

IMPROVED METHOD FOR RECOVERING PALLADIUM FROM OTHER METAL ELEMENTS PRESENT IN A NITRIC AQUEOUS PHASE USING MALONAMIDES AS EXTRACTANTS

DESCRIPTION

5 TECHNICAL FIELD

The present invention belongs to the technical field of recycling palladium and, more particularly, to the use of at least one washing step in order to increase the separation factor between the palladium and the other metal elements contained in a nitric aqueous solution, coming in particular from the recycling of waste electrical and electronic equipment, in a liquid-liquid extraction operation.

More particularly, the present invention proposes a method that makes it possible to separate then to selectively recover the palladium present, in a nitric aqueous solution, in a mixture with other metal elements, by using as extractants at least one malonamide and at least one washing step of the organic phase that contains the palladium and at least one malonamide. The present invention has applications in the treatment of waste electrical and electronic equipment and the recycling thereof.

PRIOR ART

Palladium (Pd) is a semi-precious metal the supply of which remains strategic due to a geographical location of the deposits and, consequently, of the production, limited to a few countries (mainly Russia 41% and South Africa 36%). Furthermore, although palladium does not appear as a strategic metal in the analyses of the EU, tensions can exist in the palladium market due to the end of the stocks held by Russia which would make it possible to ease the market, as well as the regular increase in the demand for palladium. Therefore, all of the metals in the platinum group, in particular platinum (Pt), palladium and rhodium (Rh) are considered as strategic by the EU and the USA, rather because of platinum, but the production of these three metals is intimately linked.

Palladium is a metal that has interesting catalytic properties, and good resistance to corrosion. It is mainly used in the manufacture of autocatalysts for the automobile (67%). The other applications are: electronics (12%), the chemical industry (5%), dental repair (5%) and jewellery (4%). This noble metal is also used as a financial investment (10% of the demand in 2010, negligible quantity in 2013). The change in the demand for palladium is substantially assured by the growth in the automobile market.

The quantity of palladium consumed annually coming from recycling is estimated to be about one-fourth. This recycling concerns exclusively autocatalysts, a homogeneous source of palladium, treated in a hydrochloric medium. The exploitation of new recycling processes should therefore be an upcoming field of economic interest. The recovery of waste electrical and electronic equipment (or WEEE) also designated by the expression "urban mining" is a booming theme, and represents a major potential source of palladium (second application market). Studies for the recycling of these materials is oriented along two lines: pyrochemicals/pyrometallurgy and hydrometallurgy. With regards to hydrometallurgy, different technologies can be used such as, for example, liquid-liquid extraction, electrochemistry, supported liquid membranes or ion exchange resins.

In the case of hydrometallurgy, the gold present in printed circuits imposes a dissolution in an acidic oxidising medium, and the only hydrochloric acid used for the recycling of autocatalysts is no longer suitable. Several solutions are considered, such as hydrochloric/nitric or sulphuric/hydrogen peroxide mixtures.

In the prior art, using an organic phase containing a malonamide to separate, recover or extract palladium from an aqueous phase in which it is located is known. Malonamides have been successfully tested on a pilot scale in several methods in a nitric medium and it has been shown that the palladium is well extracted by malonamides. In addition, the behaviour of the palladium in liquid-liquid extraction by *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide (or DMDOHEMA) was the object of a publication [1]. Finally, it has already been established that palladium is co-extracted, during a method for selectively recovering americium developed by the Applicant, with

lanthanides, which requires the adding of *N*-(2-hydroxyethyl)ethylene diamine triacetic acid (or HEDTA) in the aqueous phase [2].

Moreover, the Applicant has developed a method that uses an organic phase containing a malonamide and, more particularly, a malonamide that does not contain any sulphur atoms to selectively separate and purify the palladium contained in a mixture with other metal elements in a nitric aqueous solution [3].

In all of the data available before the method described in [3] was proposed, either the palladium was co-extracted with the lanthanides, or it was sequestered in the aqueous phase and the lanthanides were extracted. The malonamides and, more particularly, the malonamides devoid of sulphur atoms were not known to be specific extractants of palladium: they had been developed within the framework of extracting lanthanides and actinides, cations defined as "hard cations" according to the HSAB theory (for "Hard and Soft Acid and Base", a theory developed by Pearson [4]), while palladium is a cation classed as "soft".

Thus, nothing would suggest to those skilled in the art to use a malonamide to selectively recover palladium from a nitric aqueous solution containing other metal cations. It is therefore rather surprising to observe that palladium can be extracted, selectively, in relation to several metal cations, of which lanthanides, simply by adjusting the content in nitric acid of the aqueous phase, at a concentration in nitric acid less than or equal to 3 mol.L⁻¹.

However, in the method for recovery described in [3], if step (c) of back-extracting is repeated in particular in cross-currents, some of the other cations initially present in the nitric aqueous solution and driven in the organic phase such as iron are also back-extracted during said step (c) (see experimental part hereinafter). Therefore, taking account of the difference in initial concentration between the palladium (100 mg/L) and the iron (2,000 mg/L) in the solutions coming from the treatment of waste electrical and electronic equipment, it is observed that the quantity of iron extracted is substantial and even higher than that of palladium in the organic phase.

The inventors have therefore set the goal of further improving the method for recovering palladium described in [3] by developing a method that does not

have the disadvantages described hereinabove and which makes it possible to effectively separate and purify the palladium contained in a nitric aqueous solution that contains, in addition to palladium, other cations such as metal cations.

5 **DISCLOSURE OF THE INVENTION**

 This purpose and others are achieved by the present invention which proposes a method for recovering palladium from the other metal elements contained in a nitric aqueous phase via a liquid-liquid extraction that uses an organic phase containing, as an extractant, at least one malonamide and having at least one washing step of the organic phase obtained following the selective extraction step.

 Indeed, the inventors have shown that it is possible to further increase the selectivity of the recovery of palladium from nitric solutions stemming from the treatment of waste electrical and electronic equipment by proceeding with a selective washing of the organic phase obtained following the extraction step. This washing step can be considered as a selective back-extracting step of the metal element or elements different from palladium and driven in the organic phase during the extraction step.

 This washing step does not require the use of any specific chelator of this or of these metal element(s) different from palladium. In fact, any organic is overcome in the method for recovering. The latter requires only a management of the effluents of relatively low volume due to the O/A ratio implemented during this washing step.

 Moreover, the steps of extracting and of back-extracting implemented within the framework of the method according to the present invention can be implemented in cross-currents as well as in counter-current, unless explicitly mentioned otherwise.

 Thus, the present invention relates to a method for recovering palladium from a nitric aqueous phase that contains, in addition to palladium, at least one

other metal cation of which the valency is greater than or equal to 2, said method comprising the following steps of:

5 a) optionally diluting the nitric aqueous phase that contains, in addition to palladium, at least one other metal cation of which the valency is greater than or equal to 2 in such a way that the concentration in nitric acid contained in this nitric aqueous phase after dilution is at most 3 mol.L⁻¹;

10 b) extracting palladium from said nitric aqueous phase optionally diluted in step (a), which extracting comprises at least one operation in which said nitric aqueous phase is put into contact with an organic phase that is not miscible with it, containing at least one malonamide free of sulphur atoms as an extractant, then separated from this organic phase;

15 c) back-extracting at least one other metal cation of which the valency is greater than or equal to 2 present in the organic phase stemming from step (b), which back-extracting comprises at least one operation in which the organic phase stemming from step (b) is put into contact with an aqueous phase, the O/A ratio during this putting into contact being greater than or equal to 4; then

20 d) selectively back-extracting the palladium present in the organic phase stemming from step (c), which back-extracting comprises at least one operation in which the organic phase stemming from step (c) is put into contact with an aqueous phase, then separated from this aqueous phase.

25 "O/A ratio" means the ratio between the volume or the flow rate (if the phases put into presence are circulating) of the organic phase and the volume or the flow rate of the aqueous phase. Step (c) of the method of the present invention is clearly distinguished from step (c) of the method described in [3] since, in the latter, the O/A ratio is at most equal to 3. The inventors have shown that by using an O/A ratio greater than or equal to 4, it is possible to selectively back-extract the other metal cation(s) present in the organic phase while still maintaining, in this phase, the palladium.

30 As already mentioned for the method described in [3], if the nitric aqueous phase contains one or more lanthanide(s), the latter remain in the nitric aqueous

solution, following the putting into contact with the organic phase containing at least one malonamide as an extractant. In addition, the method according to the present invention does not require adding any selective complexing agent of the other multivalent cations present in the nitric aqueous phase, such as, for example, EDTA.

5 It is pointed out that, in the field of liquid-liquid extractions, i.e. using the difference in solubility of the chemical elements that are sought to be separated between an aqueous phase and an organic phase:

– the distribution coefficient between two organic and aqueous phases, of a metal element M, noted as D_M , corresponds to the ratio between the concentration (or activity) that this element has in the organic phase and the concentration that this same element has in the aqueous phase;

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– the extraction factor of a metal element M, noted as E_M , corresponds to $O/A * D_M$, i.e. to the product of the ratio between the volume or the flow rate (if the phases put into presence are circulating) of the organic phase and the volume or the flow rate of the aqueous phase by the distribution coefficient D_M of this same element; and

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– the separation factor between two metal elements M1 and M2, noted as $FS_{M1/M2}$ corresponds to D_{M1}/D_{M2} , i.e. to the ratio between the distribution coefficient of the element M1 and the distribution coefficient of the element M2.

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Within the framework of the present invention, step (a) of the method is optional. Indeed, if the concentration in nitric acid of the nitric aqueous phase containing palladium and at least one other metal cation of which the valency is greater than or equal to 2 is, before the implementation of the method for selective recovery according to the invention, less than or equal to 3 mol.L^{-1} , it is not necessary to dilute this phase further. On the contrary, if the concentration in nitric acid is greater than 3 mol.L^{-1} , it is suitable to dilute the nitric aqueous phase by adding water in order to bring the concentration within the desired range.

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Within the framework of the present invention, the nitric aqueous phase used during step (b) is characterised by the presence of different metal elements

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among which there is palladium and at least one other metal cation of which the valency is greater than or equal to 2 and by the adjusted quantity of nitric acid.

Advantageously, the quantity of nitric acid in the nitric aqueous phase is less than or equal to 3 mol.L^{-1} , notably less than or equal to 2.5 mol.L^{-1} and, in particular
5 comprised between 0.1 mol.L^{-1} and 2 mol.L^{-1} . In a particular embodiment, the nitric aqueous solution implemented within the framework of the present invention contains nitric acid at a concentration of about 1 mol.L^{-1} (i.e. $1 \text{ mol.L}^{-1} \pm 0.25 \text{ mol.L}^{-1}$). The quantities of nitric acid given hereinabove are intended prior to the putting into contact with the organic phase. Indeed, a certain quantity of nitric acid can be extracted in the
10 organic phase by the malonamide extractant.

Any nitric aqueous phase containing different metal elements among which there is palladium and at least one other metal cation of which the valency is greater than or equal to 2 can be used within the framework of the present invention. The nitric aqueous phase used within the framework of the method according to the
15 invention is advantageously a nitric aqueous solution stemming from the treatment of waste electrical and electronic equipment (WEEE). Thus, this nitric aqueous phase comprises not only palladium but also at least one metal element selected from the group consisting of iron (Fe), copper (Cu), zinc (Zn), aluminium (Al), lead (Pb), nickel (Ni), silver (Ag), cobalt (Co), neodymium (Nd), lanthanum (La), dysprosium (Dy), ytterbium (Yb) and
20 chromium (Cr). The quantity of each one of these metal elements and in particular the quantity of palladium in the nitric aqueous phase will depend on the origin of the nitric aqueous phase and in particular on the nature of the waste electrical and electronic equipment and on the treatment that they have been subjected to.

Typically, waste electrical and electronic equipment is ground, optionally
25 subjected to an acid attack, for example, by hydrochloric acid or sulphuric acid then subjected to an oxidising attack by nitric acid in particular in a quantity comprised between 3 mol.L^{-1} and 6 mol.L^{-1} , so as to dissolve metal elements such as gold, silver, palladium and certain lanthanides. The nitric aqueous phase implemented in the method according to the present invention therefore corresponds to the solution obtained

following such a treatment i.e. a leaching water of the shredded waste electrical and electronic equipment.

This aqueous phase can optionally have undergone a pre-treatment in order to already remove certain metal cations. Indeed, according to the method selected, certain majority elements such as copper or iron, or gold for its substantial value, can be selectively extracted by conventional techniques of hydrometallurgy. By way of example, Jung *et al.* have proposed a method for the selective prior recovery of the gold using dibutyl carbitol as an extractant [5], which leads to a residual acid solution that contains palladium mixed with other cations such as zinc, copper, silver or platinum.

In general and notably with regards to the above, the palladium present in the nitric aqueous phase prior to the implementation of the method for preparing is present in oxidised form i.e. in the form of Pd^{2+} cations. The latter can optionally be present partially in the form of complexes with the nitrate anions or chloride present in the solution.

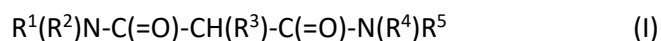
In addition, the fact that the nitric aqueous phase implemented in the method according to the present invention has to contain a quantity in nitric acid such as defined hereinabove i.e. less than or equal to 3 mol.L^{-1} appears as an optimum compromise: the dissolution during the oxidising attack of the waste electrical and electronic equipment takes place at concentrations in nitric acid that are relatively high (3 mol.L^{-1} minimum), therefore adjusting to a lower concentration can be considered by simple dilution. In this case, working with a quantity of nitric acid in the nitric aqueous phase of 1 mol.L^{-1} makes it possible to both not work with an excessive dilution, while still guaranteeing excellent selectivity.

The nitric aqueous phase implemented during step (b) of the method according to the present invention may contain, as acid, only nitric acid. Alternatively, this nitric aqueous phase can contain, in addition to nitric acid, at least one other acid in particular selected from the group consisting of hydrochloric acid, bromhydric acid, fluorhydric acid and sulphuric acid. In addition, whether or not this nitric aqueous phase contains at least one other acid different from nitric acid, it can furthermore contain hydrogen peroxide (or H_2O_2).

Within the framework of step (b) of the method for separating according to the present invention, the extractant contained in the organic phase non-miscible in water has the form of a malonamide free of sulphur atoms or of several different malonamides free of sulphur atoms. The latter are capable of forming complexes with the palladium present in the nitric aqueous phase and, more particularly, with the palladium nitrate present in this phase.

Within the framework of the present invention, explicitly excluded are extractants used alone, sulphur diamides such as the dithiodiglycolamides mentioned hereinabove. Note that such a sulphur diamide or a mixture of different sulphur diamides can however be used, within the framework of the present invention, in a mixture with at least one malonamide free of sulphur atoms.

"Malonamide free of sulphur atoms" means a substituted diamide of formula (I):



in which the R^1 , R^2 , R^3 , R^4 and R^5 groups, identical or different, represent an alkyl or a heteroalkyl, free of sulphur atoms.

Within the framework of the present invention, "alkyl group" means an alkyl group, linear, branched or cyclic, comprising from 1 to 20 carbon atoms, notably from 1 to 18 carbon atoms and in particular, from 1 to 15 carbon atoms.

Within the framework of the present invention, "heteroalkyl group" means a heteroalkyl group, linear, branched or cyclic, comprising from 1 to 20 carbon atoms, notably from 1 to 18 carbon atoms and in particular, from 1 to 15 carbon atoms, the heteroatom or heteroatoms able to be a nitrogen atom, an oxygen atom or a phosphorus atom, notably a nitrogen atom or an oxygen atom and, in particular, an oxygen atom. The heteroatom(s) can in particular interrupt an alkyl chain and/or separate an alkylene chain and an alkyl chain. In particular, within the framework of the present invention, a heteroalkyl is an alkyl such as defined hereinabove interrupted by an oxygen atom.

In accordance with the invention, the malonamide free of sulphur atoms implemented is, preferably, selected from among malonamides in which the total number of carbon atoms that together the R¹, R², R³, R⁴ and R⁵ groups have is greater than or equal to 20 and notably greater than or equal to 22. Indeed, such malonamides have a hydrophobic nature that is sufficient to be used in an organic phase non-miscible with water.

Advantageously, the malonamide free of sulphur atoms implemented within the framework of the present invention is a malonamide of formula (I) such as defined hereinabove in which the R¹ and R⁵ groups are identical and the R² and R⁴ groups are identical, the R¹ and R⁴ groups able to be identical or different.

In particular, the malonamide free of sulphur atoms implemented within the framework of the present invention is a malonamide of formula (I) such as defined hereinabove in which the R¹, R², R⁴ and R⁵ groups are such as defined hereinabove and in which the R³ group is an alkyl or a heteroalkyl and notably an alkyl interrupted by an oxygen atom.

More particularly, the malonamide free of sulphur atoms implemented within the framework of the present invention is selected from the group comprising *N,N'*-dimethyl-*N,N'*-dibutyltetradecylmalonamide (or DMDBDMA), *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide (or DMDOHEMA), *N,N'*-dimethyl-*N,N'*-dioctyloctylmalonamide (or DMDOOMA), *N,N'*-dimethyl-*N,N'*-dioctylhexylmalonamide (or DMDOHxMA), *N,N'*-dimethyl-*N,N'*-dioctylheptylmalonamide (or DMDOHpMA), *N,N'*-dimethyl-*N,N'*-dibutyl-dodecylmalonamide (or DMDBDDEMA) and *N,N'*-dimethyl-*N,N'*-dibutyl-tetradecylmalonamide (or DMDBTDEMA).

Even more particularly, the malonamide free of sulphur atoms implemented within the framework of the present invention is DMDOHEMA or DMDBTDEMA.

Within the framework of step (b) of the method according to the invention, the malonamide free of sulphur atoms is present in the organic phase in a quantity greater than or equal to 40 mM, notably in a quantity greater than or equal to 60 mM, notably in a quantity comprised between 80 mM and 2 M and, more particularly,

in a quantity comprised between 100 mM and 1 M. When the organic phase comprises several different malonamides and notably several different malonamides free of sulphur atoms, the total quantity of malonamides in the organic phase is greater than or equal to 40 mM, notably greater than or equal to 60 mM, in particular comprised between 80 mM and 2 M and, more particularly, comprised between 100 mM and 1 M.

Finally, the organic phase non-miscible in water used within the framework of step (b) of the method according to the present invention contains at least one malonamide free of sulphur atoms such as defined hereinabove, as an extractant, in an organic diluent. Advantageously, this organic diluent is selected from the polar or aliphatic organic diluents the use of which has already been proposed for the realisation of liquid-liquid extractions. More particularly, this organic diluent is selected from the group consisting of cyclopentane, pentane, cyclohexane, n-hexane, cycloheptane, n-heptane, n-octane, iso-octane, nonanes or dodecanes, linear or branched (such as n-dodecane), hexadecane, petroleum ether, benzene, n-butylbenzene, isobutylbenzene, sec-butylbenzene, tert-butylbenzene, p-cymene, triisopropylbenzene, toluene, xylene, cumenes, kerosene, hydrogenated tetrapropylene (or TPH), diethyl ether, n-butyl acetate, isopropyl myristate and the mixtures thereof. Finally, the organic diluent can comprise all or partially a molten salt i.e. a salt that has a melting temperature less than 100°C, often even less than the ambient temperature. "Ambient temperature" means a temperature of 20°C ± 5°C. These molten salts can be used as substitutes for the organic diluents such as defined hereinabove in the liquid-liquid extraction operations and are generally comprised of an organic cation and of an anion which can be organic or inorganic. As illustrative and non-limiting examples of molten salts that can be used as a solvent of the organic phase implemented during step (b) of the method according to the invention, mention can be made of compounds comprised of a cation of the family of N,N-dialkylpiperidiniums, N-alkylpyridiniums or N,N'-dialkylimidazoliums, and of a hexafluorophosphate or bis(trifluoromethanesulfonyl)imide anion.

During step (b) of the method according to the invention, the volume ratio or ratio of the flow rate between the organic phase and the nitric aqueous phase (O/A ratio) is comprised between 1/3 and 3, notably between 0.5 and 2 and, in particular,

about 1 (i.e. $1 \pm 0,2$). In addition, during this step (b), the putting into contact between the nitric aqueous phase and the organic phase lasts between 15 min and 2 h, notably between 30 min and 90 min and, in particular, about 60 min (i.e. $60 \text{ min} \pm 10 \text{ min}$).

Step (b) of the method according to the present invention is carried out at a temperature generally less than 80°C , in particular comprised between 10°C and 70°C . In a particular embodiment, the temperature during this method of separating is the ambient temperature.

Within the framework of the method according to the present invention, step (c) is a washing step of the organic phase obtained following step (b). This organic phase contains at least one malonamide free of sulphur such as defined hereinabove, palladium and at least one other metal cation of which the valency is greater than or equal to 2. This other cation is in particular selected from the group consisting of a ferrous cation, a ferric cation, a cupric cation, a nickel cation, an aluminium cation, a lead cation, or a zinc cation. During this washing step, the metal cations different from palladium are back-extracted, selectively, from the organic phase.

Advantageously, the aqueous phase implemented during step (c) of the method according to the invention is either water, or an aqueous solution of nitric acid. The nitric aqueous solution implemented during step (c) is an aqueous solution comprising nitric acid in a quantity comprised between 0.5 and 2 M and notably between 1 and 1.5 M.

During step (c) of the method according to the invention, the operation of putting into contact of the organic phase with an aqueous phase such as defined hereinabove can be repeated at least once. At each new putting into contact, the aqueous phase used can be identical to or different from the aqueous phase used during the preceding putting into contact. Thus, when the putting into contact is repeated twice, it is possible to use

- (i) water as aqueous phase during the two cases of putting into contact,
- (ii) an aqueous solution of nitric acid as an aqueous phase during the two cases of putting into contact,

(iii) water as aqueous phase during the 1st putting into contact then an aqueous solution of nitric acid as aqueous phase during the 2nd putting into contact, or

(iv) an aqueous solution of nitric acid as aqueous phase during the 1st putting into contact then water as aqueous phase during the 2nd putting into contact.

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Advantageously, when step (c) of the method according to the invention comprises two operations of putting into contact, water is used as an aqueous phase during the 1st putting into contact then an aqueous solution of nitric acid is used as an aqueous phase during the 2nd putting into contact.

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In a 1st embodiment of step (c) of the method according to the invention and notably when this step is carried out at counter-current, the O/A ratio is less than 7 and notably less than 6 and, in particular, less than 5. Typically, step (c) of the method according to the invention is carried out at counter-current, the O/A ratio is 4.

In a 2nd embodiment of step (c) of the method according to the invention and notably when this step is carried out at cross-current, the O/A ratio is greater than or equal to 7, notably greater than 7 and less than or equal to 10 and, in particular, greater than or equal to 8 and less than or equal to 10.

In addition, during this step (c), the case or cases of putting into contact between the aqueous phase and the organic phase last between 15 min and 2 h, notably between 30 min and 90 min and, in particular, about 60 min (i.e. 60 min $\pm$ 10 min).

Step (c) of the method according to the present invention is carried out at a temperature generally less than 50°C, in particular less than 40°C and, more particularly, less than 30°C. Advantageously, the temperature during this step (c) is the ambient temperature.

Step (d) of back-extracting is a conventional step of liquid-liquid extractions.

In a 1st embodiment of this step (d) of back-extracting, the aqueous phase implemented is a diluted solution of acid with a pH greater than 1. Many acids can be suitable for preparing such a diluted solution of acid, and as non-limiting examples hydrochloric acid, nitric acid, or sulphuric acid can be used. Alternatively, the aqueous

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phase put into the presence of the organic phase containing the palladium initially has a neutral pH (i.e. pH comprised between 6.5 and 7.5) which is acidified following this putting into contact and with the passage, in the aqueous phase, of acids and in particular of nitric acid present in the organic phase following step (c).

5 In a 2nd embodiment of this back-extraction step, the aqueous phase used contains a complexing agent of the palladium able to facilitate the migration in the aqueous phase of the palladium contained in the organic phase following step (c).

Advantageously, this complexing agent is selected from the agents the use of which has already been proposed for the realisation of liquid-liquid extractions.
10 Such an agent is typically capable of complexing the palladium contained in the organic phase obtained following step (c) of the method. In particular, this complexing agent is selected from the group consisting of sulphur based compounds such as thiourea, thiocyanate or thiosulphate salts, sodium or potassium metabisulphite; chloride based compounds such as hydrochloric acid or solutions of alkali metal chlorides such as lithium
15 chloride; nitrogen compounds such as ammonia, hydrazine salts, hydroxylamine salts and mixtures thereof; ammonium chloride; chelating compounds derived from carboxylic polyacids such as oxalic acid, EDTA, HEDTA and mixtures thereof.

As particular and non-exhaustive examples, the aqueous phase used during this 2nd embodiment of this step (d) of back-extracting can contain hydrochloric
20 acid at a concentration comprised between 1 M and 8 M of aqueous phase, and/or thiourea in a quantity comprised between 0.1 M and 2 M of aqueous phase and/or thiosulphate in a quantity comprised between 0.1 M and 2 M of aqueous phase. Therefore, an ammonia based aqueous phase can be used, at a content comprised between 1 and 4% (example ammonia 1 M).

25 In a 3rd embodiment of this step (d) of back-extracting the palladium contained in the organic phase stemming from step (c), a direct recovery of the metal palladium is carried out. In this case, an aqueous phase is used that comprises a palladium reducer which allows for the precipitation of metal palladium in the form of colloids at the interphase of the two phases. These particles can then be separated by any suitable
30 liquid-solid separation technique, known to those skilled in the art, such as, for example, a

filtration or a centrifugation. Many reducing agents can be used in this 3rd embodiment. As illustrative and non-limiting examples, it is possible to use a hydrazine solution in nitric acid such as an aqueous solution of diluted nitric acid (0.1 M to 1 M) containing hydrazine 0.1 M or a solution of sodium or potassium formate.

5 In step (d) of the method according to the invention, the O/A ratio between the organic phase containing the palladium and the aqueous phase is comprised between 1/12 and 12, notably between 1/5 and 10, in particular, between 1/2 and 6, more particularly between 1 and 4 and, very particularly, about 2 (i.e. 2 ± 0.5). In addition, the putting into contact of the aqueous phase the organic phase containing the palladium
10 lasts between 5 min and 90 min, notably between 15 min and 60 min and, in particular, about 30 min (i.e. $30 \text{ min} \pm 10 \text{ min}$).

 Step (d) of the method according to the invention is carried out at a temperature generally less than 50°C, in particular less than 40°C and, more particularly, less than 30°C. Advantageously, the temperature during step (d) of the method according
15 to the invention is the ambient temperature.

 Following step (d) of the method according to the invention and in particular following the 1st and the 2nd embodiments, it is easy to recover the palladium present in the aqueous phase. It is, for example, possible to recover palladium in metal form by subjecting the cations Pd^{2+} present in the aqueous phase obtained following step
20 (d) to a reduction. This reduction can be carried out according to the many known techniques available. As illustrative and non-limiting examples, this reduction can be carried out electrochemically, or by adding chemical reagents that have a reducing nature, such as boron salts (borates, borohydrides, etc.), formic acid or the salts thereof, hydrazine. The reduced palladium is able to precipitate in the aqueous phase and this
25 precipitate can be recovered by any suitable liquid-solid separation technique, known to those skilled in the art, such as, for example, a filtration or a centrifugation.

 It is also possible to recover the palladium(II) in the form of a precipitate according to the complexing agent obtained (2nd embodiment of step (d)). As illustrative and non-limiting examples, it is possible to recover the palladium in the form of a
30 precipitate of palladium(II) hydroxide, of ammonium and of palladium(II) chloride, of

palladium(II) sulphite, of palladium(II) and of sodium or of potassium disulphite. In this latter case, a precipitation will advantageously be carried out using ammonium chloride.

In addition, following step (d) of the method according to the invention, the organic phase containing at least one malonamide free of sulphur atoms can be recovered and reused, in particular in a method for selective recovering of palladium such as defined in the present invention.

Other characteristics and advantages of the present invention shall appear to those skilled in the art when reading the examples hereinbelow given for the purposes of information and in a non-limiting manner, in reference of the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the simulation of the composition of an organic phase resulting from the extraction of a nitric aqueous phase at 3 M of HNO_3 loaded with 100 mg/L in palladium and 2,000 mg/L in iron by DMDBTDMA at 0.5 M in toluene by a method described in [3] with cross-flow according to the number of stages.

Figure 2 shows the simulation of the composition of an organic phase resulting from the extraction of an aqueous phase at 2 M of HNO_3 loaded with 100 mg/L in palladium and 2,000 mg/L in iron by DMDBTDMA at 0.4 M in toluene by a method described in [3] with cross-flow according to the number of stages.

Figure 3 shows the distribution coefficients of HNO_3 determined by titration of the phases after balancing.

Figure 4 shows the modelling of the effect of a washing with water on the organic extraction phase (DMDBTDMA at 0.6 M) according to the O/A ratio.

Figure 5 shows the modelling of the effect of a washing with a solution HNO_3 at 1 M on the organic extraction phase (DMDBTDMA at 0.6 M) according to the O/A ratio.

Figure 6 shows the results of the different washing strategies tested.

DETAILED DISCLOSURE OF PARTICULAR EMBODIMENTS

I. Preliminary remarks

Within the framework of the method described in [3], if it is sought to
 5 recover, as cross-current, all of the palladium present in the organic phase following step
 (b), a method with several stages must be considered i.e. a method in which the putting
 into contact during step (c) is repeated at least twice.

In this case, even if the selectivity remains constant, the progressive
 depletion of the aqueous phase in palladium leads to a drop in the quantity of palladium
 10 extracted in the organic phase as the stages take place, while the quantity of impurities
 extracted remains constant (but low). Thus, the purity of the palladium obtained will drop
 with the number of stages.

Furthermore, in a realistic solution, there is at the start a quantity of
 iron that is much higher than the palladium, whereby this effect will be more marked. It is
 15 possible to adjust the number of stages according to the volume ratio of the aqueous
 phase over the organic phase (A/O ratio) selected and modified with respect to the
 method described in [3] (maximum 3), but the simulations carried out for the conditions
 DMDBTDMA at 0.5 M / $[\text{HNO}_3]_{\text{aq}}$ at 3 M with an A/O ratio equal to 10 show that the purity
 in palladium becomes mediocre when it is sought to recover at least 95%, even 98% of
 20 the palladium from a realistic mixture (100 mg/L of palladium for 2,000 mg/L of iron,
 Figure 1).

It is possible to consider conditions for which the selectivity in favour of
 palladium is better ($[\text{HNO}_3]_{\text{aq}}$ at 2 M, [DMDBTDMA] at 0.4 M where $\text{SPd/Fe} = 120$) and to
 seek to recover only 90%, even 95% of the Pd (by working with an A/O ratio = 12), but the
 25 final purity will not be much better (Figure 2).

It was therefore sought to optimise at the level of the laboratory a
 possible method based on this data by developing a method with cross-currents in which
 the purity of the palladium recovered is based on selective washings rather than on a
 selective extraction.

II. Method for separating palladium according to the invention

II.1. Washing strategies

The strategy proposed is based on selectivity in favour of palladium with
 5 acidities comprised between 1 and 2 M. Below the palladium is no longer extracted quantitatively in the organic phase, above the selectivity is less.

After extraction (i.e. after step (b) of the method according to the invention), the organic phase also comprises a certain content in nitric acid of about 0.6 M to 0.65 M, to the extent that the back-extraction of the latter will modify the
 10 concentration in HNO_3 of the aqueous washing phase. The concentration in HNO_3 in the final aqueous phase therefore depends on the initial content in HNO_3 of the two phases as well as on the O/A ratio used. As the distribution coefficients depend on the final concentration $[\text{HNO}_3]_{\text{aq},f}$, it is important to supplement the data acquired by the distribution coefficients of HNO_3 , especially in the targeted concentration zone $[\text{HNO}_3]_{\text{aq},f}$
 15 (Figure 3).

A certain variability of the DHNO_3 is observed between 1 and 2 M. It is however possible to calculate the concentration $[\text{HNO}_3]_{\text{aq},f}$ according to the initial data, then to model DPd and DFe via calculation. The effect of a washing with water (Figure 4) and of a washing with HNO_3 1 M (Figure 5) was thus modelled according to the O/A ratio
 20 used.

These two studies show that when there is a sufficient O/A ratio (about 7 in cross-currents), there is enough HNO_3 in the system so that the losses in palladium are minimal. Furthermore, the washing with H_2O alone makes it possible to eliminate more iron, up to an O/A ratio of 7 to 8. A first washing with H_2O alone was therefore
 25 chosen.

Therefore, the influence of the concentration $[\text{HNO}_3]_{\text{aq},f}$ on the distribution coefficients of palladium and of iron is very strong between 1.5 and 2 M, a very small error on DHNO_3 consequently has a strong impact on these distribution coefficients. The entire washing strategy was therefore optimised experimentally, based

on a first washing with H₂O, and a second washing with H₂O or HNO₃ 1 at 1.5 M, by varying the O/A ratio (Figure 6).

In the zone of [HNO₃]_{aq,f} that results from these conditions, the influence of [HNO₃]_{aq} is substantial. It can be concluded that the elimination of the Fe by the O/A ratio as well as by the residual content in HNO₃. The option was therefore made for a first washing with H₂O alone (with O/A = 10), and a second washing with HNO₃ 1M (with here again O/A = 10).

Note in the end that a few washing tests with a diluted solution of soda were carried out, without any notable improvement: the optimum concentration in soda is delicate to adjust because either it is too low and this does not change anything with respect to a simple washing with water, or it is too high and a substantial risk of precipitation of metal hydroxides (of palladium and iron) appears.

II.2. Validation test with all the metals (WEEE) and solvent recycling

All of the conditions thus developed were therefore chained in a validation test on the scale of about ten mL on a nitric aqueous phase at 3 M of starting nitric acid containing a mixture of palladium and of 5 other metal cations (Fe, Cu, Ni, Al and Zn).

This test is based on two successive extractions (10 min each) by a solution of DMDBTDMA at 0.6 M in toluene, a washing with water then with HNO₃ at 1 M (O/A = 10), and a concentrating back-extraction (O/A = 10) of the palladium by an aqueous solution of LiCl at 0.5 M (Table 1).

Metals	Pd (mg/L)	Fe (mg/L)	Ni (mg/L)	Cu (mg/L)	Zn (mg/L)	Al (mg/L)	% purity Pd
Initial aqueous phase	98	972	288	1942	484	484	-
[M] _{min,aq}	2.8	2.1	1.5	0.7	2.7	2.5	
Organic extraction phase (A/O)=2; N=2; 10min)	102	92	<QL	27	<QL	<QL	-
[M] _{min,aq}	3.5	2.6	1.9	0.9	3.4	3.1	

Organic phase after H ₂ O washing (O/A)=10; N=1; 1H)	100	20	<QL	1.7	<QL	<QL	-
[M] _{min,aq}	3.5	2.6	1.9	0.9	3.4	3.1	
Organic phase after HNO ₃ 1.0M washing (O/A)=10; N=1; 1H)	100	3.2	<QL	<QL	<QL	<QL	-
[M] _{min,aq}	3.5	2.6	1.9	0.9	3.4	3.1	
Aqueous phase after back-extraction LiCl 0.5M (O/A)=10; N=1; 1H)	854	5	<QL	<QL	<QL	<QL	99%
[M] _{min,aq}	2.8	2.1	1.5	0.7	2.7	2.5	
"New organic phase" – New cycle – (A/O=2; N=2; 10min)	132	188	<QL	23	<QL	<QL	
[M] _{min,aq}	3.5	2.6	1.9	0.9	3.4	3.1	
With	[M] _{min,aq} =QL*FD _{aq}						
	[M] _{min,org} =QL*FD _{org}						

Table 1: Characteristics of the different phases during the different steps of the method of separating the palladium carried out in the laboratory

5 An aqueous solution of palladium, loaded at 0.85 g/L, with a purity of the palladium greater than 99% (99.4%) is obtained. The rate of recovery of the palladium is 87%, knowing that the remaining 13% remains in the extraction solvent which can be reused.

10 Only iron is detected in a small quantity in the palladium solution. The copper is detected in the extraction solvent, but it is eliminated during washing. During the second washing (with HNO₃ at 1 M), in the aqueous washing phase only iron is detected in a substantial quantity, along with traces of copper and of palladium (5 and 30 mg/L respectively, corresponding to 0.03 and 0.3% respectively of the initial quantity present in the aqueous phase). The recovered solvent was finally evaluated during 15 another extraction cycle (Table 2).

		Pd (mg/L)	Fe (mg/L)	Ni (mg/L)	Cu (mg/L)	Zn (mg/L)	Al (mg/L)
Extraction by the new solvent	[M] _{aq} (mg/L)	(0.69)	821	269	1784	456	452
	% of global extraction	99.3%	16%	7%	8%	6%	7%
Extraction by the recycled solvent	[M] _{aq} (mg/L)	(1.51)	753	275	1822	466	465
	% of global extraction	98.5%	23%	4%	6%	4%	4%

5 Table 2: Compared results of the extraction of the starting aqueous phase by the new solvent (pre-balanced) and the solvent coming from a first extraction-washing cycle (back-extraction)

10 The effectiveness is comparable, knowing that the new solvent had been pre-balanced, it is delicate to make a precise comparison. However a more substantial extraction of the iron is observed: it is possible that the kinetics are somewhat modified according to the history of the solvent.

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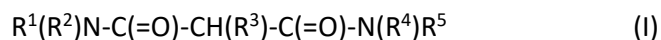
CLAIMS

- 1) Method for recovering palladium from a nitric aqueous phase that contains, in addition to palladium, at least one other metal cation of which the valency is greater than or equal to 2, said method comprising the following steps of:
- 5
- a) optionally diluting the nitric aqueous phase that contains, in addition to palladium, at least one other metal cation of which the valency is greater than or equal to 2 in such a way that the concentration in nitric acid contained in this nitric aqueous phase after dilution is at most 3 mol.L⁻¹;
- 10
- b) extracting palladium from said nitric aqueous phase optionally diluted in step (a), said extracting comprises at least one operation in which said nitric aqueous phase is put into contact with an organic phase that is not miscible with it, containing at least one malonamide free of sulphur atoms as an extractant, then separated from this organic phase;
- 15
- c) back-extracting at least one other metal cation of which the valency is greater than or equal to 2 present in the organic phase stemming from step (b), which back-extracting comprises at least one operation in which the organic phase stemming from step (b) is put into contact with an aqueous phase, the O/A ratio during this putting into contact being greater than or equal to 4; then
- 20
- d) selectively back-extracting the palladium present in the organic phase stemming from step (c), which back-extracting comprises at least one operation in which the organic phase stemming from step (c) is put into contact with an aqueous phase, then separated from this aqueous phase.
- 25
- 2) Method according to claim 1, characterised in that the quantity of nitric acid in the nitric aqueous phase is less than or equal to 2.5 mol.L⁻¹ and notably comprised between 0.1 mol.L⁻¹ and 2 mol.L⁻¹.

3) Method according to claim 1 or 2, characterised in that said nitric aqueous phase stems from the treatment of waste electrical and electronic equipment.

4) Method according to any of claims 1 to 3, characterised in that said nitric aqueous phase comprises not only palladium but also at least one metal element selected from the group consisting of iron (Fe), copper (Cu), zinc (Zn), aluminium (Al), lead (Pb), nickel (Ni), silver (Ag), cobalt (Co), neodymium (Nd), lanthanum (La), dysprosium (Dy), ytterbium (Yb) and chromium (Cr).

5) Method according to any of claims 1 to 4, characterised in that said malonamide free of sulphur atoms is a substituted diamide of formula (I):



in which the R^1 , R^2 , R^3 , R^4 and R^5 groups, identical or different, represent an alkyl or a heteroalkyl free of sulphur atoms.

6) Method according to any of claims 1 to 5, characterised in that said malonamide free of sulphur atoms is selected from the group consisting of *N,N'*-dimethyl-*N,N'*-dibutyltetradecylmalonamide (or DMDBTDMA), *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide (or DMDOHEMA), *N,N'*-dimethyl-*N,N'*-dioctyloctylmalonamide (or DMDOOMA), *N,N'*-dimethyl-*N,N'*-dioctylhexylmalonamide (or DMDOHxMA), *N,N'*-dimethyl-*N,N'*-dioctylheptylmalonamide (or DMDOHpMA), *N,N'*-dimethyl-*N,N'*-dibutyl-dodecylmalonamide (or DMDBDDEMA) and *N,N'*-dimethyl-*N,N'*-dibutyl-tetradecylmalonamide (or DMDBTDEMA).

7) Method according to any of claims 1 to 6, characterised in that the aqueous phase implemented during said step (c) is either water, or an aqueous solution of nitric acid.

8) Method according to any of claims 1 to 7, characterised in that, during said step (c), the operation of putting the organic phase into contact with an aqueous phase can be repeated at least once.

5 9) Method according to any of claims 1 to 8, characterised in that said step (c) comprises two operations of putting into contact and that the water is used as an aqueous phase during the 1st putting into contact then an aqueous solution of nitric acid is used as an aqueous phase during the 2nd putting into contact.

10 10) Method according to any of claims 1 to 9, characterised in that, during said step (c), said O/A ratio is less than 7 and notably less than 6 and, in particular, less than 5.

15 11) Method according to any of claims 1 to 9, characterised in that, during said step (c), said O/A ratio is greater than or equal to 7, notably greater than 7 and less than or equal to 10 and, in particular, greater than or equal to 8 and less than or equal to 10.

20 12) Method according to any of claims 1 to 10, characterised in that said aqueous phase implemented during said step (d) is a diluted solution of acid with a pH greater than 1.

25 13) Method according to any of claims 1 to 10, characterised in that said aqueous phase implemented during said step (d) comprises a palladium complexing agent notably selected from the group consisting of sulphur based compounds such as thiourea, thiocyanate or thiosulphate salts, sodium or potassium metabisulphite; chloride based compounds such as hydrochloric acid or solutions of alkali metal chlorides; nitrogen compounds such as ammonia, hydrazine salts, hydroxylamine salts and mixtures thereof; ammonium chloride; chelating compounds derived from carboxylic polyacids such as
30 oxalic acid, EDTA, HEDTA and mixtures thereof.

14) Method according to any of claims 1 to 10, characterised in that said aqueous phase implemented during said step (c) comprises a palladium reducer.