THE ISOTOPE-DILUTION DETERMINATION OF PLATINUM IN SOIL BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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A method of the determination of trace amounts of platinum in soils has been developed and validated. Samples were ignited, spiked by ^{198}Pt and decomposed by acid digestion ($HF–HClO_4$, $HCl–HNO_3$). Platinum was separated from the matrix by tellurium coprecipitation (recovery 55–87%) and its content was calculated by the (^{194}Pt + ^{195}Pt + ^{196}Pt)/^{198}Pt ratio measurement. In spite of the separation step (hafnium and tungsten recovery below 1%), residual spectral interference caused by HfO^+ ions was observed. This interference as well as that of ^{198}Hg were removed by mathematical correction. Accuracy of the method was confirmed by analysis of certified reference material and by the standard addition method. Detection limit of the method was 0.08 ng g^{-1} Pt. It was found out that the main component of the standard uncertainty of results was sampling uncertainty. Analysis of soil samples taken in the neighbourhood of Hřensko (Northern Bohemia) showed high platinum contents near the road with heavy traffic.

Key words: Platinum; Isotope dilution; Mass spectrometry; Soil.

Platinum and its compounds are used in industry, pharmacy and in other branches of human activity. Since the seventies, when platinum began to be used in car catalytic converters, there have been discussions about significance of emission for environment. Platinum (Pt) is released from catalytic converters probably due to mechanical and thermal impact and therefore Pt is present in car exhaust fumes[1]. However, some platinum compounds are highly toxic, even in small doses, and they are severe irritants[2]. Other platinum compounds have anticancer effects, which was for the first time reported in 1969 (ref.[3]), and are used in chemotherapy[4]. Despite the fact that catalytic converters are considered a main source of platinum contamination in the neighbourhood of roads, platinum content in contaminated soils is very low. Farago *et al.*[5] reported results of analysis of roadside soils from south London, where the mass fraction of Pt ranged from 0.3 to 8 ng g^{-1}. The fact that platinum might have entered the food chain was the reason for elaboration of methods of rapid evaluation of the platinum content in various environmental samples such as dust[5–9], soil[5,10,11] or biological materials[6,7,12–15]. On the other hand there are a whole numbers of publications for platinum determination for geological and geochemical purposes[16–20].

The determination of platinum in real samples can be performed by many instrumental methods, *e.g.* graphite furnace atomic absorption spectrometry[19] (GFAAS), inductively coupled plasma atomic emission spectrometry[21–23] (ICP-AES), inductively coupled plasma mass spectrometry[6–8,13,18,22,24,25] (ICP-MS) or neutron activation analysis[26,27] (NAA), which often require total sample decomposition. Owing to low content of Pt in most samples it is often necessary to preconcentrate elements of interest. For sample enrichment are used preconcentration method such as extraction[10], tellurium coprecipitation[17,27] or adsorptive chromatography[13,15,21,22]. Nickel sulfide fire assay is a favourite technique among geologists[18,20]. Summary of techniques and detailed information are available in reviews[28–31].

The aim of this study is the validation of determination of platinum trace (up to 10 ng g^{-1}) in soil using isotope dilution ICP-MS. The fact that the isotope dilution (ID) is the primary method with direct tracebility to the SI unit system, is an important argument for propagation of this technique. In the determination of Pt by ICP-MS, polyatomic ions YbO^+, TaO^+, WO^+ and in particular HfO^+ (refs[6,24,25]) and mercury isotopes ^{196}Hg, ^{198}Hg interfere. Therefore the separation step was included in the procedure. In fine, as a show of ability of the method, analysis of soil samples is reported from the neighbourhood of Hřensko.

EXPERIMENTAL

Standards and Reagents

Hydrochloric acid, nitric acid (Penta, Chrudim, Czech Republic) and perchloric acid (Carlo Erba, Milano, Italy) were of analytical grade, hydrofluoric acid 40 wt.% was of Suprapur® grade (Merck, Darmstadt, Germany). Iridium stock solution 1 g l^{-1} (Merck, Darmstadt, Germany) served for preparation of internal standard solution for some non-ID measurements. Deionized water (Millipore, Bedford (MA), U.S.A.) was used for preparation of all solutions.

Isotope enriched standard. Reference platinum standard (Oak Ridge National Laboratory, Oak Ridge (TN), U.S.A.) contained 95.71% of ^{198}Pt, 2.23% of ^{196}Pt, 1.23% of ^{195}Pt and 0.83% of ^{194}Pt (atomic per cent). It was weighed 10.28 mg of this standard with uncertainty of 0.02 mg (ref.[32]), dissolved in 4 ml of aqua regia and quantitatively transferred into a weighed 100-ml volumetric flask. The volume was filled to the mark with 1 M HCl and the flask with solution was weighed again. The mass fraction of Pt in this stock solution was approximately 100.0 ± 0.2 μg g^{-1} Pt. The working isotope enriched standard ^{198}Pt solution of mass fraction 10.00 ± 0.02 ng g^{-1} Pt was prepared by dilution of the stock solution and was always prepared before use. The uncertainty of the final mass fraction consist of uncertainty of weighing the of the reference platinum standard only. The uncertainty of dilution step is less by one order of magnitude and plays insignificant role. During calculation of mass fractions the weights of all solutions were corrected for air buoyancy.

Natural platinum solution. Stock solution was prepared by dissolution of 0.1021 g of Pt (99.99%, Safina, Vestec, Czech Republic) in aqua regia and quantitatively transferred into a weighed flask. The volume was made up to 100 ml with 1 M HCl and the flask with solution was weighed again. A working solution of the mass fraction 20 ng g^{-1} Pt was prepared by dilution in two steps. Standard uncertainty of this mass fraction was 0.01 ng g^{-1}. The solution was always prepared just before use. Isotopic composition of natural platinum follows: 7.16% of ^{198}Pt, 25.24% of ^{196}Pt, 33.80% of ^{195}Pt, 32.97% of ^{194}Pt, 0.78% of ^{192}Pt and 0.01% of ^{190}Pt (atomic per cent)[33].

Tellurium chloride solution. Tellurium (0.1 g) was dissolved in 5 ml of aqua regia and the solution was evaporated to dryness. The residue was three times dissolved in 2 ml of 6 M HCl and evaporated to dryness. Then the residue was dissolved in 2 M HCl, transferred into a PE bottle and the volume was made up to 100 ml with the same acid.

Tin(II) chloride solution (1 mol l^{-1}). The solution was prepared before use in a required amount. It was weighed 26.5 g of $SnCl_2 \cdot 2H_2O$ and dissolved by gentle heating in 15 ml of concentrated HCl. The solution was transferred into a PE bottle and the volume was made up to 100 ml with water.

Instrumentation

All measurements were done using an Elan 6000 mass spectrometer (Perkin–Elmer/Sciex, Norwalk (CT), U.S.A.) with a quadrupole analyzer. The tellurium precipitate was filtrated under vacuum through a paper filter Filtrak (Germany) No. 390 using a Sartorius apparatus (Göttingen, Germany).

Sample Decomposition and Preparation for Measurement

Soil sample (2 g) was weighed into a porcelain crucible and ashed over the burner. After cooling the sample was quantitatively transferred into a 150-ml Teflon beaker and 0.5 g of the working isotope enriched standard ^{198}Pt solution was added. After sample humectation with deionized water, 5 ml of concentrated HNO_3 was added and the sample was heated (70 °C) to be partly oxidized. The sample was evaporated to get moist salts and after cooling, 20 ml of concentrated HF and 2 ml of concentrated $HClO_4$ were added. The mixture was gradually heated until fumes of perchloric acid appeared. To the cooled mixture, 30 ml of aqua regia was added and the beaker was covered with a watch glass. The mixture was slowly heated (1 h), then it was heated to the boil for 3.5 h. After cooling the mixture (70 °C) and evaporation of acids to get moist salts, 5 ml of concentrated HCl was added. The mixture was again evaporated to get moist salts to remove nitric acid. Then 40 ml of deionized water and 5 ml of concentrated HCl was added to the prepared sample. The sample was heated to 50–60 °C for another 1 h. Then it was transferred into a 250-ml glass beaker, 15 ml of concentrated HCl were added, and the volume was made up to approximately 100 ml with deionized water. Tellurium solution (2 ml) was added to the boiling solution. Under permanent heating, 10 ml of tin(II) chloride solution was slowly added. The solution was boiled for a few minutes until the precipitate coagulated and then the tellurium solution (1 ml) was added again. The sample was boiled for another 5–10 min, then removed from the hot plate and cooled[17]. The mixture was filtered through a paper filter under moderate vacuum. The precipitate was rinsed with *ca* 100 ml of hot dilute 1 M HCl. The paper filter with the precipitate was transferred back into the beaker. The precipitate was treated with 3 ml of concentrated HCl and then dissolved by addition of a few drops of hot concentrated HNO_3 (*ca* 2 ml). The filter was then washed with deionized water (1–2 ml) and discarded. The sample was heated to boiling, then its temperature was decreased and the sample was evaporated to dryness. The residue was dissolved in 2 ml of HCl (1 : 1) and transferred into a 50-ml PE flask. The blank samples were prepared in the same way.

Isotope Ratio Measurement and Calculation

The isotope composition of natural platinum and the choice of ^{198}Pt as a reference isotope enables measurement of various numbers of isotope ratios, from ^{194}Pt/^{198}Pt to ^{196}Pt/^{198}Pt and their combinations. The choice of the (^{194}Pt + ^{195}Pt + ^{196}Pt)/^{198}Pt ratio leads to the most sensitive determination. The dependence of theoretical value of this isotope ratio f and sensitivity of the determination df/dw_{Pt} on platinum content in a sample dw_{Pt} is shown in Fig. 1. It was found by repeated measurements of solution sets prepared by weighing and dilution of isotope-enriched and natural platinum solutions that the chosen isotope ratio leads to the most precise and accurate results in comparison with other ratios. The operating conditions of the mass spectrometer are given in Table I.

Calculation of the platinum content in the sample from the measured isotope ratio was done according to the formula:

$$w_{Pt} = \frac{w_S\, m_S\, A_{1S} - f\, w_S\, m_S\, A_{2S}}{f\, m\, A_{2N} - m\, A_{1N}}\,\frac{M_N}{M_S}\ , \qquad (1)$$

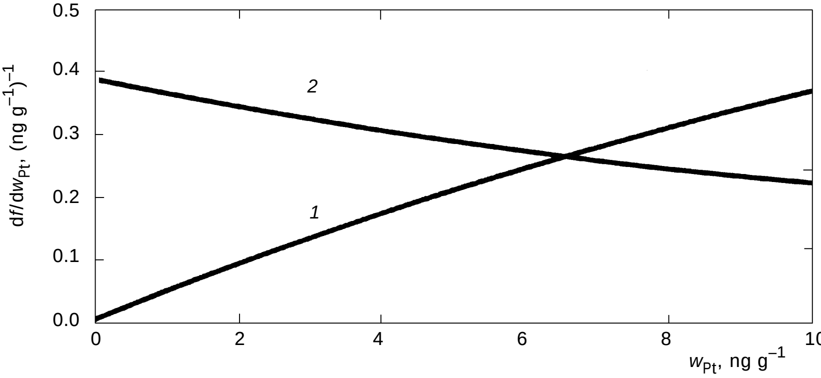

FIG. 1

Dependence of sensitivity df/dw_{Pt} and the measured ratio f on the platinum content w_{Pt} in a sample; *1* measured ratio f, *2* sensitivity of the determination df/dw_{Pt}

where w_{Pt} is the mass fraction of platinum in the sample [ng g^{-1}], w_S is the mass fraction of platinum in the working isotope enriched standard ^{198}Pt solution [μg g^{-1}], m_S is mass of spike of this solution [mg], m is sample weight [g], f is the measured isotope ratio of selected Pt isotopes corrected for mass discrimination, M_N is molar mass of natural platinum, M_S is molar mass of isotope enriched platinum, A_1 are abundances of chosen platinum isotopes (in this case the sum of ^{194}Pt, ^{195}Pt and ^{196}Pt) in the natural platinum (subscript N) and in the isotope enriched platinum (subscript S), and A_2 are abundances of the reference Pt isotope (^{198}Pt) in the natural platinum (subscript N) and in the isotope enriched platinum (subscript S).

Correction for mass discrimination was obtained by measurement of the correction solution with the known value of the isotope ratio. The weights of the isotope enriched solution (5.1110 g of mass fraction 101.0 μg g^{-1}) and solution of natural platinum (0.5202 g of mass fraction 988.9 μg g^{-1}) were used for the preparation of the stock correction solution. The working solution with mass fraction of natural platinum approximately 0.1 ng g^{-1} was prepared by subsequent dilution of the stock correction solution.

RESULTS AND DISCUSSION

Efficiency of the Platinum Separation

The effect of the HCl concentration on the separation efficiency was tested by analysis of six solutions containing the same amount 50 ng of platinum, 5 μg of hafnium and 5 μg of tungsten in 100 ml of HCl diluted subse-

TABLE I
Operating conditions of ID-MS measurements

Auxiliary gas	argon
Outer gas	argon
Plasma power	1 075 W
Nebulizer	cross-flow
Nebulizer gas flow rate	0.8 l min^{-1} (daily optimized)
Run mode	peak hopping
Dwell time	75 ms
Scan/reading	40
Replicates	10
Run time per isotope	30 s
Sample consumption	1 ml min^{-1}
Observed isotopes	^{194}Pt, ^{195}Pt, ^{196}Pt, ^{198}Pt, ^{180}Hf, ^{202}Hg, ^{181}Ta and ^{182}W

quently in the ratios 1 : 3, 1 : 3.5, 1 : 4, 1 : 4.5, 1 : 5 and 1 : 6. The platinum recovery was in the range 72–79%, the hafnium recovery in the range 0.25–1% and the tungsten recovery in the range 0.29–0.8%. No relations were found between the platinum recovery and HCl concentration. The method of standard addition was used for further confirmation of the separation efficiency in natural matrix. Ten soil samples were decomposed and the resulting solutions were combined to make a mixture and subsequently divided back to make 10 samples again. Five of them were spiked by 10 ng Pt. The platinum recovery was in the range 55–87%. This relatively low recovery does not significantly affect results of analysis since the isotope ratio of Pt isotopes is measured instead of the Pt intensity.

Interferences

In spite of the separation step was included, interferences caused by hafnium oxides ($Hf^{16}O$) on given platinum isotopes were observed. The interferences of hafnium oxides were eliminated by mathematical corrections based on the measurement of HfO/Hf ratio which was experimentally found out by analysis of hafnium solution (2 ng ml^{-1}) before and during each measurement run. The intensity of ^{180}Hf isotope was corrected for isobaric overlay with ^{180}Ta and ^{180}W isotopes through ^{181}Ta and ^{182}W isotopes measurement, respectively. During measurements of intensities of platinum isotopes in real samples, the intensity of the ^{180}Hf isotope was measured as well and consequently the intensities of platinum isotopes were corrected. On the contrary, interferences with the ^{198}Pt isotope caused by the $^{182}W^{16}O$ formation were not observed. Interferences with the isotope ^{198}Pt caused by ^{198}Hg were eliminated by correction based on the isotope ^{202}Hg measurement. The theoretical correction factor based on abundances of isotopes ^{198}Hg and ^{202}Hg led to overcorrection and to an apparently high content of Pt in the sample. However, more accurate results were obtained using an empirical correction factor. The value of this factor has been confirmed by measurement of a 2 ng ml^{-1} solution of mercury before and during each measurement run. Figure 2 shows a comparison of both corrections when samples with the same platinum contents but different mercury contents were analysed.

Validation

The detection limit was estimated as the treble of standard deviation, the determination limit as the tenfold of standard deviation of blank samples

(n = 10). Each blank sample followed whole decomposition and separation procedure. For the sample weight 2 g, the detection limit was found to be 0.08 ng g^{-1} and the determination limit 0.25 ng g^{-1}. The average value of blanks was 0.24 ng g^{-1} Pt.

Selectivity was confirmed by analyses of blank samples (n = 10) with addition of 10 µg of Hf and 5 µg of W. The added amounts of hafnium and tungsten corresponded to mean contents of these metals in soils based on analyses of 30 samples. The platinum content found in this analysis was 0.33 ng g^{-1} (s = 0.08 ng g^{-1}) and did not significantly differ from the blank level.

Repeatability of determination was established in two sets of analyses of soil sample. In the first set, eight independent samples were analysed. This trial represents repeatability of the determination itself together with sampling repeatability. In the second set, eight samples were decomposed, the solutions were poured together and divided into eight portions once again. This trial represents repeatability of the determination only. For result see Table II.

Accuracy of results was proved by analysis of a certified reference material (TDB-1) and by the method of standard addition, too. The certified value of CRM (5.8 ± 1.1 ng g^{-1} Pt) was in excellent agreement with the found value (w_{Pt} = 5.2 ng g^{-1}, s = 0.5 ng g^{-1}, n = 5). In the case of standard addition, two sets of soil samples were analysed (n = 8), the first without addition, the second with addition of 0.5 g of a working natural platinum solution. This ad-

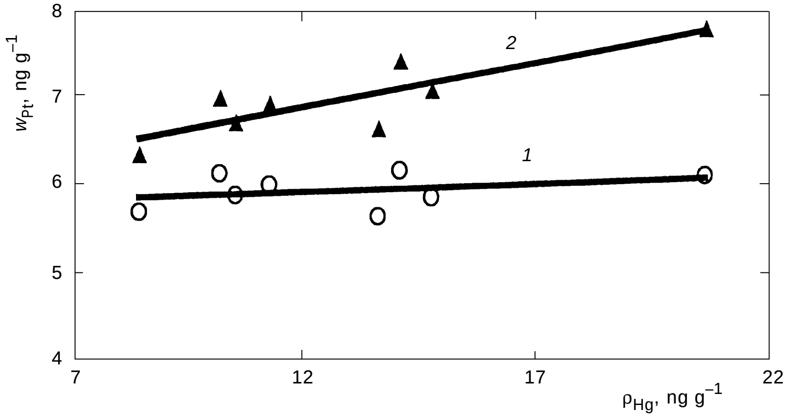

FIG. 2
Influence of the mercury concentration on the found platinum content; corrections: *1* empirical, *2* theoretical

dition corresponds to a theoretical increase in mass fraction of platinum about 5.11 ng g^{-1}. The found content was 3.07 ng g^{-1} (s = 0.13 ng g^{-1}) for the set without addition and 8.40 ng g^{-1} (s = 0.18 ng g^{-1}) for the set with addition. Homogenized solutions of decomposed samples (see the foregoing paragraph) were analysed in both cases. The platinum recovery was 104.4%.

A test of *robustness* was performed to obtain the effect of small changes of important instrument parameters (nebulizer argon flow rate, lens voltage and plasma power) of the mass spectrometer on platinum determination. The test was done through fractional factorial design for three factors[34]. The blank sample, sample, correction solution and mercury solution for determination of correction factor for ^{198}Hg were measured for each factor combination. Input parameters are listed in Table III. It was found that the method is robust for these factors, *i.e.* small changes in settings of these factors do not have a significant effect on the accuracy of the method.

TABLE II
Comparison of determination of individual soil samples and of homogenized solution

Determination	Individual soil sample	Homogenized solution
$\overline{w}_{Pt}$, ng g^{-1}	4.05	3.77
s, ng g^{-1}	1.78	0.33
RSD, %	43.9	8.7

TABLE III
Robustness test

Parameter	Factor	Normal value	Changed value
Nebulizer argon flow rate, l min^{-1}	A/a	0.85	0.8
Lens voltage, V	B/b	6.5	7.0
Plasme power, W	C/c	1 025	1 075

Estimation of Uncertainty of the Determination

Specification of analytical procedure was performed before calculation and identification of uncertainty sources contributing to total uncertainty were done. A survey of the components of total uncertainty is given in Table IV.

Uncertainties component of the platinum content caused by uncertainty of correction factors for HfO^+ and Hg^+ were calculated as residual standard deviations for nine pairs of calculated results using correction factors obtained at the beginning and at the end of a measurement set. The uncertainty of the correction factor for mass discrimination was evaluated by measurement of five solutions with different contents of natural platinum corresponding to soil samples of platinum mass fractions 2–10 ng g^{-1}. This set of solutions was measured five times. The sampling uncertainty was

TABLE IV
Survey of uncertainty sources

Component of uncertainty	Standard uncertainty	Relative standard uncertainty	Value
Pt mass fraction in working isotope enriched solution	0.01 ng g^{-1}	0.1%	10 ng g^{-1}
Correction factor for HfO, Δ_{HfO}	0.0598 ng g^{-1}		0
Correction factor for ^{198}Hg, Δ_{Hg}	0.051 ng g^{-1}		0
Correction factor for mass discrimination	0.0166	1.66%	1
Uncertainty of isotope composition of natural platinum			
Abundance of ^{198}Pt	0.0275%	0.38%	7.163%
Abundance of sum ^{194}Pt, ^{195}Pt and ^{196}Pt	for both	0.03%	92.041%
Isotope composition of isotope-enriched platinum			
Abundance of ^{198}Pt	0.03%	0.03%	95.71%
Abundance of sum ^{194}Pt, ^{195}Pt and ^{196}Pt	for both	0.7%	4.29%
Correction factor for sampling uncertainty, α_s		43.2%	1
Relative repeatability of determination, $s_r(w_{Pt})$		8.7%	0.3–10 ng g^{-1}

evaluated from the result obtained during validation study, see paragraph *Repeatability*. The repeatability of determination covers all uncertainty component nonspecified in Table IV, *viz*. sample and isotope enriched solution weighing, isotope ratio measurement *etc*.

Survey in Table IV shows that the sampling uncertainty is major component of the combine uncertainty. The material heterogeneity, probably caused by the "nugget effect", is described by other authors[7,17]. The sampling uncertainty was tested on one concentration level only. However, according to the sampling theory of Gy[35], the relative value of sampling uncertainty can be taken constant for given type of material and the same sample weight. It was found value of relative sampling standard uncertainty $u_r(\alpha_s)$ = 43.2% for soils polluted by using automobile catalysts. This uncertainty reflects taking of analytical sample (2 g) from laboratory sample (approximately 100 g) only. The area sample collection scheme was not the aim of this work, however its research would be very important.

The formal function rule for calculation platinum mass fraction covering the main sources of uncertainty is

$$w_{\mathrm{Pt,c}} = w_{\mathrm{Pt}}\, \alpha_s + \Delta_{\mathrm{Hg}} + \Delta_{\mathrm{HfO}} \tag{2}$$

and the calculation of combine uncertainty providing of rules for the uncertainty calculation from individual components[36] was done according to the Eq. (*3*)

$$u(w_{\mathrm{Pt,c}}) = \sqrt{w_{\mathrm{Pt}}^2 (s_r(w_{\mathrm{Pt}})^2 + u_r(\alpha_s)^2) + u(\Delta_{\mathrm{Hg}})^2 + u(\Delta_{\mathrm{HfO}})^2}\ , \tag{3}$$

where $w_{\mathrm{Pt,c}}$ is corrected platinum mass fraction [ng g^{-1}], w_{Pt} is measured platinum mass fraction [ng g^{-1}], α_s is factor due to heterogeneity of material [non-dimensional], Δ_{Hg} is factor due to correction on ^{198}Hg isotope [ng g^{-1}] and Δ_{HfO} is factor due to correction on HfO interferences [ng g^{-1}], $u_r(\alpha_s)$ is a relatively standard uncertainty of α_s and $s_r(w_{\mathrm{Pt}})$ is the repeatability of the determination; $u(\Delta_{\mathrm{Hg}})$, $u(\Delta_{\mathrm{HfO}})$ are standard uncertainties of Δ_{Hg} and Δ_{HfO}, respectively.

The Eq. (2) is correctly valid only when measured ratio *f* depends linearly on platinum content. This presumption is approximately fulfilled (Fig. 1). It is also evident that with decreasing platinum content in a sample increases influence of uncertainties caused by Δ_{Hg} and Δ_{HfO}.

Analysis of Samples from the Neighbourhood of Hřensko

The described method was used for analyses of soil samples from the title locality. Three sampling places were chosen for the test, places B and C were located on the opposite sides of the road in distances of 1 and 3 m. Place A was farther from the traffic, 16 m away from the road. Samples were taken four times during the year, in March, May, August and October. From each sampling site one 100 g laboratory sample was taken. The samples were collected using a small plastic shovel. The results in Fig. 3 represent mean of two independent analyses and the expanded uncertainty (coverage factor 2) of the mean. It was found that there is a higher platinum content close to the road. In addition, it is apparent that the platinum content is not constant during the year. Lower platinum contents were found in March increasing later on, probably due to the increasing traffic.

CONCLUSIONS

A method has been validated for the determination of platinum at ng g^{-1} levels in soil by isotope dilution ICP-MS. Sample decomposition included incineration of sample and acid digestion. Platinum was separated by a tellurium coprecipitation procedure. Recovery was in case of real samples in the range 55–87%. As technique of isotope dilution was used, low recovery does not significantly affect results of analysis. In spite of the separation step residual interferences caused by hafnium oxide ions were observed.

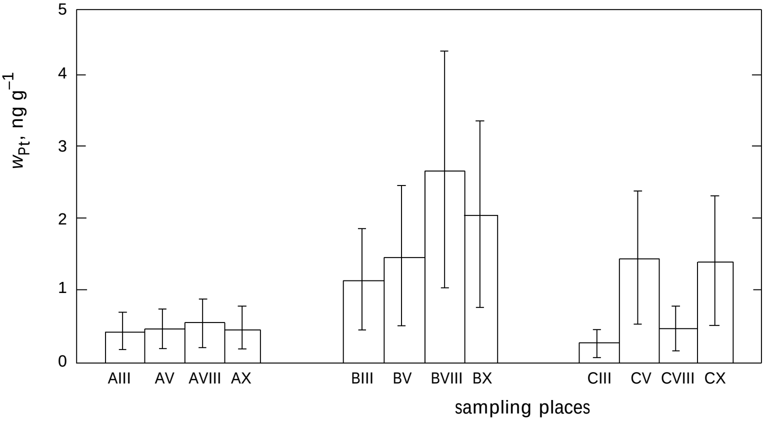

FIG. 3

Analysis of samples from the neighbourhood of Hřensko: A, B, C sampling places; III, V, VIII, X March, May, August, October

These interferences were eliminated by mathematical corrections based on the measurement of HfO/Hf ratio. Interferences on the isotope ^{198}Pt caused by isotope ^{198}Hg were eliminated by correction based on the isotope ^{202}Hg measurement. Accuracy of results was confirmed by analysis of certified reference material (TDB-1) and by the method of standard addition. The others validation parameters (detection limit, determination limit, selectivity, repeatability and robustness) were determinate too. During estimation of uncertainty of the determination the sampling uncertainty was found to be the major component of the combine uncertainty.

The described method was used for analysis of soil samples from the neighbourhood of Hřensko. Higher platinum content in the vicinity to the road was found.

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