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Uptake of platinum-group elements with the diet: A preliminary investigation*

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Abstract: Over the past decade, the increasing use of car catalytic converters based on platinum-group elements (PGEs) has been raising more and more concern. Human exposure to these metals occurs indirectly also through the diet. Thus, a pilot investigation was undertaken in order to ascertain the actual intake of PGEs through bread and cow milk. All manipulations were performed in a Class-100 clean room so as to minimize the risk of sample contamination. Digestion of samples was achieved by means of a mixture of HNO_3 and H_2O_2 with the assistance of microwave irradiation.

Determinations were performed by sector field inductively coupled plasma–mass spectrometry (SF–ICP–MS) to quantify Pd, Pt, and Rh. The isotopes $^{105}Pd^+$, $^{103}Rh^+$, and $^{195}Pt^+$ were used for the quantification. Major interferences were caused by $^{40}Ar^{65}Cu^+$ on $^{105}Pd^+$, $^{179}Hf^{16}O^+$ on $^{195}Pt^+$, and $^{87}Rb^{16}O^+$ and $^{87}Sr^{16}O^+$ on $^{103}Rh^+$. Both physical and mathematical approaches for the interference correction were used. The mean values for PGEs were found to be as follows (in ng kg^{-1}): full-cream milk: Pd, 3790; Pt, 83.2; Rh, 1680; skim milk: Pd, 12 400; Pt, 83.6; Rh, 1090; wholemeal bread: Pd, 3210; Pt, 171; Rh, 139; white bread: Pd, 27 400; Pt, 257; Rh, 2230. The preliminary data obtained in this study are probative of the significant portion of the total exposure to PGEs, which is due to the diet.

Keywords: catalytic converters; platinum-group elements; bread; milk; sector field inductively coupled plasma–mass spectrometry.

INTRODUCTION

The increasing use of catalytic converters based on platinum-group elements (PGEs) (a rough estimate for Pt ranges from 0.5–1.4 tons per year) has raised much concern as recent investigations showed that the accumulation of PGEs in roadside and airborne dust, soil, and grass, and hence in the food chain, has dramatically increased [1–16]. In fact, automotive catalytic converters consist basically of a monolithic honeycomb support made of cordierite (a phase of $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) treated with an Al_2O_3 washcoat, which in turn contains rare earth oxides and 0.10–0.15 % (w/w) Pt, Pd, and Rh. Environmental contamination by PGEs is mainly due to the release and accumulation of microparticles as a result of surface abrasion phenomena and hot-temperature chemical reactions with oil fumes.

The long-held belief that PGEs are generally harmless stems from their chemical inertness. On the other hand, their role as sensitizers in the etiology of allergenic pathologies such as asthma, conjunctivitis, dermatitis, rhinitis, and urticaria has been thoroughly ascertained. Moreover, there is some experimental evidence on the genotoxic risk posed by Pt [17–22].

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Although almost one-half of human exposure to PGEs has been estimated to occur through the diet, only scant information on the likely levels of these elements in food is available in the literature [23,24]. An investigation was thus undertaken to develop and validate new analytical methods for the ascertainment of the actual intake of Pd, Pt, and Rh through major food commodities in Italy. The preliminary results described in this paper regard the measurements performed on a set of milk and bread samples.

MATERIALS AND METHODS

Sample collection, preparation, and storage

The collection of a total of 20 different samples of each type of matrix took place in different areas in Italy. Samples were packed and frozen at –20 °C and stored at this temperature until pretreatment. In general, the more complex the sample matrix is, the wider the range of nonspectral and mass interferences that will occur with analytical techniques based on plasma–mass spectrometry. Thus, the analytical procedure for the quantification of PGEs at the expected concentrations in food commodities focuses on a number of critical steps, e.g., the procedure to be adopted to avoid chemical contamination during the sample collection, pretreatment, and storage phases, the working conditions (ancillary labware, ancillary equipment, and clean room), and the instrumental settings to be adopted.

In the case of bread, samples were chopped and crushed. Deep-frozen milk samples, in turn, were preconcentrated by freeze-drying in the precooled (–56 °C) polyethylene-protected stainless steel tray of the freeze-drier for as long as four days. After completion of the process, the freeze-dried samples were stored at room temperature in a desiccator.

Moisture determination

The humidity content of these materials was determined on separate portions of about 1 g from each sample weighed in a Petri dish on the day of analysis. Each sample was carefully and thoroughly shaken in its container for homogenizing before subsampling. The samples were then placed in a ventilated oven (WTB, Binder) set at 103 ± 2 °C, dried for 3 h, cooled down for 15 min in desiccator, and then weighed.

Sample digestion

The samples were chemically digested prior to analysis by microwave (MW)-assisted acid treatment. Approximately 0.5 g of each sample were taken from the mass, again after careful shaking, weighed into a carefully decontaminated high-pressure Teflon® vessel and added with 7 ml of a 1:6 (v/v) mixture of suprapur grade 30 % H_2O_2 and suprapur grade 65 % HNO_3 (both supplied by Merck, Darmstadt, Germany). The samples were subjected to irradiation in a high-performance MW oven (MLS 1200 MEGA, Milestone, Bergamo, Italy). The MW power applied during the digestion step varied from 250 to 650 W, and the duration of the complete cycle was less than 25 min. Details on the MW program are reported in Table 1. The same sample digestion procedure was successfully applied to milk and bread samples. At the end of the treatment, clear and homogeneous solutions were obtained. After cooling at room temperature, the content of each vessel was quantitatively transferred into polyethylene tubes (Falcon, Becton Dickinson, Lincoln Park, NJ, USA) and gravimetrically diluted with deionized water. Sample solutions were then stored at 4 °C in the dark until analysis. Blank samples were prepared along with the samples, following exactly the same procedure, but omitting the test material.

Table 1 Operative conditions for MW-assisted acidic digestion.

Step	Time (min)	Power (W)
1	2	250
2	2	0
3	5	250
4	5	400
5	5	650

The operating conditions for the acid MW-assisted digestion were optimized to give the highest possible efficiency of the digestion process, the lowest signals from the procedural blanks, and thus attain an adequate detection power. The matrix effect (nonspectral interferences), was minimized by optimizing the digestion efficiency and the dilution factor.

Strict precautions were adopted to minimize the risk of analyte loss or contamination throughout the whole analytical process. All sample manipulations took place in a Class-100 clean room (Tamco, Rome, Italy). All containers were carefully decontaminated beforehand by cleaning overnight with suprapur grade 5 % HNO_3 and rinsing with high-purity deionized water.

SAMPLES ANALYSES

Analytical measurements and instrumental settings

The determination of traces of PGEs in milk and bread was performed resorting to sector field inductively coupled plasma–mass spectrometry (SF–ICP–MS) (Element 2 model, ThermoElectron, Bremen, Germany). The relative concentration of analyte and mass interferences, as from the preliminary study on a pooled sample, requires the reduction of mass interferences by optimizing the instrumental settings and the physical resolution of the mass overlaps, when the required resolution is compatible with the isotope counts.

The radiofrequency (RF) power and the gas flows were optimized so as to give adequate detection power for the quantification of the PGEs and at the same time a low production of the relevant oxides. Instrumental settings and operating conditions are summarized in Tables 2 and 3. Double-charged ions were found to have no influence on the determination: the signal of $^{206}Pb^{2+}$ occurring at m/z 103 on the Rh isotope, in fact, can be physically separated using the appropriate resolution ($m/\Delta m \geq 1250$).

The necessary precision for measurements at the ultratrace level was achieved by coupling the high ionization efficiency of the guard electrode (GE) device and the signal stability provided by the pneumatic nebulizer (PN).

Table 2 Operative conditions for PGE determination by GE–PN SF–ICP–MS in bread and milk.

Sensitivity optimization	More than 1.2 million cps for 1 ng g^{-1} ^{115}In
Minimization of oxides	Intensity ratio $^{138}Ba/^{138}Ba^{16}O$ less than 0.001
Resolution optimization	Fe/ArO (MR), K/ArH (HR)
Analytical masses (amu)	^{105}Pd, ^{195}Pt, and ^{103}Rh

Table 3 Equipment and settings for the determination of PGEs in bread and milk.

Spectrometer	SF–ICP–MS ELEMENT 2 (ThermoElectron, Bremen, Germany) equipped with a GE device
Geometry	Double-focusing reverse Nier–Johnson
Resolution	$m/\Delta m \geq 300$, 4000, 10 000
Radio frequency generator	Frequency power output, 950.0 W
Nebulizer	Pneumatic, Meinhard type
Torch	3-turn induction coil, with alumina injector
Interface	Sampler and skimmer cones in Ni alloy
Data acquisition	Electric scan; 4 runs; 10 passes; sample scantime, 2 min 11 s
Argon flows (l min^{-1})	Plasma, 14; auxiliary, 1.15; aerosol, 0.78

The standard addition mode was used for calibration in order to minimize any matrix-induced signal variations. Matrix-matched calibration was achieved by spiking pooled sample solutions with standards. Calibrants were prepared daily by appropriate dilution of single-element calibrant stock solutions of 1000 mg l^{-1} of Pd, Pt, and Rh in 2 % HNO_3 (Spex Industry, Edison, NJ, USA) with high-purity deionized water (specific resistance of 18 MΩ cm) produced through an apparatus manufactured by PBI International (Milan, Italy).

Semiquantitative study

The expected levels of PGEs and other elements potentially affecting their analytical masses in bread and milk were obtained through a preliminary semiquantitative study.

This study provided information on the analytical conditions to be adopted, i.e., dilution of samples and mass resolution, and the applicability of mathematical corrections for interferences. The approximate apparent concentrations of elements forming atomic or molecular ions in bread and milk digested samples were obtained by comparing counts from pooled sample solutions and multi-element standard solutions containing the metals producing interferences at the level expected in the real samples.

For the semiquantitative study, single-element stock solutions of 1000 mg l^{-1} of Pd, Pt, and Rh as well as of potential interfering elements such as Cd, Cu, Ga, Hf, Mo, Rb, Sr, Y, Zn, and Zr were employed. Measurements were carried out by resorting to the operative conditions and instrumental settings given in Tables 2 and 3.

Selection of isotopes and interference study

Quantification of Pd, Pt, and Rh at levels expected in bread and milk requires adequate sensitivity and detection power such as those possessed by SF–ICP–MS. However, for the reliable analysis of trace elements in complex matrices, mass interferences should be carefully identified beforehand and the required physical resolution of interfering species from the isotope of interest should be set. When the concentration of the analyte is too low to allow for the use of the required physical resolution, the mathematical correction of the contributions to the apparent signal of the investigated isotope mass due to interfering ions should be used.

The analytical isotopes ^{105}Pd, ^{195}Pt, and ^{103}Rh were selected. This choice was based on the natural abundances of the analytical isotopes and the ascertainment of the relative abundances of the potential atomic and molecular interfering ions along with the physical resolution required to separate analyte masses from interfering masses.

The low-resolution (LR) mode provides maximum sensitivity and the highest precision, thanks to the flat top peak shape. On the other hand, the LR mode is more dramatically affected by mass inter-

ferences originating from atomic and molecular ions produced in the Ar plasma by the matrix constituents of the samples.

Platinum was determined at m/z 195 because of the highest natural abundance of this isotope (33.8 %). This mass, as well as mass 194 (natural abundance 32.9 %) might be affected by the formation of $^{177}Hf^{18}O^+$, $^{178}Hf^{17}O^+$, and $^{179}Hf^{16}O^+$. The molecular interferences originating from double ions of Hf with ^{17}O and ^{18}O were considered negligible due to the low natural abundance of these isotopes. The spectral overlap of $^{179}Hf^{16}O^+$ was taken into account because of the low concentration of Pt in bread and milk. The resolution required for this interference is high, but the low level of Pt in both matrices makes the LR mode unavoidable. The influence of $^{179}Hf^{16}O$ on the mass signal of ^{195}Pt was thus assessed by daily measuring the signal of pooled sample solutions spiked with different amounts of Hf so as to adequately cover and even exceed the range of concentration expected for Hf in bread and milk. The mathematical correction was thus applied by measuring the actual Hf concentration in each sample.

The role of trace elements, such as Cu, Pb, Rb, Sr, Y, Zn, and Zr, all being present in the matrices under test and giving rise to polyatomics overlapping the monoisotopic Rh mass, was also studied. Among the many potential mass interferences for Rh, i.e., $^{36}Ar^{67}Zn^+$, $^{68}Zn^{35}Cl^+$, $^{40}Ar^{63}Cu^+$, $^{38}Ar^{65}Cu^+$, $^{206}Pb^{2+}$, $^{87}Sr^{16}O^+$, $^{87}Rb^{16}O^+$, $^{85}Rb^{18}O^+$, $^{89}Y^{14}N^+$, and $^{91}Zr^{12}C^+$, only those originating from Zn, Cu, and Pb can be adequately separated from the analyte signal in the medium-resolution (MR) mode ($m/\Delta m = 4000$). The interfering effect of $^{89}Y^{14}N^+$ and $^{91}Zr^{12}C^+$ at m/z 103 was found to be of no practical importance because of the low concentrations of Y and Zr both in bread and milk samples. The polyatomic interferences arising from $^{85}Rb^{18}O^+$ were of no actual consequence because of the natural low abundance of isotope ^{18}O. On the basis of counting resulting from the semiquantitative study, the actual content of Sr and Rb is so high that their interferences need a resolution higher than 10 000, i.e., exceeding the maximum resolution power of the equipment used in this study. Thus, no physical separation from the analyte peak can be achieved for $^{87}Sr^{16}O^+$ and $^{87}Rb^{16}O^+$. Oxides have been ascertained to heavily affect the signal of ^{103}Rh with a total contribution so high that their formation varies greatly with time, thus making the mathematical correction inadequate. All in all, the quantification of Rh in the investigated matrices might be hampered by the occurrence of these interfering oxides, and further investigations aimed at optimizing the analytical working conditions and reducing the occurrence of such oxides are needed to make them manageable by a mathematical equation. Hence, the concentrations reported for ^{103}Rh in bread and milk are probably higher than the actual values.

The 106 and 108 isotopes of Pd are the most abundant ones (natural abundance, 27.3 and 26.5 %, respectively). These masses are affected in the MR mode by the interference of isobaric monoatomic Cd ion. On the basis of the results of the semiquantitative investigation, the Cd contributions to the signal of ^{106}Pd and ^{108} Pd cannot be disregarded and should be dealt with by measuring the $^{111}Cd^+$ signal, which, in turn, should be mathematically corrected for the influence of $^{95}Mo^{16}O$. As no monoatomic ions interfere with the measurement of ^{105}Pd (natural abundance, 22.3 %), this isotope was selected for analysis. The molecular species $^{40}Ar^{65}Cu^+$, $^{36}Ar^{69}Ga^+$, $^{89}Y^{16}O^+$, $^{88}Sr^{17}O^+$, $^{87}Sr^{18}O^+$, and $^{87}Rb^{18}O^+$ are potential interferents at mass 105. The physical separation of the polyatomics $^{40}Ar^{65}Cu^+$ and $^{36}Ar^{69}Ga^+$ was used for the quantification of Pd both in the MR and high-resolution (HR) modes. The interferences due to argides are fully physically solved by operating in the HR mode ($m/\Delta m$ = 10 000). In the MR mode, there is still a certain grade of overlap of the analyte signal with the $^{40}Ar^{65}Cu^+$ signal, but, by using a small enough mass window and integrating only the central part of the peak, the isotope of interest might be unaffected.

Signals arising from potentially interfering species at m/z 105, i.e., $^{88}Sr^{17}O^+$, $^{87}Sr^{18}O^+$, $^{87}Rb^{18}O^+$, and $^{89}Y^{16}O^+$, require a resolution power higher than that offered by the instrument. The mathematical correction of ^{105}Pd counts from runs in the MR mode could be applied, but the interfering effect of the formation of the above overlapping signals was neglected, both because of the scarce abundance of the isotopes involved (^{17}O and ^{18}O) and the low Y concentration in bread and milk.

To check the ruggedness of the method, Pd was quantified by running the samples in the MR and HR modes. The discrepancy between MR and HR results was found to be less than the uncertainty of the measurements.

The validity of both analytical approaches used was demonstrated by satisfactory recovery tests and good agreement of results, as detailed in Table 4.

Table 4 Ruggedness test for Pd determination. Recovery tests and consistency of results between two sets of measurements (MR and HR modes).

	Recovery (%) (MR)	Recovery (%) (HR)	Consistency of MR and HR results (%) (AVG)	Uncertainty (%) (HR)
Milk	118	125	9	14
Bread	107	90	7	16

RESULTS AND DISCUSSION

Performance of the analytical method: Reliability criteria and validation

Tables 5 and 6 report the figures of merit for PGE determination by GE–PN SF–ICP–MS in a milk certified reference material (BCR 151), which, however, has no certified values for PGEs, and bread internal working reference material (internal code no. 880). The detection power offered by the technique in the investigated matrices was checked by analyzing 10 independent procedural blanks and calculating the net signal after spiking the matrix. Limits of detection (LoDs), based on the 3σ criterion applied to the matrix solution, turned out to be adequate for the quantification of PGEs in bread and milk samples.

Table 5 Method's parameters for PGE determination by GE–PN SF–ICP–MS in milk samples.

	Pd (HR)	Pt (LR)	Rh (MR)
LoDs (ng kg^{-1})[a]	59.5	0.8	7.4
Reporting limit (ng kg^{-1})[b]	198	2.8	24.7
Whole process reproducibility (%)[c]	6.9	4.1	4.6
Recovery (%)[d]	125	97	154
Uncertainty (%)[e]	14	8	10

[a]Calculated on the basis of the 3σ criterion in the matrix.
[b]Calculated on the basis of the 10σ criterion in the matrix.
[c]Five independent aliquots were analyzed.
[d]Calculated on five independent fortified samples.
[e]Calculated according to the EURACHEM/CITAC Guide.

Table 6 Method's parameters for PGE determination by GE–PN SF–ICP–MS in bread samples.

	Pd (HR)	Pt (LR)	Rh (MR)
LoDs (ng kg^{-1})[a]	13.5	1.9	0.1
Reporting limit (ng kg^{-1})[b]	45.1	6.3	0.3
Whole process reproducibility (%)[c]	8	2	6
Recovery (%)[d]	90	101	108
Uncertainty (%)[e]	16	4	12

[a]Calculated on the basis of the 3σ criterion in the matrix.
[b]Calculated on the basis of the 10σ criterion in the matrix.
[c]Five independent aliquots were analyzed.
[d]Calculated on five independent fortified samples.
[e]Calculated according to the EURACHEM/CITAC Guide.

The same procedure was applied to calculate the limits of quantification (LoQs) and, therefore, the reporting limits (equal to or higher than the LoQs). The whole process reproducibility was assessed by calculating the RSD (%) of measurements performed on 5 independent aliquots in the same analytical run. The instrumental imprecision was evaluated and monitored over the entire working range by performing replicate analyses of standards.

As regards the test for accuracy, unfortunately, no reference materials certified for PGEs in the said matrices are commercially available. Consequently, reliability of measurements was checked through recovery tests by including in the analytical runs a set of 5 independent samples which were fortified with the expected mass of the analytes prior to the digestion process.

To establish the comparability of results, the uncertainty associated to the analytical methods developed was estimated according to the EURACHEM/CITAC Guide [25].

Control charts were set up to check the performance of the method by daily plotting results from the measurement of the pooled sample.

Provisional PGE concentration ranges in bread and milk

Tables 7 and 8 list the Pd, Pt, and Rh levels found in a set of 20 milk samples and 20 bread samples, respectively. In particular, the minimum and maximum results are reported, along with the mean values and standard deviations.

Table 7 Results of the preliminary investigation of milk matrix. Results are calculated on the basis of the sample dry weight. For Rh, the apparent concentration range is reported.

	Milk samples		
	Pd (HR)	Pt (LR)	Rh (MR)
Full-cream			
Concentration ranges (ng kg^{-1})	949–8155	16.9–154	1036–3203
Mean values (ng kg^{-1})	3790 ± 3090	83.2 ± 38.7	1680 ± 719
Skim			
Concentration ranges (ng kg^{-1})	10 536–14 286	48.1–183	569–2024
Mean values (ng kg^{-1})	12 400 ± 2650	83.6 ± 41.3	1090 ± 642

Table 8 Results of the preliminary investigation of bread matrix. Results are calculated on the basis of the sample dry weight. For Rh, the apparent concentration range is reported.

	Bread samples		
	Pd (HR)	Pt (LR)	Rh (MR)
Wholemeal bread			
Concentration ranges (ng kg^{-1})	2225–3970	13.2–703	45.6–238
Mean values (ng kg^{-1})	3210 ± 700	171 ± 204	139 ± 74.4
White bread			
Concentration ranges (ng kg^{-1})	1067–84 065	110–547	1587–3774
Mean values (ng kg^{-1})	27 400 ± 33 500	257 ± 149	2230 ± 702

As anticipated, Pt results were obtained by resorting to the LR mode. Indicative concentration levels for Rh, in turn, derive from runs in the MR mode with daily ad hoc mathematical correction of the contributions of oxides produced by the samples in the Ar plasma. For the time being, data on Rh are to be considered only indicative, as shown by the poor recovery, and further investigations would be necessary for minimizing the production of interfering oxides ions, while at the same time maintaining a good detection power for Rh in the MR mode. In the case of Pd, results from the HR mode are given.

Table 9 shows the concentration values of ^{195}Pt (this study) as compared to those determined by Vaughan and Florence (1992), by means of adsorptive voltammetry [23]. In the above paper, the authors detail their pretreatment procedure consisting of wet ashing followed by quantitative convertion to chloroplatinates. The much higher data found by these authors are difficult to understand, unless one would admit that their determinations were affected by poor control of the contamination of samples during the pretreatment and analytical phases.

Table 9 Concentration values of ^{195}Pt (this study) as compared with those already published*.

	Pt concentration (ng kg^{-1}) (DW)	
	Present study	*Vaughan and Florence, 1992
Full-cream milk	83, RSD = 49 %	1030, RSD = 14 %
Skim milk	83, RSD = 49 %	1450, RSD = 14 %
Wholemeal bread	171, RSD = 119 %	1090, RSD = 12 %
White bread	258, RSD = 58 %	900, RSD = 11 %

CONCLUSIONS

The analytical capabilities of the SF–ICP–MS instrumental technique and the potential interferences affecting the quantification of the said elements in bread and milk were assessed in order to set up a reliable analytical procedure to be exploited for the ascertainment of undue exposure to the above metals.

Further studies are necessary for substantiating these initial results as well as for understanding and mastering unknown mass interferences, which are still present in the HR mode and could not be completely disregarded.

The proposed methodological approach appears to be fully adequate for the reliable quantification of Pd and Pt and the preliminary data obtained in this investigation, although still rather low, are probative of the significant portion of the total exposure to PGEs, which is due to the diet.

In this context, the investigation of the PGE content in food will be further extended to cover a variety of food commodities. Contamination or losses of PGEs due to the most common cooking methods will be also investigated.

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