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Voltammetry for Monitoring Platinum, Palladium and Rhodium in Environmental and Food Matrices

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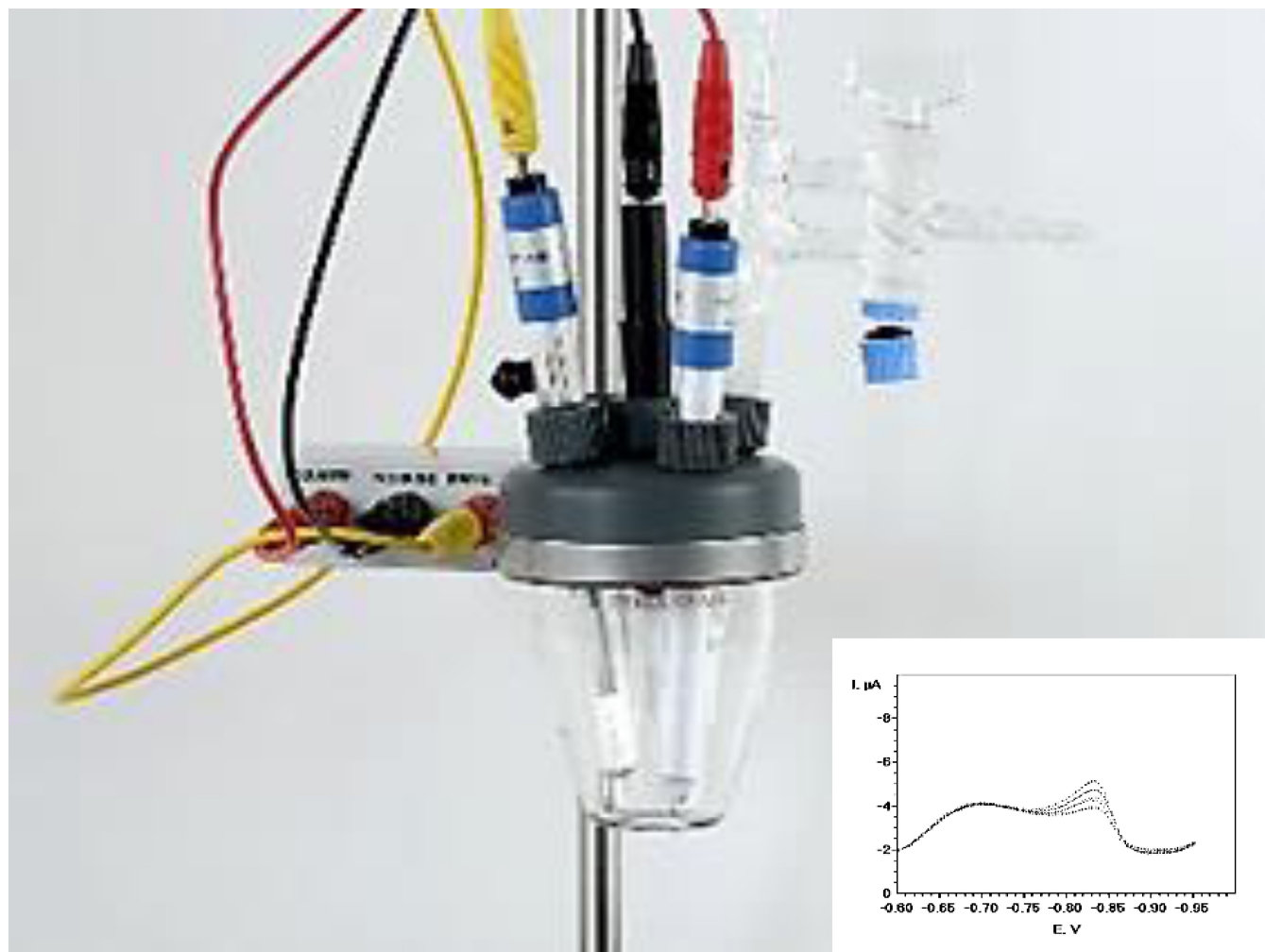
The interest of researchers on quantification of Pt, Pd and Rh in the environmental and food matrices is the consequence of the production of catalytic converters for car engines. Sensitization, mutagenic effects in bacterial and mammalian cells, and increased tumour incidence are the effects of Pt, Pd and Rh at high concentrations reported in medical and occupational researches while their effects at the low environmental concentrations have not been determined. Voltammetric techniques are very advantageous to quantify PGEs in environmental and food matrices due to their intrinsic sensitivity derived from the electrochemical pre-concentration of the analyte at the electrode surface, the capability to distinguish between different redox species and/or labile from non-labile metal complexes, with applications for metal speciation studies. The analysis of PGEs by spectrophotometric methods (atomic absorption, ICP-MS, ICP-OES, etc.) suffers from several practical problems. In this article we take into consideration the research concerning environmental and food matrices from 1996 to 2022.

Introduction

The Platinum Group Elements (PGE) includes 6 metals: Ir, Os, Pd, Pt, Rh and Ru. Their natural abundance on the earth's crust is highly variable (Table 1), however, almost always about parts per billion (ppb).

The increasing interest of researchers in quantification of Pt, Pd and Rh in the environmental and food matrices is the consequence of the production of catalytic converters for car engines (in USA since 1975 and in Europe since 1986).[3–6]

In particular, they are used to limit CO, NO_x and unburned hydrocarbons amounts in exhaust gases from engine vehicles. Usually, the converter comprises a metallic substrate, a ceramic monolith with a honeycomb structure, a wash coat of aluminum and cerium oxides and the catalyst material, a mixture of Pt, Pd and Rh deposited on the metal oxide.

Generally, Pt is the most active and is widely used, but is not appropriate for all applications because of unwanted reactions and high cost. Palladium and rhodium are two other elements used. Rhodium is a reduction catalyst, palladium an oxidation catalyst while platinum is used for both reduction and oxidation. The particulate matter emitted by the engines contains PGE due to thermal and mechanical actions during vehicle operation. PGEs, once released to the air, are transported over short and long distances and then might enter the environmental matrices and, hence, the food cycle.[7,8] A fast accumulation in the environmental matrices was observed in German soils between 1999 and 2005, nearly alongside heavy traffic roads[9,10] with enrichment factors between 2.1 and 8.9, once even a factor of 15 was found. Also, elevated Pt and Rh concentrations were measured in airborne dust.[10–11] High PGE concentrations are not limited to the vicinity of emission points, having been measured in remote areas. By Inductively coupled plasma mass spectrometry (ICP-MS), Barbante et al.[12] measured PGEs concentrations in snow sampled in Greenland area that were approximatively 40 (Pt), 80 (Pd) and 120 times (Rh) higher than the values in old ice (7000 years).

For people exposure to this metal class, inhalation of fine particulate containing PGEs, skin contact and nutritional intake represent the main ways. People exposure and uptake have been studied comparing citizens with different contacts to car traffic. Adults from Rome with high traffic density had greater urinary Pt and Rh amounts than adults from Foligno (a smaller town) with relatively low traffic density, but no clear trend was found for Pd.[13] While, a significant correlation among urinary palladium and rhodium concentrations and traffic density was found in children, but no correlation was observed for platinum.[14] Despite some inconsistencies, the studies show that human exposure results in the uptake of PGE, although PGE may not be transferred to organs.[14] Though PGEs are mostly emitted in elemental and oxide form,[3–6] there is evidence that in the environment they can be converted into soluble compounds by complexation with natural ligands and can enter the food chain.[15–17]

In addition to be used in catalytic converters, the PGEs have a high economic value because are involved in many fields such as electronics, drugs, jewellery and catalysts in the

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Table 1. Natural abundance in Earth's crust (ppb).

Element	[1]	[2]
Ir	1	1
Os	5	1.5
Pd	15	15
Pt	1–5	5
Rh	0.1	1
Ru	0.1	1

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chemical industry. Several platinum compounds, in particular the coordination complexes such as cisplatin, carboplatin and oxaliplatin, have anticancer effects and are used against solid, testicular, ovarian, lung, head and of the neck.[18] Pt is excreted by the patients after the treatments and released into the hospital sewage. Researchers[19] concluded that the Pt contribution of hospitals into the environment is of minor importance as compared to other anthropogenic sources, particularly the auto vehicular traffic.

The continue increasing use of Platinum Group Elements and their discharge, over the last thirty years have led to the occurrence of environmental and food contamination.

Health risks

Sensitization, mutagenic effects in bacterial and mammalian cells, and increased tumour incidence are the effects of Pt, Pd and Rh at high concentrations reported in medical and occupational researches[20,21] while their effects at the low environmental concentrations have not been determined. A no-effect limit concentration of $1.5 \, \text{ng m}^{-3}$ has been set for exposure to Pt salts in the catalyst-manufacturing industry[20,21] and airborne Pt concentrations should not exceed $100 \, \text{pg m}^{-3}$ and only approximately 10% may be in the form of soluble salt. Available similar data on Pd and Rh are still not enough to establish the consequences on human health.[20,21]

Even if the PGE emissions are increasing, in common environmental matrices their concentrations remain low, consequentially, associated risks for people are supposed to be limited. Considering the chemical-physical properties of PGEs and the type of substances presents in air where they are released in the form of very fine particles, it is possible to hypothesize that the aforementioned analytes can be mobilized and solubilized, thus increasing their bioavailability, they can be converted into substances to greater toxicity, especially after introduction into the body, moreover, the presence of chloride in the pulmonary fluids could give rise to formation of halogenated compounds which can cause cellular damage.[22] However, it should be noticed that today known data are not enough for accurate valuation of risks. The information about
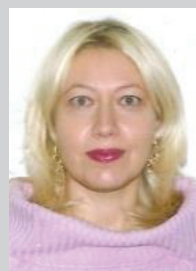
Diana Amorello born in Palermo on 1972, graduated in Chemistry in 1996 and in 2000 obtain the 2° Level Master on Chemical Methodologies for Control and Analysis at Bologna University. She started his career at the University of Palermo (Italy) on 2002 as researcher of Analytical Chemistry. This discipline constitutes the predominant part of the research activity and concerns the following lines of research: development of voltammetric analytical methodologies, in particular, for platinum group elements; study on environmental and food matrices. The scientific production to date consists of 24 publications mostly in international journals.

Santino Orecchio born in Palermo on 1955, graduated in Chemistry in 1980, started his career on 1984 at the University of Palermo as researcher of Analytical Chemistry. From 2002 is Associate Professor of Chemistry of the Environment and Cultural Heritage. These disciplines constitute the predominant part of the research activity of Prof. Santino Orecchio and concerns the following lines of research: Development of analytical methodologies; Study of environmental matrices (causes and effects of pollutants, analytical techniques, biomonitoring, etc.); Adsorption and photo-degradation studies of organic contaminants (PAHs, nitro-phenols, phthalates, etc.); Study of matrices concerning Cultural Heritage. The scientific production to date consists of 133 publications mostly in international journals.

Silvia Orecchio born in Palermo on 1990, in 2019 she got a degree in Pharmaceutical Chemistry and Technology by the University of Palermo, with a graduation thesis on novel food analysis. From September 2019 to February 2021 she worked by the University of Pavia, on a research project aimed to optimize the methods of analysis of hazardous trace compounds (PAHs) in matrices that have been contaminated as result of fires. She is currently a Ph.D. student at the University of Palermo. Her research interests are focused on the synthesis of molecular and polymeric systems as interface additives in organic and perovskite photovoltaic devices and in the production of the latter.
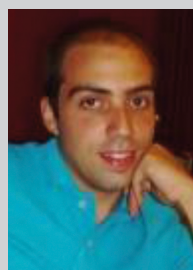
Salvatore Barreca born in Palermo (Italy) on 1986. From October 2022 is Assistant Professor in the Department of Chemical Science, University of Catania. His researches concern: on the development and validation of analytical procedures for quantification of pollutants in different matrix; photochemistry of surface and atmospheric waters; heterogeneous photo-catalysis and its applications in the environmental fields, application of advanced oxidation processes (Fenton reaction,) to water and soil remediation. chemical education. He also authored one patent, one book chapter. The scientific production to date consists of 36 publications mostly in international journals.

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the migration, accumulation, physicochemical form, bio effects are limited for risk evaluation. Also, very little information is available on the subclinical effects of continue low dose exposures to PGE.

So it is very important to continue measure the environmental concentrations and study their properties, physico-chemical behaviour, bioavailability, and associated toxicity to organism, which ensure us to better assess their potential risk in human.

Analytical techniques

Voltammetric techniques are very advantageous to quantify PGEs in environmental and food matrices due to their intrinsic sensitivity derived from the electrochemical pre-concentration of the analyte at the electrode surface, the capability to distinguish between different redox species and/or labile from non-labile metal complexes, with applications for metal speciation studies. In Figure 1 and 2 are showed a Voltammetric device and voltammetric cell respectively.

The analysis of an only rhodium isotope by ICP-MS suffers from possible interferences with polyatomic ions[23] (e.g., $^{63}Cu^{40}Ar$, $^{80}Kr^{23}Na^+$, $^{40}Ar_2^{23}Na^+$, $^{206}Pb^{2+}$, $^{102}RuH^+$, $^{87}Sr^{16}O^+$, $^{89}Y^{14}N^+$, $^{91}Zr^{12}C^+$).

Figure 1. – Voltammetry device.

Figure 2. – Voltammetric cell.

Considering Pd analysis, the signals relative to the isotopes 104 and 108, after correction for mass spectral interferences, could be selected for quantification. Anyway, these isotopes have spectral interferences that are not fully minimized working in high-resolution mode. Also, the masses ^{105}Pd and ^{106}Pd can be measured, but mathematical corrections for unresolved spectral interferences provided many negative results. Measure of ^{194}Pt could be was used for statistical analyses.

In the quantification of PGEs by ICP-MS, the presence of interfering elements in environmental matrices (street dust and roadside soils) in much higher concentrations than the analytes, isobaric and double-charged ions disturbs the determination of Pd. The reason is the presence of mono ($^{106}Cd^+$, $^{108}Cd^+$ and $^{110}Cd^+$, etc.) and polyatomic isobaric ions ($^{105}Pd^+$, $^{68}Zn^{37}Cl^+$, $^{106}Pd^+$, ^{66}Zr, $^{40}Ar^+$, $^{108}Pd^+$, $^{68}Zn^{40}Ar^+$, $^{110}Pd^+$, $^{94}Mo^{16}O^+$, etc.).[80,81] For Pt analysis by ICP-MS, mathematical corrections based on signal ratio measurements were need for HfO^+, $CuAr^+$, YO^+, SrO^+, RbO^+ and Pb^{2+} interferences.[24] The interference contributions of HfO^+ in ^{195}Pt determination, of Pb^{2+}, $ArCu^+$, SrO^+ and RbO^+ in ^{103}Rh quantification and that of YO^+, $ArCu^+$ and $ArGa^+$ in ^{105}Pd determination were studied by Gomez in order to find the best analyte/interferent signal ratio.[24] The conclusions of this research showed that argon gas flow rate cannot be used for interference mitigation and that a medium plasma power of 1350 W yields the best results, although Pb^{2+} formation is minimised at 1150 W. A potential method to overcome the spectral interferences is by matrix separation/PGE preconcentration methods (ion exchange resins, chelation, etc.).

The same researchers[24] affirm that to avoid matrix separation procedures, a possibility is the direct determination by high resolution magnetic sector field ICP-MS (HR-ICP-MS) using ultrasonic nebulisation which reduces the formation of some molecular interferences on the plasma. However, the results are not satisfactory.

Moreover, ICP-MS needs expert specialists, principally for the mass spectrometry and many constituent parts of the ICP-MS instrument are very delicate, for example, the injection system gets dirty very easily and is often necessary to replace it, in any case, the operating costs of voltammetric systems are decidedly lower than those of other techniques which require large quantities of gas (argon). Other instruments such as Graphite furnace atomic absorption spectroscopy (GF-AAS), instead, has not adequate detection limit for Rh analysis if it is not preceded by a pre-concentration step. Also, GF-AAS, needs an accurate setting of the instrumental parameters especially when the matrix contains organic compounds or is rich in salts. This analytical technique, for each detectable element, needs the specific hollow cathode lamps and the instrument needs a frequent replacement of graphite tubes and consumes inert gas (argon).

Fortunately, several inorganic pollutants, such as PGE after acid decomposition, may be quantified at ultra-trace levels by direct differential pulse cathodic stripping voltammetry (DPCSV or CSV). In this context, voltammetric instrumentation can be considered an important tool for PGE analyses in different matrix. However, extensive knowledge of electrochemistry is

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required to take full advantage of all the possibilities that voltammetry can offer.

Voltammetric techniques

Voltammetric techniques are based on the measure of the current flowing through an electrode immersed in a solution containing electroactive compounds, while a potential scanning is imposed upon it. This type of electrodes, are named working electrodes (WE) and could be constituted of different solid materials (gold, platinum or glassy carbon) or formed by a drop of mercury hanging from a capillary. Generally, it has a very little surface to assume quickly and accurately the potential imposed by the electrical circuit.

Rapid scan Voltammetry is the simplest technique. At the working electrode is applied a rapid potential scanning that varies linearly (20–100 mV s^{-1}). The scanning starts before the discharging potential and stops afterwards. The potentiality of this technique are strongly limited because the capacitive current increases when the velocity of scanning is increased and cannot be electronically compensated.[25]

During an analysis by differential pulse voltammetry (DPV), a series of periodical pulses of potential are superimposed to the linear scanning, in this way, a consistent improvement of the signal (current) is obtained. Furthermore, if the difference between the current just before and at the end of the pulse is measured, a result less influenced by the capacitive current can be obtained. In this case it produced a peak shaped voltammogram (Figure 3). This technique is very sensitive and detection limits, generally, range from 10 to 100 μg L^{-1}.[25]

In the stripping Voltammetry (SV), anodic stripping voltammetry, (ASV), cathodic stripping voltammetry (CSV), several metals dissolve in mercury (working electrode) forming an amalgam while some anions form insoluble salts with it. This procedure consents improve the limits of quantification because in the pre-concentration phase a great quantity of analyte is accumulated in a small volume of mercury and consequentially, the measured stripping currents are greater than the ones obtained using a non-accumulative technique. In this case the detection limits are lower the μg L^{-1}.[25]
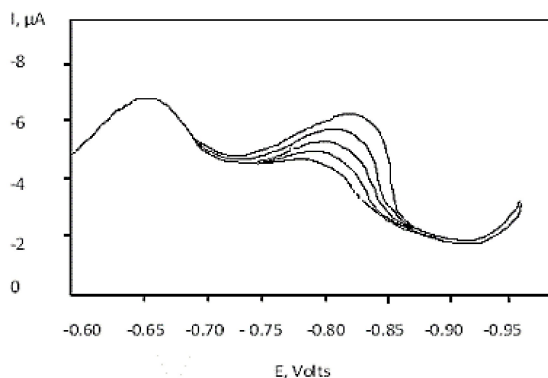
In these analytical techniques are important the two main steps: pre-concentration of analyte onto the electrode surface and the following stripping of the cumulate compound in the solution.

The stripping process occurs during the scanning by the previous described techniques (linear or differential pulsed or square wave scanning). Generally, the working electrode is a dropping or a film mercury. The most used technique is the anodic stripping: a negative potential is applied to the electrode and the cations are discharged as element into the mercury (amalgam). Successively the atoms are oxidised again, during an anodic scanning of potential. During the scanning of the potential, the current is measured and plotted in a voltammogram where a peak shaped is shown. The position (potential) and the height of the peak are related, respectively, to the specific analyte and to their concentration respectively.[25]

In the adsorptive voltammetry (AdV) and adsorptive stripping voltammetry (AdSV) many metal complex and some organic substances are adsorbed onto the surface of the electrode at a specific potential. This artifice can be employed if the metals do not form amalgam onto the mercury, but form complex (with a complexing added to the solution) that can be adsorbed onto the latter and analysed with a direct scanning or a stripping method. The detection limits are below the μg L^{-1}, while the linear range is often short.[25]

Researches 1996–2022

Researches 1996–2002

By complex with dimethylglyoxime, Georgieva et al.[26] used adsorptive stripping voltammetry to analyse palladium concentration in aqueous and solid samples, in addition, the recovery from biological and inorganic materials was evaluated changing different parameters. The sensitivity of the proposed analytical method and the linearity between the peak current and the concentration of analita is influenced by the ionic strength, the electrode area, the pre-concentration time, the transport rate to the electrode and the potential scan rate. The most appropriate medium was 0.1 mol L^{-1} acetate buffer between pH 3.5 and 4. Using 2 min of pre-concentration at a 2.6 mm^2 electrode and the differential pulse mode, a detection limit of 0.05 μg L^{-1} Pd was achieved for liquid samples and 50 ng g^{-1} for solid samples.

Adsorptive stripping voltammetry[27] it was also employed to measure airborne platinum concentrations in Munich local buses during regular ride. Sampling 5 m^3 of air, the detection limit was 0.5 pg m^{-3}. The mean concentration of air sampled during a year (1993–94) was 7.3 pg m^{-3}. The highest concentration of Pt (33 pg m^{-3}) was measured during the bus voyage in a high-traffic area compared to 3.0 pg m^{-3} shown on a suburban bus route.

Leon et al.[23] quantify simultaneously ultra-traces of Pt and Rh in electrolyte solutions by catalytic adsorptive stripping voltammetry using a hanging mercury drop electrode. Optimal instrumental parameters were: accumulation potential 0 volts

Figure 3. – Platinum voltammograms at different concentrations.

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(vs. Ag/AgCl), second accumulation potential −0.8 V, pre-concentration times 90 s and 120 s respectively, scan rate 20 mV s^{-1}. In this study, many possible interferences were evaluated. The optimized method was employed to quantify traces of Pt and Rh in spruce shoots samples after high pressure mineralization. Pt and Rh concentrations in the spruce shoots were 543 pg g^{-1} and 22 pg g^{-1} respectively.

Traces of platinum in gasoline, after combustion in a Wickbold modified apparatus, and subsequent UV digestion (T > 90 °C, t > 90 min) were quantified by differential pulse cathodic stripping voltammetry (DPCSV)[28] and ICP-MS was used for comparison. In diverse type of gasoline (unleaded Normal, Super and Super Plus), platinum concentrations were in the order of 5 pg g^{-1}.

By driving test,[29–31] some researchers measured emission from new catalysts of 0.1 mg km^{-1} for Pt, while for aged ones the emissions decreased to 0.006–0.008 mg km^{-1}.[31]

Helmers[19] by cathodic stripping voltammetry quantifies Pt and Rh in polluted and unpolluted grass and in the hospital waste water samples. The authors established that in 1997, concentrations of Pt and Rh in grass samples were 2.7 times higher than in 1994 and in dust samples 3.9 times higher than in 1994, respectively. Percentage of cars supplied with catalytic converters was 2.4 times higher in 1997 than 1994.

Zimmermann[32] carried out a research to quantify Pt trace levels in eel liver and mussel soft tissue, using two different analytical techniques: sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) combined with microwave digestion and adsorptive cathodic stripping voltammetry (ACSV) following high pressure ashing (HPA). The results of this research demonstrated that the detection power of ACSV after digestion was about 20 times more sensitive than spectrometric method, because, in the last case, high dilution to reduce acid concentration is need. The concentrations of two methods differed between 16 and 30% for Pt concentrations below 1 ng/g and were almost identical above this amount. The platinum concentrations in the tissues analyzed were in the range from 0.1 to 2.3 ng g^{-1}. Similarly, other researchers,[33] in pilot experiments, (Klueppel) digested grass samples by HPA followed by Pt-determination by both, adsorptive cathodic stripping voltammetry (ACSV) and ICP-MS and demonstrated satisfactory agreement at Pt concentrations above 50 ng g^{-1}. At lower concentrations (0.5–2.5 μg L^{-1} Pt) the determination of Pt in blood showed also a good agreement between ICP-MS and ACSV.[32]

Optimal instrumental parameters were found[34] for the analysis of Pd^{2+} complexed with α(2-benzimidazolyl)-α′,α″-(N-5-nitro-2-pyridylhydrazone)-toluene (BINPHT) by adsorptive cathodic stripping voltammetry using hanging mercury drop electrode. Pd^{2+} in the sample solution can be determined in BINPHT and EDTA. Accumulation is achieved by adsorption of Pd(II)-BINPHT complex on a hanging mercury drop electrode. The optimized method was used to quantify untreated river water spiked with a solution of platinum obtaining concentrations of 40 and 80 ppb.

Researches 2003–2009

Huszał[35] describes a catalytic adsorptive stripping voltammetry (CAdSV) method to quantify, at the same time, traces of platinum and rhodium in plant material using new supporting electrolyte containing hydroxylamine or acetone oxime and formaldehyde in H$_2$SO$_4$. Pre-accumulating Pt and Rh for 120 s at 0.0 V, the detection limits, in presence of acetone oxime, were 0.1 ng L^{-1} and 0.2 ng L^{-1} respectively while 0.6 ng L^{-1} and 0.2 ng L^{-1} in presence of hydroxylamine. ICP MS was used to compare the results of CAdSV measurements and comparable results were obtained.

Obata[36] compared the results related the concentrations of platinum, at pico molar levels, in the estuarine waters around Tokyo Bay using two different analytical techniques: cathodic stripping voltammetry (CSV) and isotope dilution-inductively coupled plasma mass spectrometry (ID-ICPMS) combined with anion resin column extraction method. Results using successive UV irradiations were comparable. Without UV illumination, the Pt concentrations obtained using voltammetry were usually lower than those obtained using ICP-MS. This shows that the platinum in the estuary water, partly, was in an organic form. In the analysed estuarine waters samples, platinum concentrations ranged from 5.0 to 13.6 pM in the Ara River and from 4.8 to 35.2 pM in the Tama River.

Locatelli[37] proposed a method to quantify at the same time Pd and Rh at ultra-traces level, by square wave adsorption stripping voltammetry (SWAdSV), using dimethylglyoxime (DMG) as complexing agent and a process for the sequential determination of Pt(II), Rh(III), Pd(II) and Pb in surface water. The authors tested the obtained data by analysis of the certified reference material as standard sea water BCR-CRM 403 and fresh water NIST-SRM 1643d. In conclusion, author affirms that voltammetry is a good alternative to atomic absorption spectrometry, which, in the case of quantification of analytes in complex matrices and with high salts amounts as sea water, needs expensive apparatus like Zeeman background corrector.

The same previous author[38] proposed an analytical method to quantify sequentially by square wave voltammetry, at trace and ultra-trace levels, Pd, Pt, Rh and Pb in environmental matrices, principally, in presence of interference metals as Cu, Zn, Co, Ni, that show, signal potentials very similar to analytes, causing voltammetric interferences. The method was verified analysing standard reference materials and by comparison with spectroscopic results. In the case of water standard reference materials not containing PGEs (standard sea water BCR-CRM 403 and fresh water NIST-SRM 1643d), the solutions were spiked with known element concentrations, successively verifying the percentage recovery. The standard addition method permitted to solve or minimize complications linked to voltammetric interferences. For the aqueous solutions, detection limits (LoD) for Pt, Pd and Rh were 0.021, 0.019 and 0.027 μg L^{-1} respectively. The optimized procedure was applied to sediments, soils and superficial waters sampled in proximity of superhighway and in the Po River mouth area.

Monticelli[39] proposed a new automated method to quantify ultra-traces of several heavy metals (Cd, Pb, Cu, Ni, Co,

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Rh and U). Rhodium was quantified by adsorptive cathodic stripping voltammetry (AdCSV) by the catalytic effect on H_2 discharge of its formaldehyde complex. In this case, an acidic pH is required and the complexing agent was added directly in the test tube. In this research, the authors optimized the instrumental and chemical parameters affecting the performance of the method. The automation of the proposed analytical method was validated following IUPAC technical report.[40] The validated method was verified on surface water samples collected from Lake Como.

Osterauer[41] investigated the effects of different concentrations of Pt on the early development of the snail and the zebrafish Ramshorn. The use of an antimony film coated on a screen-printed carbon electrode was suggested for the determination of palladium at ppb concentrations in environmental matrices by adsorptive stripping voltammetry using dimethylglyoxime as chelating agent. Metal bio-accumulated in the organisms was measured by adsorptive cathodic stripping voltammetry (ACSV) after digestion by high pressure ashing.

In 2008 and 2011, the concentrations of Pt in sediments, water and suspended particulate matter, sampled in the Lérez River estuary (Pontevedra Ria, Iberian Peninsula), were determined by Cobello,[42] by means of catalytic adsorptive stripping voltammetry using a modification of the method proposed by Jacinto.[43] In this study, the authors quantified the concentrations of dissolved and particulate Pt and confirm the decrease in Pt particle-reactivity across the salinity gradient. The transfer from neutral Pt(II) (Pt(OH)$_2$) to Pt(IV). The range of Pt concentrations obtained (0.2–1.6 pM) is similar to that found previously in the Pacific Ocean.

Haus[44] proposed a high pressure microwave method using nitric and hydrochloric acids to mineralize plant and animal tissue to quantify Pt by adsorptive cathodic stripping voltammetry according to Zimmermann et al..[45] The authors established that the aging of the Teflon vessels produces an irregular loss of Pt over time. The determination of Pt in the animal tissue samples by means of ACSV was performed.

Researches 2010–2016

Differential pulse voltammetry (DPV/a) and adsorptive stripping voltammetry (AdSV) were used by Orecchio[46] for the determination of Pt and Rh in *Nerium oleander* leaves prevalently collected in the Palermo area. Metals emitted from engine exhausts (Pt, Pd and Rh and in the past also Pb) are deposited along roadways, on adjacent vegetation, and the deposition on plant foliage is a function of air concentrations,[47] so leaves represent a convenient biological sampler for monitoring atmospheric contaminants.[48–52] Pt quantification was carried out in aqueous H_2SO_4 1 M as supporting electrolyte, in the presence of hydrazine sulphate and formaldehyde. Formaldehyde and hydrazine condense in situ to form the corresponding hydrazone, which forms a complex with Pt(II). Subsequently, a potential changing from −0.3 to −1.0 V in the differential pulse mode was applied to the working electrode, and the catalytic current of the hydrogen formation was measured at −0.85 V (versus Ag/AgCl); its intensity is propor-

tional to analyte concentration. The catalytic effect of Pt makes this determination extremely sensitive. Quantification of Rh was carried out by adsorptive stripping voltammetry (AdSV). This technique is known to give an excellent sensitivity for trace metals at a mercury film or drop electrode. This method implicates complexation of Rh with specific ligands. The complex is electrochemically removed by scanning the electrode potential, usually in a reductive direction. Analyses were carried out in hydrochloric acid solution, in the presence of formaldehyde, a complex rhodium–formaldehyde is adsorbed on a hanging mercury electrode at −0.7 V. The potential of working electrode was improved from −0.9 to −1.2 V, giving a peak at −1.1 V due to hydrogen reduction, catalyzed by Rh complex. Quantitative determinations of Pt and Rh were done using the standard addition procedure. In the *Nerium oleander* leaves Pt and Rh concentrations were found in the ranges 0.33–25 and 0.40–4.6 µg kg^{-1}, respectively. Authors carried out linear regression investigation between Pt and total PAHs concentrations in *Oleander* and *Quercus ilex* leaves measured in previous researches[49,50] referred to the same area. The good correlation demonstrates that oleander leaves can be used to establish the presence and the distribution of pollutants in a chosen area. The same researchers[53] employed differential pulse voltammetry (DPV/a) to quantify platinum in soils sampled in Palermo area. All samples show concentrations of Pt above average upper crust values; Pt concentrations were in the range 0.6–2240 µg kg^{-1}. The higher concentration of platinum detected in soils from the urban areas compared to the control sites and to the deep samples are diagnostic of conspicuous air contamination of Palermo area.

Platinum contamination[54] of estuarine and coastal sediments from the Tagus Estuary and Prodelta shelf sediments has been studied. After mineralization, platinum analyses were carried out by catalytic adsorptive cathodic stripping voltammetry (catalytic AdCSV). In this study, the detection limit for a mass of 0.15 g of sample was 0.05 ng g^{-1}. The accuracy was monitored using river sediment certified reference material and good agreement was obtained with the certified concentrations. The time profile shows an elevated input of Pt from the early 1970s to the mid1980s related to recent years. However, car converters were not used in Europe until sometime in the late 1980s or early 1990s and no Pt enrichment was observed in the deep layers of the cores sampled in the past. Consequently, sub-surface Pt enrichment in the *Tagus Prodelta* may not reflect the actual anthropogenic inputs but post-depositional mobility. The authors suggest that the Pt maximum amount found at the base of the surface mixed layer is probably driven by the scavenging of Pt at the oxic/anoxic boundary.

Considering that data on traces of PGEs in biological matrices are rare, researchers[18] proposed a voltammetric method to quantify Pt in blood of patients after infusion of oxaliplatin. The perfusate and blood samples of cancer patients on oxaliplatin chemotherapy were collected and analysed at different times. After heating at 550 °C of 250 µL of sample, the ashes were treated with a hot mixture of $HNO_3 + HCl$ in a microwave oven equipped with high-pressure Teflon contain-

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ers. The obtained solution was analysed by differential pulse voltammetry (DPV/a). The concentrations of platinum in the blood samples of untreated citizen were similar to quantification limit (1.5 $\mu g L^{-1}$) while in the treated cancer patients the concentration ranged from 1.5 to 360 $\mu g L^{-1}$ while in perfusate ranged from 0.7 to 9700 $\mu g L^{-1}$.

An anodic stripping voltammetric method[55] was proposed to quantify Pd in simulated high level nuclear water waste. Before analysis, the metal was extracted and precipitate using oximes (α-benzoin oxime in Solvesso-100). The organic phase was scrubbed with water prior to the stripping of palladium using thiourea in HNO_3 and NH_4OH separately.[56] The results quality (accuracy, precision, etc.) were tested by analyzing synthetic samples of Pd solutions in 0.01 M HCl at different 5×10^{-7}, 2×10^{-6} and 5×10^{-6} M concentration levels. Single and multiple addition methods were carried out.

Platinum has been successfully measured in natural waters, biological matrices, soils and sediments, even at ambient background levels using a highly sensitive catalytic method at the HMDE.[57]

A comparable method has been used to quantify Rh in sediments, taking advantage of the improved detection obtained with the aid of the second derivative signal transformation of the stripping scans.[58] The low detection limit testified, 0.02 $ng L^{-1}$, using a relatively short deposition time (120 s), suggests that this method could also be useful in determining this element in natural waters.

Kowalska[59] quantifies Pt (263 $ng g^{-1}$) and Rh (47 $ng g^{-1}$) in soil and quarts samples contaminated by automobile exhausts by voltammetry (AdSV). To validate the obtained results an ICP-MS was applied. In the Kowalska research the attempts to quantify palladium failed, because voltammetric determination was impossible without elaborate sample preparation aiming at simplification of the matrix. It was achieved by solid phase extraction. Two methods for that were established and described in 2020 by Sadowska[60] and the following year by Kińska.[61]

Silwana[62] uses an adsorptive differential pulse stripping voltammetric procedure for Pd, Pt and Rh analysis in samples collected from rivers in close proximity to mining activities in South Africa. A screen-printed carbon electrode coated with a bismuth film, SPCE/BiF was used. The paper describes the experimental parameters, including data on buffer for coating and the supporting electrolyte solution. In this research, analytes were pre-concentrate using dimethylglyoxime. In natural water Pd ranged from 2.56 to 5.17 ppb, Pt from 0.41 to 17 ppb and Rh from 0.14 to 0.38 ppb.

Kolpakova[63] quantifies gold, platinum and palladium in gold–sulfide quartz minerals with a high content of carbon (1–1.5%). The determination of Pd(II) complexed with (2-benzimidazolyl)-(N-5-nitro-2-pyridylhydrazone)-toluene INPHT) was carried out by adsorptive cathodic stripping voltammetry using hanging mercury drop electrode. Pd in the sample solution was determined in BINPHT and ethylenediaminetetraacetic acid (EDTA). Accumulation was obtained by adsorption of Pd(II)-BINPHT complex on a hanging mercury drop electrode. In this

paper, the comparison of the results obtained by stripping voltammetry and atomic absorption is presented.

It is known that European people[64] spend 90% of their time in indoors environments (house, school, car, bus, train, plane, etc.). As consequence, indoor air quality has an important role in exposure to hazardous substances. In a paper[65] Pt analysis and the results relative to dust samples collected in indoor (homes and cars) settled dust, used as passive samplers, are described. The research is finalized to value the magnitude and distribution of Pt concentrations inside common environments and their possible origins. The Pt concentrations in settled indoor dust were measured by differe0ntial pulsed voltammetry (DPV). Concentrations of Pt in dust sampled in houses are in the range from 30 to 1460 $\mu g kg^{-1}$ while, in the cars from 30 to 1750 $\mu g kg^{-1}$. Considering the geo-accumulation index (I_{geo}) [Eq. (1)]:[66]

$$I_{geo} = \log_2 (C_{Pt}/1.5 \cdot B_{Pt}) \tag{1}$$

where C_{Pt} is the measured concentration of Pt in the sample and B_{Pt} is the geochemical background concentration in the hearth crust (5 $\mu g kg^{-1}$).[64,65] Only in two cases, the I_{geo} [Eq. (1)] indicates environments extremely contaminated and regarding settled dust sampled in the cars, about 11% corresponds to practically unpolluted.

Almécija et al.[67] quantify Rh in sediment sampled near a motorway in close proximity to the Tagus Estuary (Lisbon, Portugal) by catalytic adsorptive cathodic stripping voltammetry applying second-derivative signal transformation. This transformation provided well-defined peaks due to the minimization of background interferences, leading to a significant decrease in the detection limits. The optimized analytical method was applied to the analysis of Rh in a sediment core collected close to a motorway bridge. Here, Rh concentrations ranged from 0.06 to 0.47 $ng g^{-1}$, showing a surface Rh-enrichment.

Stripping voltammetry, was used to quantify platinum in sediments and oysters sampled in the Gironde fluvial–estuarine area (France).[68] Sediment cores from the Lot River were representative of the period 1952 to 2001. These samples revealed the phasing-out of an historical Pt contamination with Pt/Th (Thorium) values of $11 \cdot 10^{-5}$ for the oldest part of the section which is greater than the regional geochemical background value (Pt/Th $\sim 2.2 \cdot 10^{-5}$). The oysters from the mouth of the Gironde Estuary sampled from 1981 to 2013 contained Pt amounts in the range 0.80 $p mol g^{-1}$ to 3.10 $p mol g^{-1}$. Pt concentrations were related to industrial melting activity and to other sources. Variations of Pt amounts in oysters was attributed to the exponential increase of Pt use for car catalytic converters. These marine organisms acted as excellent bio-indicators, in fact, they may concentrate the Pt with bio-concentration factor about 1000 and transfer this contaminant to the higher food chain.

Platinum, rhodium and creatinine concentrations were quantified[70] in urine samples of 259 German participants (subdivided in three groups) also assessment of the dental status was taken into account. At the same time, an interview including demands characterising potential exposure to traffic

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exhaust was carried out. For platinum quantification samples were mineralized by UV-photolysis and analysed by inverse voltammetry, while rhodium was quantified by inductively-coupled-plasma mass-spectrometry (ICP-MS) equipped with a dynamic reaction cell (DRC) for the removal of isobaric interferences. The median platinum excretion was 2.42 ng Pt g^{-1} creatinine and 7.27 ng Rh g^{-1} creatinine. The results related to the collected data showed a significant higher Pt excretion concentration with increasing number of surfaces with repairs containing PGE, but also higher values for people of urban areas compared with those of countryside. Also, people working in urban areas showed higher platinum excretion values. Males living and working next to highly frequented roads showed higher rhodium excretion concentrations.

Researches 2017–2022

The quantification of Pt and Rh in 42 alcoholic beverages (white and red wines, vodka and brandy) produced in Italy, Malta and Gozo, for the first time, were investigated.[70] In this case, 10–50 mL of sample, dried at 105 °C for one night was ashed for 5 hours in a muffle at 600 °C. The ashes were solubilized in HCl. Differential Pulse Voltammetry (DPV/a) and Adsorptive Stripping Voltammetry (AdSV) were used for the quantitative determinations of the two analytes. In analysed wine samples, Pt and Rh concentrations ranged from 3 to 470 μg L^{-1} and from 0.0006 to 0.36 μg L^{-1} respectively. The author calculated Pt/Rh ratios ranging from 37 to 180000, in quite disagreement with the ratio in catalytic converters. Unlike other investigated matrices (settled dust matter),[65] the concentrations of the two PGEs are not correlated, suggesting that the grape or the plant (*vitis vinifera*) accumulate the two metals differently. Daily intakes (DIM) of Pt and Rh are reported: consuming 200 mL day^{-1} of wine, this supply from 0.6 to 94 μg and from 0.00012 to 0.072 μg of platinum and rhodium for person respectively.

By voltammetry, usually, palladium is analysed using the hanging mercury drop electrode (HMDE), but, the high toxicity of this metal, has led to their replacement by other electrodes more environmentally friendly but with similar analytical characteristics.[71] An antimony film coated via ex-situ on a commercial screen-printed carbon electrode (ex-situ SbSPCE) was used to quantify Pd(II) in natural samples spiked with 180 μg L^{-1} of Pd by adsorptive stripping voltammetry using dimethylglyoxime as chelating agent by means of the standard addition method.[70]

Van der Horst[72] quantifies Pd, Pt and Rh by spectroscopy and voltammetric methods, studying possible interferences of Na, Fe(III), Ni(II) and Co(II). In this study, the differential pulse absorption stripping voltammetric and a screen-printed carbon film/bismuth–silver (SPC/Bi–AgF) electrode sensor were used. In all the sampling sites very low concentrations of Pd, Pt, and Rh were found at levels that range from 0.48 to 5.4 ng/g for Pd(II), with 17.28 to 81.44 pg g^{-1} for platinum, and 14.34 53.35 pg g^{-1} for rhodium.

Abdou,[73] for the duration of 35 days, exposed *Crassostrea gigas*, a species of oysters, sampled in an unpolluted estuary, to

the isotope 194Pt in seawater. Seawater was renewed daily and spiked to three nominal Pt concentrations (50, 100, and 10,000 ng L^{-1}). In the same time, control conditions were monitored. Five oysters from each tank were analysed by ICP-MS after 3, 7, 14, 21, 28, 35 days of Pt exposure. The results of this method applied to marine organisms were compared to those obtained by voltammetry. In the oysters, the Pt concentration increasing with exposure period.

Dissolved Pt in samples collected along the Atlantic Ocean[74] was analysed by means of catalytic adsorptive cathodic stripping voltammetry (Cat-AdCSV), using a method described in in the 2013 by Cobelo-García et al.).[42] Dissolved Pt concentrations ranged from 0.11 to 0.32 pM, with an average value of 0.22 ± 0.04 pM.

Platinum in sediments core and mussel samples[75] from the north western Mediterranean coast was quantified by Adsorptive Cathodic Stripping Voltammetry (AdCSV) as described in Cobelo-García.[57] The historical (> 100 years) record of Pt in sediments from the Toulon Bay suggests the absence of Pt origins older than those related to vehicle emission converters, such as petrol industry and coal-fired combustion.

From the time when PGEs were used in car converters and as anticancer drugs, very few researches on the platinum and rhodium concentrations in food are available.[70] A paper[76] reports an analytical approach to quantify the two elements in vegetal food. In particular, this study takes in consideration different potato samples produced in Europe and one in Australia. Quantifications of Pt and Rh in potato samples were carried out by Differential pulse voltammetry (DPV/a) for platinum and by Adsorptive stripping voltammetry (AdSV) for Rh using the standard addition procedure. In the potatoes samples, Pt and Rh concentrations ranged from 0.007 to 109 μg kg^{-1} and from 0.0008 to 0.030 μg kg^{-1} respectively. For both metals, in many cases the concentrations are near the quantification limits (0.007 and 0.0008 μg kg^{-1}). The highest Pt concentrations were measured in two samples cultivated in the Syracuse (Italy) area, which is in a highly industrialized zone for the presence of refineries and other chemical industries. In this case, I$_{geo}$ [Eq. (1)] is in the range −11.2 to 2.9 with a mean of −0.27, and from −7.6 to −2.3 with a mean of −5.0 for Pt and Rh, respectively. It results that, for platinum, about 80 % of the samples could be definite as practically uncontaminated, five moderately contaminated, and three from moderately to heavily contaminated. For rhodium, in all the cases, the I$_{geo}$ [Eq.(1)] indicates practically uncontaminated potato samples.

Carlos E. Monteiro[77] proposed, an arrangement of analytical approaches to obtain the speciation of Pt and Rh in the leachates of urban road dust deposited in a section of 30 m of a high-traffic road (Lisbon, Portugal). A sample of road dust was treated over 7 days with artificial rainwater and seawater. In the liquid obtain by filtration (< 0.45 μm), dissolved Pt and Rh concentrations were quantified by adsorptive cathodic stripping voltammetry, while total metal concentrations were measured by ICP-MS. The quantification of Pt and Rh was done, as in other researches using the standard addition method.[78] The species in solution corresponded to a small fraction of total metals in the road dust.

The concentration of total filter-passing species predominates for both elements by a factor of 10 and 2–3 for Pt and Rh, respectively, evidencing that particulate species coexist with truly dissolved forms. Temporal variations were observed for Pt, as opposed to Rh.

The first analytical research[80] to evaluate Pt concentrations in edible mushroom samples uses the Differential Pulse Voltammetry (DPV). Because there are no available on the market certified reference mushrooms containing platinum group elements also in this case was applied the standard addition method. In the 28 analysed samples from Italy, Pt concentration ranged from 0.03–73 μg kg^{-1}. The authors calculated the enrichment factor (EF) [Eq. (2)][80,81] to differentiate between the Pt from human activities and those from natural sources and to value the degree of anthropogenic influence. EF values near to 1 indicate a natural origin of pollutants, while values higher than 10 are considered to be related to human activities.

$$EF = Pt_{\text{conc. in the mushroom}}/Pt_{\text{conc. in the earth crust}} \cdot \qquad (2)$$

Pt in earth crust $= 10$ μg kg^{-1}.

Based on the EF [Eq. (2)] values five contamination categories are acknowledged (Table 2).

The EF [Eq. (2)] of the analyzed mushroom ranged from 0.003 to 7.3. The EFs of Pt calculated for most of the samples are lower than 2, indicating either deficiency or minimal enrichment. Considering the EF values obtained, authors conclude that three samples can be considered as only moderately enriched, while two samples are significantly enriched. In these last cases, the analita certainly is from anthropogenic origin.

A voltammetric application was proposed by Meluccia[83] to quantify at the ultra-trace level Pd(II), Pt(II) and Rh(III) in herbal medicines containing different plants (*Eucalyptus globulus, Harpagophytum procumbens* DC and *Taraxacun officinale weber*), by means of square-wave adsorption voltammetry (SWAdSV). The method was tested both on certified plant samples and by comparing the results obtained by voltammetry with those determined by Atomic Absorption Spectrometer equipped with deuterium background corrector and graphite furnace. Good agreement between the spectroscopic and voltammetric results were obtained. In the analysed herbal medicines samples Pt, Pd and Rh were in the ranges 19.7–27.3, 16.5–29.9 and 10.7–15.0 μg g^{-1} respectively. Moreover, if compared with the average values on the lithosphere is as implicit as their bioaccumulation can lead to serious harms for the consumer's health.

Adsorptive stripping voltammetry was applied[84] to differentiate between labile (ionic) and non-labile forms of Rh in cultivated plants (*Sinapis alba* L.) in enriched soil. For this scope, authors optimize the mineralization process. These bioavailability studies demonstrated that rhodium is absorbed by plants independently on its form, although with different efficiency and that it is accumulated mainly in roots. Bioaccumulation and translocation factors indicate that the transport of Rh to the above-ground parts is negligible. Soil constituents strongly immobilize all the forms of rhodium.

In a paper[84] Krasnodębska-Ostręga et al. proposed a method based on quantification of CO adsorption on the surface of metallic Pd to quantify its nanoparticles in water and plant tissues.

In this case, the detection limit was 4.5 μg Pd as nanoparticles. If the sample dissolution is carried out at low temperature in ultrasound bath using HNO$_3$ it is possible to discriminate Pd from Pt nanoparticles.

In a paper in press[85] we report the voltammetric analytical method for the Pt and Rh quantification in coffee brew prepared using a Moka coffee maker and ground coffee available on the market and not pre-packaged pods or capsules. The brew coffee samples (thirty) were prepared in our laboratory, using a two-cup stainless steel coffee maker, 8 grams of coffee powder and 70 mL of water. As far as possible, the temperature of the heating plate was kept constant for all samples. Platinum concentrations in beverages made from different powders range from 58 to 430 ng L^{-1}. The average value is 183 ± 214 ng L^{-1}. Rhodium is always less than the detection limits. Considering that there are no Dietary References Intakes (RDI) values for platinum and rhodium with regard to the health risks derived from the intake of the two elements, the results obtained in this research have been compared with the available toxicological values.[86] European Medicines Agency guidelines recommend Permitted daily strength (PDE) for residues of Pt (100 μg day^{-1}) and Rh (100 μg day^{-1}) in pharmaceutical substances. In conclusion, the coffee samples analysed contain lower concentrations of Pt than those recommended by international bodies. Therefore, for coffee consumers, the estimated intake of this metal is several orders of magnitude lower than that which could give rise to health effects, and assuming that, in Italy and in other European countries, many people consume daily quantities even ten times higher than those we have considered (70 mL), even in this case, the health effects would be nought or negligible.

Summary and Outlook section

The content of this review represents the first available data on the most Voltammetric methods of the last 25 years, to quantify and, in some cases, to carried out a speciation, of platinum palladium and rhodium in environmental and food matrices. The quantitative data obtained by voltammetry, in several cases, were compared to those measured by other analytical techniques. In general, the literature data show an increased accumulation of PGE concentrations during last

Table 2. Contamination categories based on EF values.	
EF	
<2	Deficiency to minimal enrichment
2–5	Moderate enrichment
5–20	Significant enrichment
20–40	Very high enrichment
>40	Extremely high enrichment

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Table 3. – Summary of what is reported in the text.

Year	Author	Ref	PGE	Technique	Matrix	C_{Pt}	C_{Rh}	C_{Pd}	Place
1997	Georgieva	26	Pd	AdSV	Liquid samples			0.05 µg L^{-1}	
1997	Georgieva	26	Pd	AdSV	Solid samples			50 ng g^{-1}	
1996	Schierl	27	Pt	AdSV	Airborne bus	3–33 pg m^{-3}			Munich
1997	Leon	23	Pt, Rh	CSV	Spruce shoots	543 pg g^{-1}	22 pg g^{-1}	–	
1997	Hoppstock	28	Pt	DPCSV	Gasoline	1.8–7 pg g^{-1}			
1998	Helmers	19	Pt,Rh	CSV	Grass	0.03–10 µg Kg^{-1}	0.03–2.1 µg Kg^{-1}	–	Stuttgart
1998	Helmers	19	Pt,Rh	CSV	Dust (car tunnel)	>730 µg Kg^{-1}	>60 µg Kg^{-1}	–	Stuttgart
1998	Helmers	19	Pt,Rh	CSV	Unpolluted Dust	<0.03 µg Kg^{-1}	<0.03 µg Kg^{-1}	–	Stuttgart
1998	Helmers	19	Pt,Rh	CSV	Airborne particulate matter (urban)	68 µg Kg^{-1}	8 µg Kg^{-1}	–	Stuttgart
1998	Helmers	19	Pt,Rh	CSV	Hospital effluent	2.2 µg L^{-1}	<0.01 µg L^{-1}	–	Stuttgart
2001	Zimmermann	32	Pt	ACSV	Animal tissues	0.1–2.3 ng g^{-1}		–	
2002	Sung-Il Kim	34	Pd	AdsCSV	Spiked drinking water			40–80 ng mL^{-1}	
2006	Obata	36	Pt	CSV	Estuarine water	5–13.6 pM	–	–	Ara River, Tokio
2006	Obata	36	Pt	CSV	Estuarine water	4.8–35.2 pM	–	–	Tama River, Tokio
2006	Locatelli	37	Pt, Pd, Rh	SWAdSV	Surface water	0.069–0.18 µg L^{-1}	0.041 µg L^{-1}	0.023 µg L^{-1}	
2006	Locatelli	38	Pt, Pd,Rh	SWAdSV	Sediments	28.6 ng g^{-1}	<LOD	5.9 ng g^{-1}	Portomaggiore area (Italy)
2006	Locatelli	38	Pt, Pd,Rh	SWAdSV	Soil	<LOD	<LOD	>LOD	Portomaggiore area (Italy)
2006	Locatelli	38	Pt, Pd,Rh	SWAdSV	Sea water	LOD −0.177	<LOD	LOD −0.195 µg L^{-1}	Po river and Goro area (Italy)
2007	Monticelli	39	Rh		Lake water		<0.30 ng L^{-1}		Como Lake (Italy)
2009	Osterauer	41	Pt	AdsCSV					
1989	Jacinto	43	Pt						
2010	Orecchio	46	Pt, Rh	DPV/a-AdsV	Oleander leaves	0.33–25 µg Kg^{-1}	0.40–4.6 µg Kg^{-1}		Palermo (Italy)
2011	Orecchio	51	Pt		Soil	0.6–2240 ng g^{-1}		–	Palermo
2011	Cobelo	54	Pt	Cat-AdCSV	Sediment core	0.5–9.5 ng g^{-1}			Tagus estuary (Portugal)
2011	Cobelo	54	Pt	Cat-AdCSV	Sediment core	0.6–0.9 ng g^{-1}			Tagus Prodelta (Portugal)
2012	Orecchio	18	Pt	DPV/a	Blood	1.5 µg Kg^{-1}			
2012	Bhardwaj	55	Pd	ASV	Nuclear Waste			264.9 mg L^{-1}	
2014	Kowalska	59	Pt, Rh	AdSV	Soil, quartz	263 ng g^{-1}	47 ng g^{-1}	–	
2014	Silwana	62	Pt, Pd, Rh	AdDPSV	Natural water	0.41–0.71 µg L^{-1}	0.14–0.38 µg L^{-1}	2.56–5.17 µg L^{-1}	South Africa
2015	Kolpakova	63	Pt, Pd	SV	Gold–sulfide quartz minerals	1.4–14.5 g t^{-1}		0.013–4.6 g t^{-1}	Russia
2015	Amorello	65	Pt	DPV	Home dust	30–1460 µg Kg^{-1}			Palermo (Italy)
2015	Amorello	65	Pt	DPV	Car dust	30–1750 µg Kg^{-1}			
2016	Almécija	67	Rh	CaSV	Sediment core	–	0.06–0.47 ng g^{-1}	–	Tagus Estuary (Lisbon)
2017	Silwana	62	Pt	AdsCSV	Freshwater close to PGE mining areas	0.02–1.1 ng L^{-1}	0.04–0.1? ng L^{-1}	1–10 ng L^{-1}	
2016	Abdou	68	Pt	SV	Oysters	0.80–3.10 pmol.g^{-1}			Gironde estuarine (France)
2017	Abdou	68	Pt	AdsCSV	Oysters	0.1–0.7 ng g^{-1}	–	–	
2017	Cobelo-Garcia	57	Pt		Natural water	0.02–2.9 ng L^{-1}	–	–	
2017	Amorello	70	Pt, Rh	DPV/a-AdsV	Alcoholic beverages	3–470 µg L^{-1}	0.0006–0.36 µg L^{-1}		Sicily (Italy), Malta
2017	Pérez-Ràfols	71	Pd	AdSV	Enriched natural water			178.6 µg L^{-1}	
2018	van der Horst	72	Pt, Pd, Rh	DPAdSV	Road dust and soil	17.3–81 pg g	14.3–53.3 pg g^{-1}	0.48–5.44 ng g^{-1}	South Africa
2019	López-Sánchez	74	Pt	Cat-AdCSV	Sea water	0.11–0.32 pM			Atlantic Ocean
2019	Abdou	75	Pt	AdCSV)	Sediment core	12–16 ng g^{-1}			North western Mediterranean
2019	Abdou	75	Pt	AdCSV)	Mussel	0.09–0.66 ng g^{-1}			North western Mediterranean

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Table 3. continued

Year	Author	Ref	PGE	Technique	Matrix	C_{Pt}	C_{Rh}	C_{Pd}	Place
2019	Orecchio	76	Pt, Rh	DPV/a-AdsV	Potatoes	0.007–109 µg Kg^{-1}	0.0008–0.030 µg Kg^{-1}		
2020	Monteiro	77	Pt, Rh	AdCSV	road dust leachates	–	–	–	Lisbon, Portugal
2021	Amorello	79	Pt	DPV	Mushrooms	0.03–71 µg Kg^{-1}			Italy
2022	Meluccia	82	Pt, Pd,Rh	SWAdSV	Herbal medicines	19.7–23.7 µg g^{-1}	10.7–15 µg g^{-1}	16.5–29.9 µg g^{-1}	

decades as a consequence of continuing increase in the use of vehicles with catalytic converters.

Table 3 shows that the number of publications on palladium (13) is smaller than on platinum (36) and rhodium (20). This is justified by the fact that, before the voltammetric analysis of the Pd, it is often necessary to isolate the analyte from the matrix. Considering the increasing diffusion in the analysis and research laboratories of ICP-MS and the improvement of analytical performance, this technique is far more used especially in the case of samples in which the concentrations of the analytes are not particularly low or after appropriate concentration of the solutions. However, it is always to be kept in mind that voltammetric techniques are always the least expensive and, often, the equipment is available, both for educational and for research purposes, in universities that have less economic resources.

At present, platinum group metals can be classified as emerging contaminants, therefore, there are no concentration limits regarding the different environmental matrices with which people is in contact and, in particular, for food. In our opinion, more toxicological studies are needed on these trace analytes and, subsequently, the legislators of the various countries should propose concentration limits in drinking water and in food, similar to what has been established for other substances that have long been considered dangerous.

With regard to platinum group metals, for the evaluation of air quality, in our opinion, it may be advantageous to use plants as bioindicators and/or bioaccumators. Biomonitoring methods using organisms, or part of them, offer a feasible low cost alternative, especially in terms of high spatial resolution and time-averaged data series. This approach is particularly useful, for example, in monitoring areas where the origin of platinum is not only related to vehicular traffic but the metal can be produced by hospital incinerators that treat tissues containing Pt-based drugs or in areas where catalytic converters are dismantled, legally or not.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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