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Mineral content of foodstuffs – Palladium in food

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SUMMARY

Palladium is one of the platinum group metals, a microelement. Within the platinum group metals, it belongs to the group of light platinum metals. It is not an essential element and not stimulative either. It is present in the food chain at very low, $\mu\text{g}/\text{kg}$ concentrations, therefore, even though it forms some decidedly toxic compounds, its toxic effect has no practical importance from an agricultural production, environmental protection or human nutrition point of view. The discussion of palladium-related knowledge was undertaken to complete a series of communications that started years ago.

INTRODUCTION

The topic of minerals was discussed in a series of 48 articles between 2005 and 2009 in the former scientific journal *Food Industry* until it was discontinued. In this series of papers, the food chemical characteristics of macroelements, essential microelements, stimulative elements, and a group of toxic elements were described. However, a discussion of the entire periodic table, with the exception of the 4 biogenic elements and the 6 noble gases which are not mineral elements, was not carried out, of course. An opportunity was recently offered by the editors of the *Journal of Food Investigation* to compile articles about the remaining elements, and to make the collection describing the minerals in foods complete. Thus, in connection with the previous series of articles, the characterization of microelements that are considered toxic or mildly toxic is continued in this new series. The present paper provides brief information on the topic related to palladium (Pd), a microelement of the platinum group metals.

THE PHYSIOLOGICAL ROLE OF PALLADIUM

Palladium is a heavy metal microelement belonging to the platinum group metals, a member of the second triad of group 8 of the periodic table, classified into the group of light platinum group metal (Ru, Rh and Pd), similarly to ruthenium and rhodium. Its physical and chemical characteristics are well known [1, 2], however, we are less familiar with its biological and, especially, toxicological role.

Palladium is an element that rarely occurs in nature. The metal was discovered in raw platinum by the British physician and chemist William Hyde Wollaston in 1803, and it was named after the asteroid Pallas [3]. It has its own mineral called palladite (PdO). Chemically, among platinum group metals it is primarily similar to platinum. In its compounds it is usually divalent, but trivalent and tetravalent palladium compounds are also known. Its compounds are yellow, brown, red or black in color, its simple salts hydrolyze easily, its complex compounds are more stable.

Industrially, its alloys are used in the catalysts in cars, e.g., the so-called “white gold” contains 10% palladium, but only very small amounts of it enter the environment as a pollutant, despite the fact that, under natural conditions, palladium is the platinum group metal that occurs in the highest amounts. In the lithosphere, it is present at a rate of about $4 \mu\text{g}/\text{kg}$ on average, but typical concentrations in rocks and soils are generally lower than this [4, 5].

The physiological role of palladium is not known, and can typically be classified as non-essential. There are no reliable literature data on its possible biopositive effects. Therefore, the role of Pd from a biological or physiological point of view can only be judged on the basis of its toxicity. Although the metal has several toxic compounds, this is of little practical significance, because its very low prevalence, since its prevalence in the biosphere is significantly lower than that of typical microelements considered to be physiologically important. From a theoretical point

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of view, it may be a subject of discussion whether palladium should be classified as a toxic element or rather a microelement with no biological-physiological effect. On the other hand, there is a characteristic property that exhibits a fundamental divergence between vital and non-essential elements, and this is the concentration distribution [6].

Palladium metabolism in the human body

The amount of Pd entering the human body daily is quite small, although it is generally higher than the values characteristic of other platinum group metals. The total daily Pd intake is likely to be well below 0.1 mg, and this comes mainly from food and, to a lesser extent, from drinking water. Based on data from the United Kingdom, in the 1990s, 98% of the population had a daily palladium intake of typically less than 0.002, and the average daily Pd intake was estimated to be 0.001 mg [7]. Little data is available on the absorption, but it is well known that the absorption ratio, and thus the amount of palladium excreted in urine and faeces, is strongly dependent on the chemical form of the element, i.e., the speciation.

THE PALLADIUM CONTENT OF FOODS

The palladium concentration of plants and, thus, of the plant-animal-human food chain, is mainly determined under natural conditions by the Pd-providing ability of the soil, if no special contamination source is expected. Since the Pd concentration of soil and groundwater is mostly low, although the geological origin of the soil plays a decisive role, the Pd content that can be measured in foods typically quite low. Mostly, it is in the $\mu\text{g}/\text{kg}$, rather than the mg/kg concentration range. Platinum group metals, even though they are not essential from a plant physiology point of view according to our current knowledge, can be taken up relatively easily by the plants from the soil, and thanks to this the ratio of Pd in plant ash is much higher than it is in the soil [8]. The average Pd content of food plants is roughly $30 \mu\text{g}/\text{kg}$ dry matter, and the Pd content of powdered Bowen's kale, used as an analytical reference material, was $25 \mu\text{g}/\text{kg}$ [9]. According to Frazzoli et al., the lowest Pd content in Italy was measured in eggs ($2.8 \mu\text{g}/\text{kg}$), while the highest value was obtained in vegetables ($47.8 \mu\text{g}/\text{kg}$). Values are based on dry matter content [10].

In foods of animal origin, Pd concentrations lower than in plant-based ones can be measured, and according to Bowen, the average Pd content of animal muscle tissue is only $2.0 \mu\text{g}/\text{kg}$ dry matter [4] [5]. According to Reilly [11], in the United Kingdom, the average Pd content of meat products is $0.6 \mu\text{g}/\text{kg}$, while it is $2.0 \mu\text{g}/\text{kg}$ in fish, on an as is basis. In the book of Nordberg et al. [7], the palladium content of several foods is published:

- Dairy products and poultry: $0.3 \mu\text{g}/\text{kg}$
- Fruits, vegetables, various drinks: $0.4 - 0.9 \mu\text{g}/\text{kg}$

- Fish and breads: $2.0 \mu\text{g}/\text{kg}$
- Nuts: $3.0 \mu\text{g}/\text{kg}$

Even though palladium has compounds of certain toxicity, because of their low concentrations the potential toxic effects of Pd are of little practical significance in the case of agricultural production or in human nutrition. There are no data available on organisms that would enrich palladium heavily or on foods with significant Pd concentrations.

RELATIONSHIP BETWEEN THE ENVIRONMENTAL PALLADIUM LOAD AND VEHICLE TRAFFIC

A certain amount of palladium is released into the environment and into the air from the catalytic afterburner motor vehicles. For the time being, this load does not pose a significant risk of environmental pollution or a real toxicological risk to warm-blooded animals [12]. At the same time, the worldwide spread of catalytic vehicles can significantly increase the Pd emission into the environment. For example, between 2002 and 2010, the average palladium concentration of roadside dust in Beijing increased from 36 to $113 \mu\text{g}/\text{kg}$, while in Munich the Pd content of tunnel dust increased from 18 to $389 \mu\text{g}/\text{kg}$ between 1994 and 2007 [7].

CONCLUSIONS

According to our present knowledge, palladium has no considerable biological or food toxicological significance. Of course, the metal and its compounds as heavy metals would be toxic were they to appear in foods in concentrations greater than the current ones, but this risk is not yet present. The palladium content in the environment is low. However, it should be taken into account that the palladium emitted by the catalytic afterburners of combustion engines operated in accordance with environmental regulations is also released into the environment with the exhaust gases thus, it can be incorporated into plants grown near busy roads with airborne dust or through absorption from the soil. The palladium content of food raw materials produced in such areas may therefore increase, but due to the spread of electric vehicles, the environment is not expected to be burdened by the palladium emitted.

From an analytical point of view, the detection and quantification of palladium do not present any difficulty. Even a few nanograms of palladium can be detected in 1 kg of sample by inductively coupled plasma-optical emission spectrometry (ICP-AES) or by neutron activation analysis.

We plan to continue this series of articles, the next installations will describe the remaining platinum group metals, heavy platinum group metals, and information will be provided about the presence of these heavy metal microelements in the food chain.

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