$ (15 mmol L^{-1}) were placed.

The solution was purged with argon gas for 15 min. The preconcentration was carried out at the potential of 0.0 V in a stirred solution for 15 s. After the resting time of 10 s the voltammetric curve – base line – was recorded in the potential range from –0.57 to –1.0 V using differential pulse technique with scan rate 20 mV s^{-1} and amplitude 50 mV.

Then an aliquot of the sample solution was added and voltammetric determination was continued. The catalytic current of the hydrogen reduction was recorded at about –0.9 V.

For quantitative determinations the double standard addition method was used.

In all cases the automatic subtraction of base line was performed.

ICP-MS determination

ICP-MS measurements were performed with following parameters: sweep 5, replicates 5, dwell time 0.1 s, ICP RF power 1100 W, lens voltage 7 V, nebulizer gas flow 0.98 l min^{-1}, plasma gas flow 15 l min^{-1}, measured isotope ^{96}Pt. Quantitative Analysis Program, automatically corrected intensities for interferences from isobaric and molecular ions, was used. For quantitative determinations the calibration curve method was applied.

Results and discussion

Before platinum determination in plant materials some experiments with standard solutions were carried out. For platinum determination two analytical methods were applied – mainly mass spectrometry with inductively coupled plasma (ICP-MS) and as a reference one – adsorptive stripping voltammetry (AdSV) at a hanging mercury drop electrode. As both applied methods require liquid samples, before determination the digestion procedure had to be carried out.

To shorten the duration of this analysis stage pressurized digestion with microwave energy source was used. Additionally as adsorptive stripping peaks are seriously affected by the presence of organic compounds, to assure complete decomposition of samples additional UV irradiation of the digested solutions obtained after microwave digestion was performed. To control this analysis stage

Table 1. Recovery of platinum in the digestion step (mean ± $t_{95\%}$SD).

Analytical method	Pt added [ng]	Pt found [ng]	Recovery [%]
ICP-MS	100.0	101.1 ± 7.3	101
AdSV	100.0	111.4 ± 2.4	111

100.0 ng of Pt and mixture of nitric, perchloric and hydrochloric acid were placed in the teflon vessels and digestion procedure was carried out according to the previously described procedure [5]. The determinations of platinum by ICP-MS and AdSV in obtained solutions showed good recovery of the analyte – 101% and 111% (Table 1).

Then described procedures were applied for determination of platinum content in analysed plants organs – leaves, stems and roots in case of Indian mustard and shoots and roots in case of Anawa maize. The obtained results are presented in Table 2. To control the quality of the analysis in one of the samples – leaves of Indian mustard 1 – platinum content was determined by adsorptive stripping voltammetry (Fig. 1). Good agreement was obtained (42.9 ± 0.3 μg g^{-1} by ICP-MS and 39.5 ± 1.0 μg g^{-1} by AdSV).

Based on the studies it can be concluded that both plant species have uptaken platinum from the growing medium in considerable high amounts. Platinum was translocated to all plant organs, although they essentially differed in platinum concentration. In case of Indian mustard platinum concentration in roots (444 μg g^{-1}) was about 10 times higher than in leaves and stems (about 44 μg g^{-1}). While in case of maize concentration of platinum in roots (239 μg g^{-1}) was nearly 20 times higher than in shoots (12.2 μg g^{-1}) (Table 2).

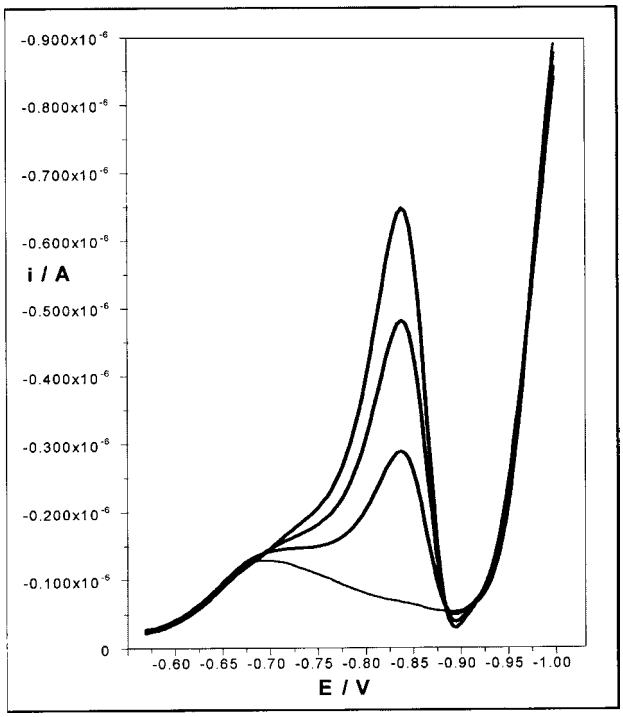

Fig. 1. Quantification of platinum in digested Indian mustard sample (39.5 ± 1.0 μg g^{-1}) by double standard addition (100 and 200 pg of platinum).

In case of total amount of accumulated Pt these differences are less evident (Fig. 2). Roots accumulated 3–4 times more than above ground organs for mustard plants and 6–7 times for maize. Summarizing it can be emphasize

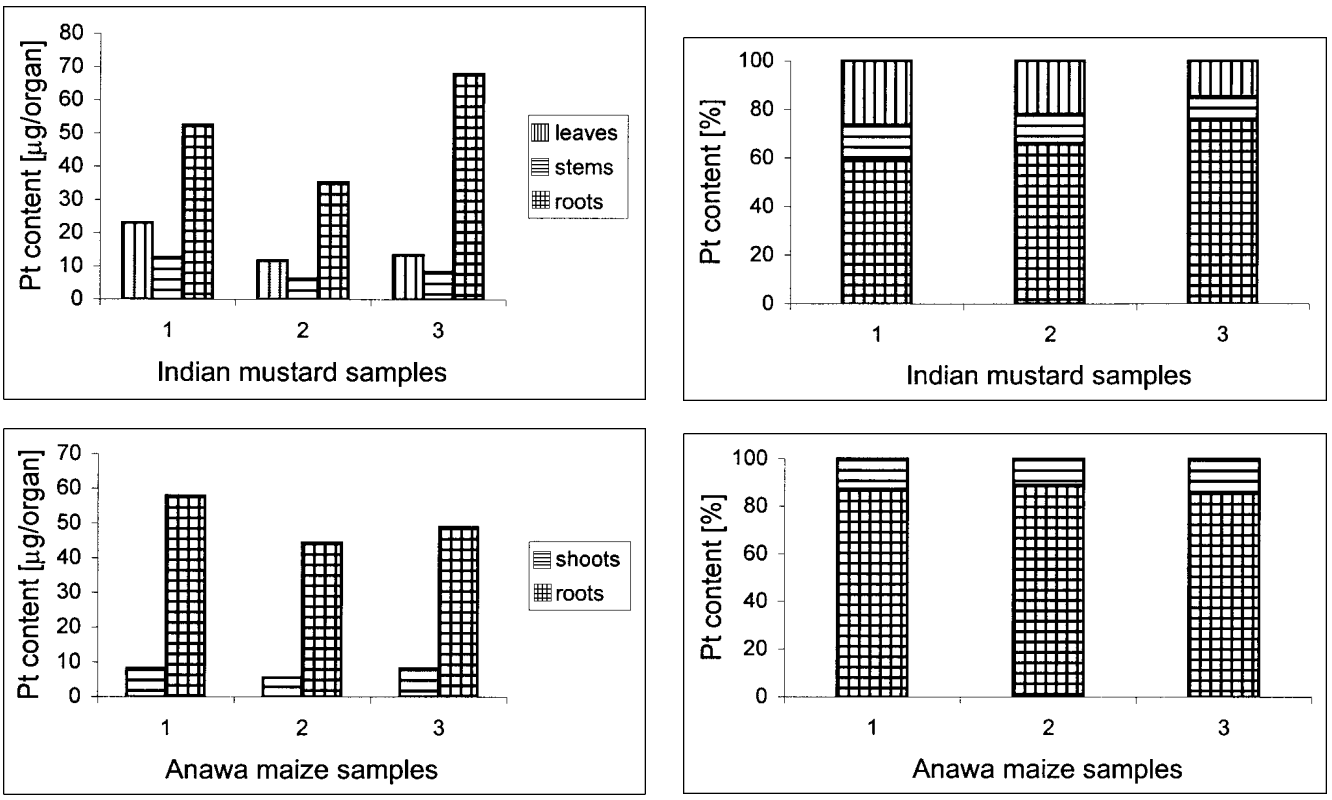

Fig. 2. Platinum content in analysed organs of Indian mustard and Anawa maize.

Table 2. Results of platinum determination in plants (mean ± $t_{95\%}$SD).

Sample		Platinum content [μg g^{-1}]		
Indian mustard	leaves	42.9 ± 0.3	36.4 ± 0.4	34.1 ± 0.3
	stems	44.8 ± 0.1	49.9 ± 0.4	48.4 ± 0.1
	roots	444 ± 6	349 ± 2	470 ± 2
Anawa maize	shoots	12.2 ± 0.3	13.8 ± 0.6	13.5 ± 0.2
	roots	239 ± 4	244 ± 18	182 ± 5

Table 3. Accumulation factors (AF) of platinum in analysed plant organs.

Sample		Accumulation factor		
Indian mustard	leaves	85.8	72.8	68.2
	stems	89.6	99.8	96.8
	roots	888	698	940
Anawa maize	shoots	24.4	27.6	27.0
	roots	478	488	364

that Indian mustard transport platinum to the above ground organs much more effective than maize.

Accumulation factor (AF) defined as the ratio of Pt concentration in plant organ to Pt concentration in nutrient solution can be estimated as (Table 3): for Indian mustard 840 for roots, 95 for stems and nearly 76 for leaves, while for Anawa maize it was 444 and 26 for roots and leaves, respectively.

To conclude it can be said that both studied plant species posses tolerance to relatively high Pt concentration in nutrient solution and efficient Pt uptake and translocation to above ground parts. As we could observe, plants exposed to Pt did not differ from control ones, both in morphology and in biomass production. So it can be assumed that they are tolerant to the toxicity of the investigated element at least at the level of 500 μg L^{-1} Pt.

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