Benign recovery of platinum group metals from spent automotive catalysts using choline-based deep eutectic solvents

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ABSTRACT
The recovery of platinum group metals (PGMs) from secondary raw materials has become a topic of critical importance mainly due to the gradual depletion of their natural resources and their continuously increasing demand. However, the insufficient recovery of PGMs coupled with the negative environmental impact of the state-of-the-art recycling procedures mandate the investigation and development of alternative recovery processes that will assist in minimizing or even eliminating these drawbacks. Herein, we present a process for the extraction of platinum group metals from spent car catalysts relying on benign deep eutectic solvents (DESs). It is demonstrated that with addition of small amounts of an oxidizing agent, deep eutectic solvents can act as excellent leaching media for the quantitative extraction of platinum group metals. Despite its inertness towards acidic and oxidizing agents, Rh can be leached in a considerable amount which can be further increased by physical pre-treatment of the spent car catalyst material.

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Introduction
Platinum, palladium and rhodium along with ruthenium, osmium and iridium, constitute the group of PGMs. The former three have gained the most attention due to their unique properties and they have found a number of different applications, ranging from construction of dental materials to electric and electronic equipment. Thus, they are currently the most significant of all PGMs, both from a financial and industrial perspective (1).

The largest percentage of PGMs is exploited by the automotive industry in the construction of catalytic converters of which they constitute indispensable components. They are responsible for the chemical processes (oxidation/reduction) that convert the harmful pollutants of vehicle exhaust emissions to compounds that are more environmentally benign (2).

In the past few years, the steadily increasing demand for PGMs exceeds the attainable supply, which relies both on natural resources and recovery from secondary raw materials. Their relatively low abundance and limited localized natural supply on a global level (mainly encountered in South Africa and Russia) has rendered them a critical raw material status (3, 4). Therefore, their recycling is of paramount importance since it signifies conservation of the already limited primary resources and consequent stability in their market price (5,6).

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A review of the available literature data indicates that hydrometallurgical and pyrometallurgical procedures are primarily used for the extraction of PGMs from secondary raw materials (7–11). However, these processes have numerous drawbacks mainly associated with negative environmental impact and potential health risks. The major drawbacks associated with hydrometallurgy arise from the use of strongly basic or acidic media, which can generate dangerous and toxic compounds, while, at the same time, severe conditions of pressure (2800–6200 kPa) and temperature (up to 270 °C) are required. The temperatures employed in pyrometallurgical processes are even higher (up to 800 °C), rendering them expensive and insufficient from an energy consumption perspective (12).

Various alternative approaches for the recovery of PGMs from spent car catalysts have been reported in the literature, such as leaching with mineral acid and oxidizing agent mixtures (13), microwave-assisted PGM leaching (14, 15), extraction with supercritical CO₂ (16), leaching with the aid of cyanide-producing bacteria (17, 18), magnetic separation (19, 20) and recovery of PGMs from an acidic leach liquor into an ionic liquid medium (21). Additionally, environmentally benign and energy efficient processes relying on DESs, which are regarded to be ionic liquid analogues (22), have been reported for the recovery of precious metals, such as gold (23). An overview of available industrial- and lab-scale technologies is presented in Figure 1. DESs constitute a solvent group on which the emerging branch of solvometallurgy relies, which is a sustainable alternative to traditional extractive metallurgy (24). Besides their low toxicity and low vapor pressure, which renders them ideally suited to replace commonly used organic solvents, DESs allow for simple tuning of their properties, by varying their individual building components or their respective mixing ratio. Additionally, their comparably low price and biodegradable nature makes them both financially desirable and environmentally compatible (25).

Specifically, DESs comprising the quaternary ammonium salt choline chloride and a hydrogen bond donor (DES type III) (22), have been employed in a wide range of applications due to their versatile nature. The simplicity of their preparation, low reactivity with water, biodegradability and low cost along with their wide solvation range and tunability of their properties, which is largely attributed to the large number of available hydrogen bond donors, renders these DESs particularly interesting (22). With respect to metal extraction, choline-based DES applications have, among others, been reported in the extraction of rare earth elements from magnets (26), the selective extraction of transition metals from mixed metal oxide matrixes (27) and the extraction of metal traces from barley (28), while p-toluenesulfonic acid-based DESs have

![Figure 1](image-url)

**Figure 1.** Industrial- (top) and lab-scale (bottom) approaches for PGM extraction vs our procedure (presented in green letters). TBP = tributyl phosphate, LOD = limit of detection. Note: we should point out that comparing efficiencies of industrial- and lab-scale approaches is not sensible considering the significant difference in scale, thus, the figure simply aims to give a quick overview of the available processes.
demonstrated the ability to solubilize metal oxides (29). Despite their notable extractive properties, no industrial-scale application for DESs has been reported to date. This could be attributed partly to the fact that fundamental knowledge on DESs is still at a nascent stage. Additionally, the technological application of DESs is a rather new field and marketing a new technology to the industry can be a long and difficult process (30). Herein, we present the application of choline-based DESs for the extraction of PGMs from spent car catalysts.

**Experimental section**

**Materials and methods**

All reagents employed in the method development were of analytical grade, unless otherwise stated. Individual stock solutions of Pt, Pd and Rh, 1000 ppm in 5% HCl, were obtained from Sigma-Aldrich, Germany and used for the preparation of the calibration standard solutions. Stock solution of In, 1000 ppm in 2–3% HNO₃, was also obtained from Sigma-Aldrich, Germany. Concentrated HCl 37% and HNO₃ 65% were purchased from Merck, Germany. H₂O₂ 30% was obtained from Sigma, Germany. NaCl was purchased from Sigma-Aldrich, Spain. Choline chloride ≥ 98% was purchased from Sigma, Germany. The following compounds that were used as hydrogen bond donors were purchased from Sigma Aldrich; p-toluene sulfonic acid from Sigma, Germany, oxalic and lactic acid from Sigma, Germany, citric acid, glucose, glycerol, ethylene glycol, sorbitol, thiourea, urea, xylitol, malic acid and malonic acid. High purity water was supplied by an Easipure water system (Thermo, U.S.A., resistivity 18 MΩ·cm).

The car catalyst material employed in this work was provided by Monolithos Ltd. (Athens, Greece). The grinding size of the provided catalyst powder was < 0.16 mm. The PGM composition of the powder catalyst was provided in the supporting information (ESI, Table S2). The separation of the catalyst material from the leaching solution was performed via centrifugation in a Microstar 12 tabletop centrifuge (VWR, Germany).

The leaching efficiencies of the PGMs were quantified with the aid of a radial ICP-OES (Thermo icAP 6500, Thermo Scientific, U.S.A.) with a sample introduction kit consisting of a parallel path nebulizer (PEEK Mira Mist, Thermo Scientific, Canada), a gas cyclonic spray chamber with a riser tube and a torch injector tube with 2 mm inner diameter (for details, see ESI Tables S3 and S4). Prior to measurement, appropriate sample dilution and matrix matching were performed to accommodate for the high carbon content of the DESs. The quantification of PGMs in the recovered DESs was conducted within a 24 h frame after the completion of the leaching process. Background corrected emission signals in ICP-OES were recorded and processed using Qtegra 2.10 software (Thermo Scientific, U.S.A.).

**Characterization of spent car catalyst material**

The car catalyst material was fully characterized before the DES-based leaching experiments. The catalyst (100 mg) was digested with the aid of a mixture of mineral acids (4 mL HCl, 3 mL HNO₃, 2 mL HF) in a microwave oven (Multiwave 3000, Anton Paar, Germany), prior to measurement, for the complete dissolution of the ceramic material, which primarily comprises the car catalyst. The following digestion program was employed; 8 min at 500 W, hold 8 min, 15 min at 900 W, hold 35 min, which allowed complete mineralization of the powdered catalyst material, resulting in clear sample solutions without any remaining solid residues. The elemental quantification was performed by ICP-OES with appropriate sample dilution. The fitness for purpose of the analytical measurement method was initially verified with the aid of the certified reference material ERM-EB504.

**Selection of deep eutectic solvents**

Various DESs based on choline chloride (choline Cl) were synthesized and a number of different hydrogen bond donors were tested (Table 1 and ESI, Figs. S1 and S2). Their production in bulk combined with their low price (compared to fine chemicals), makes the selected hydrogen bond donors ideal candidates for considering the developed process viable for industrial scale. It should be taken into account that the amount of H₂O added to a DES can impact its structure; however, in choline-based DESs, the solvophobic sequestration of water into nanostructured domains around cholinium cations enables retention of the DES nanostructure at water content up to 50% wt. (31) In our systems, the H₂O always remained below 15% wt.

**Table 1. Evaluated hydrogen bond donors in the synthesis of DESs.**

| hydrogen bond donors | Ethylene glycol | Urea | Thiourea | Sorbitol | Xylitol | Glycerol | Glycerol + urea | Glucose + water |
|----------------------|---------------|------|----------|----------|---------|---------|----------------|----------------|
| p-toluene sulfonic acid | Lactic acid | Citric acid | Citric acid + water | Lactic acid + oxalic acid | Lactic acid + citric acid | Malic acid | Malonic acid |               |

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The oxidizing agents HNO₃, H₂O₂, I₂, thiourea, and KH₂SO₅ were used and in certain/selected systems HCl and NaCl were employed as additives. The specific details of all tested combinations are presented in the ESI, Table S1.

**Leaching procedure**

The leaching process was performed as follows: (0.1000 ± 0.0050) g grinded car catalyst were mixed with (0.5000 ± 0.0100) g DES (solid:liquid 1:5) and (0.1000 ± 0.0050) g oxidizing agent and the mixture was stirred at 80 °C for 4 h. The mixture was subsequently centrifuged for 30 min at 13500 rpm for the sedimentation of the solid car catalyst material. The liquid phase was recovered and appropriately diluted prior to PGM quantification by ICP-OES analysis.

The leaching efficiency was calculated based on the following equation:

\[
\% \text{ leaching efficiency} = \frac{\mu g \text{ of } [M] \text{ in the leachate}}{\mu g \text{ of } [M] \text{ in amount of catalyst powder (prior to leaching)}} \times 100,
\]

where \([M] = \text{metal}\)

**Measurement procedure**

The calibration curves consisted of a set of six standards in the range of 500–12000 ppb for the PGMs and a set of five calibration standards in the range of 1000–30000 ppb for the other quantified elements. The standard and sample solutions were appropriately diluted in a 1% EtOH-5% HCl diluent. The EtOH was added and accordingly adjusted in the diluent to account for the high carbon content of the DESs (matrix matching between standards and samples).

Five replicas of each sample were prepared and each replica was measured five times. Blank solutions with composition identical to the diluent were used for the determination of limits of detection and quantification. Indium was used as internal standard and the output signals were corrected using the emission line at 230.606 nm.

**Results and discussion**

**Characterization of spent car catalyst material**

The spent car catalyst used in this study was fully characterized prior to the experiments and the quantification results are presented in Figure 2 and ESI, Table S2.

The recorded X-Ray diffractogram of the spent car catalyst material (Figure 3) indicates that the car catalyst comprises a cordierite support. Hydroxides present in the catalyst were also detected.

**Investigation of PGM leaching efficiency**

The selection of the evaluated DES systems was based on different parameters, such as, the extraction efficiency for all 3 target PGMs, the difficulty of preparation and cost of the DES and the properties that make the DES an easy-handling and environmentally friendly system. The PGM leaching capacity of the selected DESs was assessed at variable conditions. Specifically, parameters such as the solid:liquid ratio, the leaching temperature, the leaching duration, the amount and nature of the added oxidizing agent, the

![Figure 2. Concentration of elements present in the car catalyst material.](image-url)
presence or absence of additives and the dilution of the leaching medium with water, were evaluated for their effect on the PGM leaching behavior of the system. The effect of these parameters is presented in the following sections on the example of the DES system relying on choline Cl/p-toluene sulfonic acid (pTsOH) 1:1.8 eq due to its simple preparation and promising performance in pre-studies. This particular DES is simple and easy to prepare, and during initial assessment of various DES-based leaching systems it demonstrated a very promising performance in terms of extraction efficiency for all 3 target PGMs.

The dissolution of PGMs in various acidic media is easier when they are encountered in their elemental form (32). Even though they are originally deposited on the catalyst support as metallic particles, in the end-of-life catalysts they have been partly converted to their respective oxides (33).

PGMs form stable complexes with soft ligands, such as Cl, and are soluble as chloro-complexes in acidic and oxidizing environments. According to thermodynamic data, Pd has the highest solubility in its chloride form, followed by Pt and Rh (34). Rhodium, particularly, is quite inert and not soluble or only slightly soluble in acids (35). This is also the case for rhodium oxide, which is less readily chlorinated than metallic Rh and stable over a wide range of temperature and pressure (36).

Effect of solid: liquid ratio

Multiple ratios of car catalyst:DES were tested with the choline Cl/pTsOH system with HNO₃ as the oxidizing agent.
agent, employing a temperature of 80 °C, for 4 h. The extraction efficiency is almost quantitative in all cases for Pd, indicating that it is easily accessible to the Cl⁻ anions for complexation, while, at the same time, its dissolution is particularly assisted by the presence of HNO₃ (1). On the other hand, quantitative extraction for Pt is obtained only at the car catalyst:DES ratio of 1:5, whereas any ratio above or below that does not yield comparably high extraction efficiencies for any of the 3 PGMs. Due to its inert nature, Rh can only be leached partly, with the highest efficiency reached at a car catalyst:DES 1:5. The latter ratio is the optimum in order to obtain maximum leaching efficiencies for all 3 target PGMs (Figure 5).

The possibility of reducing the solid:liquid ratio in the selected system was investigated as an alternative to decrease the amount of employed DES and to lower the viscosity of the mixture. To this end, the leaching was performed with solid:DES:H₂O:HNO₃ ratio of 1:4:1:1 yielding similar results with the solid:liquid ratio 1:5. The addition of water in the 1:4 system is deemed necessary to reduce the viscosity, while the excellent extraction performance could be maintained.

**Effect of leaching temperature**

It is quite evident that the selected DES system has a considerable extraction capacity for Pd at temperatures close to room temperature (Figure 6). Additionally, it can be seen that the leaching of the PGMs is dependent on the process temperature, with the highest extraction yield for all 3 PGMs observed at 80 °C. Employing the solid:DES ratio of 1:5, quantitative recovery of Pt and Pd is achieved with temperatures as low as 80 °C, whereas the partial extraction of Rh is not affected by any further increase in temperature. Additionally, temperatures above or below 80 °C appear to hamper the extraction capacity of the DES, indicating that the temperature needs to be carefully selected and monitored in order to fully exploit the advantageous effect of the DES in the extraction process. We should also point out that working with choline-based DESs at temperatures exceeding 80 °C is not recommended since it has been reported that over this temperature the progressive degradation of the DES takes place (37).

The kinetic and thermodynamic behavior of PGM-chlorocomplexes is contingent upon the oxidation
state in which the metal is encountered in solution. Additionally, certain properties, such as solubility, are directly affected by the charge and size of the formed complex species. Varying amounts of DES imply various concentrations of $H^+$ and $Cl^-$ in solution, therefore, variable composition in terms of formed PGM-chlorocomplexes (38). The formation of various complexes of different kinetic and thermodynamic properties and solubilities could be a plausible explanation as to why the PGMs do not yield constant extraction efficiency with the modification of the temperature. As the temperature increases, a drop in the yield for all 3 PGMs, which is most pronounced for Pd, is observed; this could be attributed to the fact that choline-based DESs progressively degrade at temperatures exceeding 80 °C, therefore, they most probably lose their extracting capacity (37).

**Effect of leaching duration**

The leaching efficiency of the system (solid:DES:$HNO_3$ 1:5:1, 80 °C) was evaluated over a period of 12 h at regular intervals. The equilibrium was reached after 4 h; lower leaching duration was not enough for quantitative extraction of Pt and Pd, while durations over the 4 h mark had no added advantage on the extraction efficiency of Rh and no effect on Pt and Pd (Figure 7).

**Preconcentration of platinum group metals in the leachate**

The possibility to reuse the DES in subsequent leaching cycles, thus, the pre-concentration of PGMs in cumulative steps, was investigated with the objective of preserving DES while at the same time maximizing the leached PGM amount in a constant amount of DES. The PGM-rich leachate obtained from a leaching cycle was recovered and used for subsequent leaching cycles with new catalyst material, re-dosing DES as necessary and adding new amount of oxidizing agent (Figure 8). The observed loss of DES after every leaching cycle can be attributed to its high viscosity which renders its handling, especially on a lab-scale, very challenging and susceptible to losses.

The number of PGM pre-concentration cycles as well as the cumulative PGM leaching (%) and DES recovery (%) per leaching cycle are presented in Table 2. The experiments were performed on a 1 g car catalyst scale. The reported results refer to solid:DES:$H_2O$:HNO$_3$ 1:4:1:1 system, since the cumulative recovery of the PGMs was slightly higher in that case (as opposed to solid:DES:$HNO_3$ 1:5:1). The reason that the leaching experiments were also performed with addition of $H_2O$ was to investigate whether the viscosity of the system could be decreased without any impact on its extraction capacity, since a potential industrial-scale application is envisioned.

The DES medium allows the preconcentration of Pt in subsequent leaching steps, however, there is a considerable drop in the leached amount after the third leaching cycle. The preconcentration of Pd was also successful, reaching a plateau after the second leaching cycle. In contrast, no additional Rh could be extracted beyond the first leaching step.

**Table 2.** Cumulative amount of leached PGMs (ppm) and DES recovery (%) per leaching cycle.

| Cycle No | 1  | 2  | 3  | 4  |
|----------|----|----|----|----|
| % DES recovery | 90 | 86 | 77 | 80 |
| Cumulative amount of leached PGMs (ppm) | 911 ± 19 | 1445 ± 29 | 1940 ± 35 | 2037 ± 30 |
| Pd | 1590 ± 11 | 2798 ± 116 | 2878 ± 45 | 3116 ± 221 |
| Rh | 127 ± 3 | 172 ± 25 | 144 ± 13 | 137 ± 31 |

![Figure 7. PGM leaching efficiency (%) at different leaching times, solid:DES:$HNO_3$ 1:5:1, at 80 °C.](image)

![Figure 8. DES reuse in the process flowsheet of PGM recovery.](image)
Multi-element profile of DES Leachate from spent car catalyst

In order to access the selectivity of the employed DES system, the obtained leachate was investigated for the presence of other elements, which were subsequently quantified.

A catalytic converter mainly consists of a honeycomb structured ceramic (cordierite, 2MgO·2Al2O3·5SiO2) or metal material coated largely with γ-Al2O3 and additional chemical solutions (rare earth and alkaline earth oxides). The noble metals, which are located on the washcoat (alumina layer that contains the PGMs), are supported by α-Al2O3 or zirconia. A small percentage of other elements, which function as additives, is present in the catalyst (2, 32, 39). It is, thus, clear that the catalyst matrix comprises an abundance of elements in addition to PGMs.

It is apparent that along with PGMs a number of other elements from the catalyst matrix has been extracted in the DES, with Al, Fe and Zn dominating as the major co-extracted elements in the leachate (Figure 9). The presence of large amounts of Al in the matrix comes as no surprise, considering the fact that it constitutes an essential component of the catalyst support. The presented results for PGMs and accompanying elements have been verified by standard addition experiments.

As previously reported by our research group, the leached PGMs can be effectively separated from major interfering elements co-extracted from the car catalysts matrix with the aid of ionic liquids immobilized on a silica support (40).

Pre-treatment of the car catalyst material

A challenging aspect of PGM leaching was the significantly lower extraction efficiency of Rh compared to the other target PGMs, Pt and Pd, a behavior which was not entirely unexpected given its inert nature (41). This can be possibly attributed to the fact that in the high temperature that car catalysts operate, Rh2O3 is formed which does not readily convert to its metallic form and is poorly soluble even in aqua regia.

The possibility of increasing the extraction efficiency of Rh was investigated. To this end, different pre-treatment pathways, chemical (32, 33, 42) and thermal (32, 33, 43), of the grinded car catalyst material were evaluated for their effect on the extraction efficiency of Rh. In addition to the Ar-based pre-treatment, N2 was also evaluated as an alternative and more viable option, from a financial perspective, to Ar for industrial-scale applications. An overview of the pre-treatment conditions is presented in Table 3. The pre-treatment experimental set-up was adapted from the respective referenced literature and the reported mass loss was determined gravimetrically.

In all pre-treatment processes, loss in the mass of the treated car catalyst material was observed; we presume that this could be attributed to the loss of humidity and the evaporation of volatile compounds present in the car catalyst matrix, occurring when the sample is subjected to high temperatures during the pre-treatment process. In the case of pre-treatment with HCOOH, we observe a significant mass loss, unlike in the other cases, which could be attributed to the loss of certain elements been washed off the catalyst matrix. Specifically, significant Al amount contributes predominantly to the loss, followed by considerable amounts of Zn and Fe, as well as traces of La, Mn, Ni and Cr. Measurements on the recovered HCOOH via ICP-OES after the completion of the pre-treatment, verified that no PGMs are washed off.

Car catalyst samples which were pre-treated with the methods summarized in Table 3 were subsequently

Table 3. Conditions of chemical and physical pre-treatment of the car catalyst material.

| Conditions     | T (°C) | t (h) | Treatment scale (g) | Mass loss (%) |
|----------------|--------|-------|---------------------|---------------|
| Chemical pre-treatment |        |       |                     |               |
| H2             | 300    | 3     | 10                  | 1.1           |
| i. Ar, ii. H2  | i. 500, ii. 300 | iii. 300 | ii. 3           | 2.4           |
|                | 15%    | 60    | 1                   | 11.4          |
|                | 25%    | 60    | 1                   | 12.5          |
| HCOOH          |        |       |                     |               |
| Thermal pre-treatment |        |       |                     |               |
| Ar             | 1200   | 2     | 10                  | 3             |
| Ar             | 1200   | 2     | 100                 | 3             |
| Ar             | 1200   | 1     | 10                  | 2.9           |
| N2             | 1200   | 2     | 10                  | 2.8           |
| N2             | 1200   | 0.5   | 10                  | 2.9           |
leached with the optimized system (choline Cl/pTsOH/HNO₃, solid:liquid 1:5, 80°C, 4 h).

The chemical pre-treatment of the samples had no effect on the PGM extraction efficiencies, yielding comparable efficiencies to the untreated car catalyst. In contrast, all the physical pre-treatment strategies were effective in increasing the extraction efficiency of Rh by approximately 25% (Figure 10). Surprisingly, the extraction efficiencies for both Pt and Pd in the physically pre-treated sample dropped by 20%. In temperatures exceeding 300 °C, the metal particles undergo sintering (growth into larger particles) and their specific surface area, thus, their active sites, decreases leading to a loss in their extractability (44). Repeated experiments with pre-treated catalyst yielded reproducible extraction efficiencies.

Recycling of DES

The possibility to recover and reuse the DES was considered, since this can minimize both the environmental impact and the cost of the process. The procedure that has been developed for the recycling of the DES system discussed herein, is the topic of another publication from our group. The recovery of the three PGMs in a hydrophobic ionic liquid medium allows the recycling of the DES as well as the recovery of the three PGMs via electrodeposition (45).

Conclusions

Numerous choline-based DESs were evaluated for their potential in extracting PGMs (Pt, Pd, Rh) from solid car catalyst material. The effect of different parameters on the outcome of the leaching efficiency of the evaluated systems was assessed. The leaching temperature and time, the solid and liquid ratios used as well as the oxidizing agents and their respective amounts, were all varied until the ideal combination of parameters, which led to the highest extraction efficiencies, was obtained.

Several systems yielded quantitative extraction efficiencies for Pt and Pd, however, complete extraction of Rh was not possible under any conditions, a behavior which can be attributed both to the inertness of Rh as well as the presence of the hardly soluble Rh₂O₃ species in the car catalyst sample. Nevertheless, the leaching system choline Cl/pTsOH/HNO₃ was selected as the optimum system in terms of high extraction efficiency, relatively simple scalability and reasonable price.

The possibility of increasing the extraction efficiency of Rh was investigated by pre-treatment (physical and chemical) of the car catalyst sample under various conditions which would allow the conversion of inert Rh species to ones that would be easier accessible to the leaching solvent. The physical pre-treatment strategies indeed affected the extraction efficiency of Rh, increasing it by 25%.

In conclusion, we are confident that the developed method is an alternative approach to the extraction of PGMs from end-of-life car catalysts with a more environmentally friendly and energy efficient outcome than the state-of-the-art methods. Furthermore, we foresee the possibility of using DESs for the recovery of PGMs from different sources, such as electrical and electronic waste and slag, and investigations towards different input materials as well as the recovery of PGMs from the DES systems are currently ongoing in our lab.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

Data availability statement

The data that support the findings of this study will be openly available in reposiTUm.

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