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Investigation of palladium and platinum contamination in food by means of Sector Field Inductively Coupled Plasma Mass Spectrometry

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3 **Investigation of palladium and platinum contamination in food by means of**
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6 **Sector Field Inductively Coupled Plasma Mass Spectrometry**
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11 **Chiara Frazzoli, Roberta Cammarone, Sergio Caroli***
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Abstract

Over the last two decades some noble metals such as Pd and Pt have been raising much concern as regards their impact on human health. These elements pollute the various environmental compartments due to the wide variety of their uses ranging from catalytic properties to medical applications. The risk they pose to human health and the environment is, from many viewpoints, still a controversial issue. Whatever its extent may be, however, literature data point to the diet as an important source of their uptake by the human body. In this context, the total Pd and Pt contents of several Italian food commodities have been investigated. A total number of 90 samples, including flour products, vegetables and foodstuffs of animal origin (meat, milk and eggs), were collected and freeze-dried. Samples were analyzed by Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP- MS) after chopping or crushing followed by freeze-drying and microwave (MW)-assisted acid digestion in a Class-100 clean room. A mathematical approach was adopted to correct the mass signals for the still unresolved interferences ($m/\Delta m = 300, 10,000$). The lowest and the highest concentrations of Pt, *i.e.* 17 and 93 ng kg⁻¹ (dry weight, dw), were found in vegetables and flour products, respectively. In turn, the lowest Pd level (2,830 ng kg⁻¹, dw) was found in eggs and the highest one (47,800 ng kg⁻¹, dw) in vegetables.

Keywords: Platinum in food; Palladium in food; Sector Field Inductively Coupled Plasma- Mass Spectrometry (SF-ICP-MS).

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Introduction

As documented by a large number of studies, the increase in environmental levels of Pd and Pt can mainly be ascribed to the introduction of car catalytic converters (Leśniewska et al. 2004, Bocca et al. 2003, Gómez et al. 2002, Moldovan et al. 2002, Merget and Rosner 2001, Palacios et al. 2000, Petrucci et al. 2000, Rouch and Morrison 2000, König et al. 1992), even if other sources of these metals can be traced back to various industry compartments, from catalysis to chemical and dental uses, from the exploitation in the electricity and petrol sectors to jewellery.

The dramatic increase in the environmental contamination by these metals and the high allergenic and cytotoxic potential of even very low doses of Pt compounds (the health effects caused by exposure to Pd are not so well known as those of Pt) (EHC no. 125, 226) have prompted a host of studies on biomarkers of total exposure (Bocca et al. 2004, Záray et al. 2004, Caroli et al. 2001, Begerow and Dunemann 2000, Caroli et al. 2000, Hees et al. 1998, Balcerzak 1997, Merget et al. 1991, Gebel et al., 1997) and occupational investigations (Merget et al. 2002, Baker et al. 1990). On the other hand, only a very few studies have dealt so far with the extent to which Pt and Pd compounds can enter the food chain *via* accumulation or biotransformation in agricultural and zootechnical products (Frazzoli et al. 2006, Ysart et al. 1999, Zhou and Liu 1997, Vaughan and Florence 1992, Koch and Roesmer 1962).

Palladium and Pt can be taken up through different pathways, such as aerosol deposition caused by car or industrial emissions, contaminated waste-water from hospital effluents or artificial fertilisation of soils. Vaughan and Florence (1992) investigated the role of diet as a source of Pt and observed that the levels of this element in human samples were higher than anticipated. On the basis of a standard diet, it was speculated that as high as 42 % of the total intake of Pt might be due to the diet.

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3 The present study deals with the analysis of a variety of Italian food commodities (meat, milk,
4 eggs, flour products and vegetables) by means of Guard Electrode (GE) Sector Field Inductively
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8 Coupled Plasma Mass Spectrometry (SF-ICP- MS). All possible precautions were adopted to
9
10 preserve the integrity of the samples. The detection power of the technique employed, along with
11
12 its resolving power, allow for the direct determination of ultratrace levels of the analytes of
13
14 interest, even if complex mass interferences can dramatically hamper the measurements.
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18 19 20 **Experimental**

21 22 **Samples collection and treatment**

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24 A total of 90 different samples representative of the major food commodities in Italy were
25
26 collected from several Italian areas. In particular, 50 samples of food of animal origin were
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28 gathered, including 20 samples of milk (both full cream and skimmed milk, 10 samples each), 20
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30 meat samples (of which 7 of poultry) and 10 eggs. The remaining 40 samples consisted of flour
31
32 wholemeal and white flour (10 samples each), 10 tubers (5 potatoes, 5 carrots), 5 bulbs (2 onions
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34 and 3 garlics) and 5 green vegetables. All vegetables were sampled and stored without washing
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36 and peeling. Samples were assigned an identification code, packed, frozen at - 20 °C and stored at
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38 this temperature until analysis.
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45 Prior to digestion, aliquots of each sample were, depending on their nature, chopped or crushed
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47 and then freeze-dried. Freeze-drying was included in the analytical protocol to normalize the
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49 water content (70-80 % for eggs and meat, 90 % for vegetables and milk and 20-40 % for flour)
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51 and thus facilitate the obtainment of readily comparable data. Moreover, the removal of water
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53 increases the relative concentration of the analytes by a factor of 1.5-10, thus making easier their
54
55 determination. The freeze-dried samples were stored at room temperature in a desiccator. After
56
57 careful shaking of the mass, aliquots of *ca.* 0.5 g of each sample were loaded into decontaminated
58
59 high pressure microwave (MW) Teflon vessels and added with 7 ml of a 1:6 (v/v) mixture of 30 %
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3 H₂O₂ and 65 % HNO₃, both of Suprapur grade (Merck, Darmstadt, Germany). The samples were
4
5 then subjected to MW-assisted digestion as detailed in Table 1. A high performance MW oven
6
7 (MLS 1200 MEGA, Milestone, Bergamo, Italy) was used. Upon completion of the MW treatment,
8
9 the vessels were allowed to gradually equilibrate to room temperature. The content of each vessel
10
11 was then poured into decontaminated polyethylene tubes (Falcon, Becton Dickinson, Lincoln Park,
12
13 NJ, USA) and gravimetrically diluted to 15 g with deionized water.
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20 In order to perform recovery tests, one independent aliquot from each food group was subsampled,
21
22 fortified with the expected content of the analytes and loaded for digestion. Procedural blanks
23
24 were obtained by subjecting the digestion mixture to the same treatment adopted for the samples.
25
26 To facilitate the comparison, all analytical results were corrected to dry mass. To this end, a
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28 separate aliquot from each sample was weighed in a Petri dish on the very day of the sample
29
30 digestion treatment. For the determination of the water content a mass of at least 1g was necessary
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32 so as to easily quantify the moisture loss. Each sample was thoroughly shaken for re-
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34 homogenizing the whole mass before sub-sampling. The samples were then placed in a ventilated
35
36 oven (WTB, Binder, Tuttlingen Germany), dried for 3 hours at 103 ± 2 °C, cooled down in
37
38 desiccator and then weighed. All sample manipulations took place in a Class 100- clean room
39
40 (Tamco, Rome, Italy) and all sample containers and other materials were decontaminated with
41
42 high purity HNO₃ 5 % v/v for 24 hours, then rinsed with deionized water and shaken dry prior to
43
44 use so as to minimize the risk of sample contamination throughout the analytical process. Sample
45
46 solutions were then stored at 4 °C in the dark until analysis. Because of the high detection power
47
48 of the spectrometer, namely, *ca.* 1600 kcps/(ng g⁻¹) In at a resolution of $m/\Delta m = 300$, solutions
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50 were further diluted to minimize matrix effects.
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Instrumentation

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3 A double-focusing SF-ICP-MS (Element 2, ThermoElectron, Bremen, Germany) with reversed
4
5 Nier-Johnson geometry and mass resolution $m/\Delta m$ up to 10,000 was used in this study. The
6
7 spectrometer was equipped with a standard inlet system (Meinhard Pneumatic Nebulizer, Fassel
8
9 torch with 1.5 mm i.d. injector, Ni cones) working with a sample uptake rate of $11 \mu\text{l min}^{-1}$ and a
10
11 GE device. The spectrometer settings were as follows: RF power, 950 W; coolant Ar flow rate, 13
12
13 l min^{-1} ; auxiliary Ar flow rate, $0.90 - 1.15 \text{ l min}^{-1}$; nebulizer Ar flow rate, 0.8 l min^{-1} . Data
14
15 were acquired in the electrostatic scanning mode (E-Scan), with 4 runs and 10 passes.
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22 The instrumental limits of detection (LoDs), calculated as the concentration associated with 3
23
24 times the standard deviation (SD) of 10 independent measurements of the procedural blanks, were
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26 0.5 and 0.2 ng l^{-1} for Pd and Pt, respectively. The instrumental limits of quantification (LoQs)
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28 were expressed as 10 times the above SD.
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34 **Interference correction**

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36 Most papers dealing with Pd and Pt determination recognize the severity of problems associated
37
38 with mass interferences on these analytes and extensive studies of potential interferences have
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40 been published (Petrucci et al. 2004, Bruzzoniti et al. 2003, Simpson et al. 2001, Krachler et al.
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42 1998, Parent et al. 1996). On the basis of a previous study on food matrices (Frazzoli et al. 2006),
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44 the analytical masses ^{105}Pd and ^{195}Pt were selected for performing this investigation.
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51 Platinum was quantified at mass 195, although this mass is affected by the formation of $^{179}\text{Hf}^{16}\text{O}^+$.
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53 The level of Hf present in the tested matrices makes the mathematical approach for the
54
55 interference correction reliable enough for the determination of trace Pt in the Low Resolution
56
57 (LR) mode ($m/\Delta m = 300$). The mathematical equation used to correct for the influence of
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59 $^{179}\text{Hf}^{16}\text{O}$ on the mass signal of ^{195}Pt was checked daily for each food matrix by measuring the
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increase in the analyte signal when running pooled sample solutions spiked with different amounts

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3 of Hf (Spex Industry, Edison, NJ, USA). The spikes of Hf were chosen so as to cover and even
4
5 exceed the expected concentration range. As regards Pd, mass 105 is seriously affected by
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7 multiple interferences. The variety and complexity of the interferences identified ($^{40}\text{Ar}^{65}\text{Cu}^+$,
8
9 $^{36}\text{Ar}^{69}\text{Ga}^+$, $^{89}\text{Y}^{16}\text{O}^+$, $^{88}\text{Sr}^{17}\text{O}^+$, $^{87}\text{Sr}^{18}\text{O}^+$ and $^{87}\text{Rb}^{18}\text{O}^+$) required the use of the High Resolution (HR)
10
11 mode ($m/\Delta m = 10\,000$). The mass interference due to $^{89}\text{Y}^{16}\text{O}^+$, however, cannot be overcome at
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13 this resolution. Thus, the mathematical correction is inescapable as the double ion exerts an
14
15 appreciable influence on the total counts of $^{105}\text{Pd}^+$. Even if the less sensitive HR mode may
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17 overestimate the analyte, the physical resolving power of the equipment was used in order to
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19 minimize the resorting to the mathematical correction and therefore the possibility of
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21 underestimating the analyte content due to the mathematical subtraction of more than one
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23 overlapping peak on the same target signal.
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32 In the interference study, the effects of Sr and Rb oxides ($^{88}\text{Sr}^{17}\text{O}^+$, $^{87}\text{Sr}^{18}\text{O}^+$ and $^{87}\text{Rb}^{18}\text{O}^+$) were
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34 neglected because of the low natural abundance of the involved oxygen isotope. Samples with
35
36 high content of Sr and Rb (e.g., vegetables) may give falsely higher Pd results, also in the HR
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38 mode, due to the presence of the above oxides in the plasma. In this case, the direct determination
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40 with mathematical correction should be compared with other analytical approaches, such as the
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42 introduction of a matrix removal step or the Dynamic Reaction Cell (DRC) prior to the actual
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44 determination by the SF-ICP-MS (Bruzzoniti et al.2003, Simpson et al. 2001).
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50 51 **Samples analyses**

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53 An estimate of the expected concentration ranges of Hf, Pd, Pt and Y in the food samples
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55 investigated was achieved through preliminary semi-quantitative analyses. For the quantification
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57 of the analytes, the standard addition calibration method was used. Calibrants and standards were
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59 prepared daily by diluting single-element calibrant stock solutions of 1000 mg l^{-1} of Hf, Pd, Pt and
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3 Y in 2 % HNO₃ (Spex Industry) with high purity deionized water (specific resistance of 18 MΩ
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5 cm) produced through an apparatus manufactured by PBI International (Milan, Italy).
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10 Although the most straightforward approach for the assessment of accuracy is the analysis of
11 Certified Reference Materials (CRMs), this is of limited application for Pd and Pt due to the lack
12 of CRMs with reported figures for these elements in food matrices. The reliability of
13 measurements was thus determined through recovery tests which yielded 97-116 % for Pt and
14 107-111 % for Pd, *i.e.*, rather satisfactory. The repeatability of the whole analytical protocol, from
15 sub-sampling to quantification, calculated as relative standard deviation from nine independent
16 aliquots of the same sample, ranged from 3 % to 5 % for Pt and 9-11 % for Pd, this also being
17 quite acceptable.
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31 To monitor the instrumental stability, a pooled sample was used as internal Quality Control
32 Sample (QCS). The QCS was run regularly and frequently during the analytical sequence to
33 compensate for possible instrumental drifts.
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41 **Results and discussion**

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43 Tables 2 and 3 list the results for Pt and Pd, respectively, as found in the set of the 90 food freeze-
44 dried samples investigated. In order to compare data, results for flour and milk from the pilot
45 study are shown. For each different food group, the minimum and maximum concentrations are
46 reported on a dry weight (dw) basis, along with the mean and median values. For both analytes,
47 the high RSD values found were indicative of the high heterogeneity of the samples and sampling
48 sites and make the food matrices classification for Pd and Pt levels unfeasible. In fact, as regards
49 the median concentration values, the Pt content (Table 2) was found to be between 17 and 93 ng
50 kg⁻¹. From a general viewpoint, vegetables were the food matrix with the lowest level of Pt,
51 followed by meat and eggs (23 and 33 ng kg⁻¹), poultry (65 ng kg⁻¹) and skimmed and full cream
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3 milk (73 and 74 ng kg⁻¹). The highest levels of Pt were found in wholemeal (87 ng kg⁻¹) and white
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5 flour samples (93 ng kg⁻¹). The food group with the lowest level of Pd, in turn were eggs, full
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7 cream milk, wholemeal flour and poultry (between 2800-3500 ng kg⁻¹), followed by meat, skim
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9 milk and white flour (between 11 200-13 600 ng kg⁻¹). Higher levels were found in vegetables
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11 (Table 3).
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17 Apart from the studies aimed at quantifying Pt-group elements in environmental samples, only a
18
19 few studies seem to have focused on the determination of Pt in food. Results for Pt in different
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21 matrices (this investigation) are always at least ten times lower than those reported by Vaughan
22
23 and Florence in 1992. In their work, the authors used adsorptive voltametry to determine the Pt
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25 content in a set of foodstuffs (see Table 4). Foods were prepared using normal cooking procedures
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27 and 20-100 mg aliquots of the freeze-dried material were sub-sampled for the analysis. After pre-
28
29 concentration and matrix removal, Pt was converted into chloroplatinates.
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36 In order to explain the differences between the present results and the already published data, the
37
38 Pt determinations were repeated on other aliquots of the collected samples, which were
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40 preliminarily subjected to conventional cooking. The samples were then freeze-dried and digested
41
42 as described above. Cooking was found to increase by a factor of 25-50 % the analyte
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44 concentrations. Apart from the always possible occurrence of exogenous contamination, it
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46 understandable that Pt has been concentrated through the cooking process. It is self-evident,
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48 however, that results are still much lower than those obtained by Vaughan and Florence.
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55 The actual concentration of Pd and Pt in food greatly depend on various parameters (e.g., breeding
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57 conditions, rearing areas, animal age, geocomposition of soil and vicinity to contaminated sites) as
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59 well as the sampling year. In 1962, Koch and Roesmer measured Pd by Instrumental Neutron
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Activation Analysis (INAA) in different meat samples and the mean concentrations per kg (wet

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3 weight) were found to be as follows (in ng kg^{-1}): chicken, 600; beef, 700; pork, 500. The highest
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5 concentration of 2000 ng kg^{-1} was detected in ham. On the other hand, Zhou and Liu determined
6
7 Pd by means of Q-ICP-MS and mathematical correction of interferences in various foodstuffs in
8
9 the People's Republic of China (1996-1997) and reported 3000 ng kg^{-1} of this metal in beef,
10
11 chicken stomach and pork liver. In the same years, Ysart *et al.* collected a number of food samples.
12
13 Among these, milk and poultry contained Pd concentrations below the LoD of 300 ng kg^{-1} (fresh
14
15 weight, fw), whereas flour contained well detectable mean Pd concentrations (2000 ng kg^{-1}). Also
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17 in this case, Pd concentrations were higher than the corresponding Pt concentrations, which were
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19 very close to the LoDs (100 ng kg^{-1} , fw). The difference with the mentioned Pd contents could be
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21 also ascribed to the high water content present in food samples, which in some cases was
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23 eliminated during the sample pre-treatment procedures.
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32 The data obtained in this study are in agreement with previous bioavailability studies indicating
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34 that the soil plays an important role in reducing the mobility of Pt compounds (Rauch and
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36 Morrison, 1999) and that only a small amount of the total intake of Pt with food can be traced
37
38 back to endogenous accumulation. Hence, the higher Pt mean concentration level found in the
39
40 upper part of the plant (41 ng kg^{-1}) may indicate the occurrence and predominance of exogenous
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42 contamination by this element when compared with tuber mean concentration level (18 ng kg^{-1}),
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44 i.e., endogenous contamination, and further support the findings of Fragnière and coworkers.
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50
51 Presently, there are no studies dealing with this kind of results for the Pd compounds and the data
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53 concerning Pd levels in tubers, bulbs and green vegetables given in the present study are rather
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55 low to substantiate any sound interpretation. To better characterize the obtained data set
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57 distribution, the degree of asymmetry of each distribution around its mode (skewness) and the
58
59 relative peakedness or flatness (kurtosis) were also calculated and reported in Tables 2 and 3 along
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with ranges, mean and median values. Data set with values of 2 standard errors of skewness,

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3 estimated as radq (6/no. of samples), or more (regardless of sign) are significantly skewed. Data
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5 set with values equal to or higher than 2 standard errors of the kurtosis, estimated as radq (24/no.
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7 of sample), indicate a distribution with significant kurtosis problem. When skewness and kurtosis
8
9 fall within the range ± 2 standard errors, it is assumed a normal fluctuations range (Tabachnick
10
11 and Fidell, 2001). A significantly skewed distribution was found for Pd and Pt in meat samples,
12
13 with a narrow peak declining rapidly and a long tail. As regards vegetables, eggs, full cream and
14
15 skimmed milk and white and wholemeal flour, no significant asymmetry problem were found for
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17 Pd and flat top peaks were observed. The same outcomes were shown by Pt data distributions in
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19 all these food groups but eggs, wholemeal flour and skimmed milk, for which a significantly
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21 skewed data distributions with narrow peaks and a long tail were observed.
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29 **Conclusions**

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31 Although environmental concentrations of Pd and Pt are still relatively low, several reports testify
32
33 to a progressive increase in their levels. Further, an increasing Pd contamination of food is also
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35 considered likely to occur in the light of preliminary data indicating that Pd ends up in wastes or
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37 incineration ashes during recycling processes (Cowley, 1999) and is characterized by higher
38
39 environmental mobility than Pt (Rauch et al., 1999). In consideration of the still debated relatively
40
41 serious allergenic potential and other possible adverse effects on human health of Pt and Pd,
42
43 further research to assess the human risk following exposure to Pt and Pd compounds is needed.
44
45 At present, there are very few published data concerning the dietary exposure to Pd and Pt. The
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47 levels found in the food samples investigated appears to be compatible with those typical of
48
49 different environmental compartments, if one considers that the materials object of this study had
50
51 been freeze-dried and therefore the analytes are more concentrated. The results obtained are
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53 supportive of the assumption that a significant exposure to these elements occurs through the food
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55 chain. Nevertheless, the complexity of the described analytical problems requires further
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3 development of fit-for-purpose analytical approaches, especially as regards the minimization of
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5 mass interferences.
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3 Table 1. Settings of the MW-assisted acid digestion (10 high pressure vessels) for all food items
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5 investigated. The figures within brackets refer to flour.
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Step	Time (min)	Power (W)
1	2	250
2	2	0
3	5	250
4	5	500 (400)
5	5	650
6	5	250 (none)

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Table 2. Platinum concentrations as measured by GE-SF-ICP-MS in freeze-dried foodstuffs.

Pt (LR mode)	No. of samples	Concentration ranges (ng kg ⁻¹) (dw)	Mean values (ng kg ⁻¹) (dw)	Median values (ng kg ⁻¹ , dw)	Skewness	Kurtosis
Full cream milk	10	17 - 154	80	74	0.23	-0.01
Skimmed milk	10	48 - 183	84	73	1.76	3.31
Meat (beef, pork, veal)	13	3 - 347	80	23	1.89	3.83
Meat (chicken, turkey)	7	12 - 534	122	65	2.51	6.45
Eggs	10	7 - 260	62	33	2.17	4.97
Wholemeal flour	10	13 - 703	171	87	2.32	5.95
White flour	10	31 - 462	174	93	0.86	-0.46
Vegetables (tubers, bulbs, leaves)	20	< LoQ - 76	24	17	1.13	0.44

Table 3. Palladium concentrations as measured by GE-SF-ICP-MS in freeze-dried foodstuffs.

Pd (HR mode)	Freeze-dried samples					
	No. of samples	Concentration ranges (ng kg ⁻¹ , dw)	Mean values (ng kg ⁻¹ , dw)	Median values (ng kg ⁻¹ , dw)	Skewness	Kurtosis
Full cream milk	10	949 - 8160	3790	3040	1.33	2.29
Skimmed milk	10	10 500 - 14 300	12 400	12 700	-0.12	-2.34
Meat (beef, pork, veal)	13	42 - 452 000	73 100	11 200	2.20	3.50
Meat (chicken, turkey)	7	235 - 457 000	95 600	3460	1.99	3.70
Eggs	10	993 - 8660	3120	2830	1.38	2.18
Wholemeal flour	10	2230 - 3970	3200	3280	-0.30	-1.87
White flour	10	1060 - 84 100	27 400	13 600	1.33	-0.08
Vegetables (tubers, bulbs, leaves)	20	385 - 206 000	69 600	47 800	1.04	0.00

Table 4. Comparison of results obtained for ^{195}Pt in this study with those from literature.

	Pt concentration (ng kg^{-1})		
	Present study (dw) Median values	Vaughan and Florence (dw) RSD in % within brackets	Ysart et al. (fw)
	Full cream milk	74	1030 (14)
Skimmed milk	73	1450 (14)	
Wholemeal flour	87	1090 (12)	100
White flour	93	900 (11)	
Beef	19	10 400 (5)	<100
Pork	45	5840 (12)	
Chicken	71	12 900 (9)	100
Eggs	33	14 300 (9)	<100
Carrots	16	2740 (9)	-
Potatoes	18	3880 (6)	<100
Onions	LoQ	6620 (9)	-