

METHOD FOR SEPARATING PALLADIUM FROM OTHER METAL ELEMENTS PRESENT IN AN AQUEOUS NITRIC PHASE USING SPECIFIC 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 particular malonamides as extractants in order to increase the separation factor between the palladium and the other metal elements contained in a nitric aqueous solution, stemming notably from the recycling of waste electrical and electronic equipment and this, 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 and this, by using particular malonamides as extractants. 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.

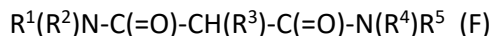
In the prior art, using an organic phase containing a malonamide to separate, recover or extract palladium from an aqueous phase in which it is located is known. Malonamides have been successfully tested on a pilot scale in several methods in a nitric medium and it has been shown that the palladium is 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 adding *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].

5 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
10 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
15 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 and this, at a concentration in nitric acid less than or equal to 3 mol.L⁻¹.

In the method described in [3], the extractant used is a malonamide free
20 of sulphur atoms and of formula (F):



in which the R¹, R², R³, R⁴ and R⁵ groups, identical or different, represent an alkyl or a heteroalkyl, free of sulphur atoms.

The malonamide more particularly exemplified in [3] is DMDOHEMA.
25 Although such a malonamide and, in general, malonamides of formula (F) are robust in a nitric medium, they remain expensive to prepare (3 custom synthesis steps), which therefore makes a competitive method dependent on very good recycling of the solvent. Furthermore, these malonamides are used at 0.6 M, which is about 300 g/L for DMDOHEMA, which renders the initial investment in solvent substantial.

The inventors have therefore set the goal to further improve the method described in [3] by developing an extractant that does not have the disadvantages of the malonamides of formula (F) while still making it possible to effectively separate and purify the palladium contained in a nitric aqueous solution that contains palladium and other cations such as metal cations.

DISCLOSURE OF THE INVENTION

This purpose and others are achieved by the present invention which proposes a method for separating palladium from other metal elements contained in a nitric aqueous phase via a liquid-liquid extraction that uses an organic phase containing, as an extractant, new malonamides that are different from the malonamides of formula (F) used in [3].

The malonamides implemented within the framework of the present invention have the following advantages:

- they are easy to prepare from industrial reagents. Moreover, the inventors have shown that it was not necessary to use these malonamides in purified form in order to retain good selectivity (cf. in the experimental portion hereinafter, the results obtained with THEMA – batch B);
- they are robust and can be reused in a method for separating palladium: indeed, as the extractants implemented in the present invention belong to the family of malonamides, no problem with chemical stability is expected;
- they can be used in a lesser quantity compared to malonamides of formula (F);
- they are effective and selective, making it possible to achieve D_{Pd} greater than 20 and $FS_{Pd/Fe}$ greater than 1,000 respectively.

Recall 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 phases, organic and aqueous, 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;

5 – 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

10 – 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.

It is suitable to note that, as the malonamides used within the framework
15 of the present invention, have a selectivity for palladium that is further improved with respect to that obtained with the malonamides of formula (F) used in [3], the quantity of nitric acid in the aqueous phase is no longer to be adjusted. In other terms, the method according to the invention makes it possible to separate then selectively recover the palladium present, in a nitric aqueous solution, in a mixture with other metal elements and
20 this, regardless of the quantity of nitric acid in this solution.

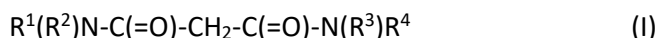
Moreover, the steps of extraction and of back-extraction implemented within the framework of the methods for separating and for recovering according to the invention can be implemented in cross-currents as well as in counter-current, unless explicitly mentioned otherwise. In addition, in the present invention, "O/A ratio" means the
25 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.

More particularly, the method for separating palladium from the other metal elements contained in a nitric aqueous phase comprises:

– putting into contact a nitric aqueous phase containing, in addition to palladium, at least one other metal cation of which the valency is greater than or equal to 2 with an organic phase immiscible with water then

– separating the nitric aqueous phase and the organic phase in which
5 the palladium was extracted,

said organic phase containing at least one malonamide free of sulphur atoms as an extractant of formula (I):



in which the R^1 , R^2 , R^3 and R^4 groups, identical or different, represent an alkyl, an heteroalkyl
10 or an arylalkyl, said alkyl, heteroalkyl and arylalkyl being free of sulphur atoms and each having at least 5 carbon atoms.

Using malonamides of formula (I) in liquid-liquid extractions is not new in itself. Such malonamides have been successfully tested on a pilot scale in several extraction
15 methods in a nitric medium.

However, Bao and Sun have compared the extraction of uranium(VI) from nitric solutions by using, as an extractant in an organic phase with a toluene base, either N,N,N',N'-tetrabutylmalonamide (TBMA), or N,N,N',N'-tetrahexylmalonamide (THEMA) which have the formula (I) [5]. The results presented in this article show that the
20 effectiveness of extracting TBMA is better than that of THEMA, this difference being explained by the greater steric hindrance at nitrogen atoms for THEMA compared to TBMA.

Likewise, Mowafy and Aly have studied the extraction of lanthanides(III) by using 8 different malonamides among which is THEMA [6]. In the conclusion of [6], it is stated that the extracting capacity of lanthanides(III) is influenced by the substituents and
25 the length of the carbon chain of the malonamides and that the malonamides of which the central methylenic carbon is monosubstituted have a higher extraction capacity than that of non-substituted malonamides.

These various teachings would have dissuaded those skilled in the art from replacing malonamides of formula (F) such as implemented in [3] with malonamides
30 of formula (I) such as implemented in the present invention. *A fortiori*, it was difficult to

consider that this replacing could result in an improvement in the effectiveness and in the selectivity of the extraction of the palladium present, in a nitric aqueous solution, in a mixture with other metal elements.

In the method according to the present invention, if the nitric aqueous phase contains one or more lanthanides, the latter remain in the nitric aqueous solution, following the putting into contact with the organic phase containing at least one malonamide of formula (I) 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.

Within the framework of the present invention, the nitric aqueous phase used is characterised by the presence of different metal elements among which there is palladium and at least one other metal cation the valence of which is greater than or equal to 2.

Any nitric aqueous phase containing different metal elements among which there is palladium and at least one other metal cation the valence of which 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 invention is advantageously a nitric aqueous solution stemming from the treatment of waste electrical and electronic equipment. 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 chromium (Cr). The quantity of each one of these metal elements and notably the quantity of palladium in the nitric aqueous phase will depend on the origin of the nitric aqueous phase and notably 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 subjected to an acid attack, for example, by hydrochloric acid or sulphuric acid then subjected to an oxidising attack by nitric acid notably in a quantity comprised between 3 mol.L⁻¹ and 6 mol.L⁻¹ and this, 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.

5 As already mentioned, it is not necessary to adjust the quantity of nitric acid in the nitric aqueous phase implemented in the method according to the invention, when this nitric aqueous phase comes from the oxidising attack of waste electrical and electronic equipment by nitric acid. The quantity of nitric acid in the nitric aqueous phase implemented in the method according to the invention is advantageously comprised
10 between 0.1 mol.L^{-1} and 6 mol.L^{-1} and notably between 0.5 mol.L^{-1} and 5.5 mol.L^{-1} . By way of illustrative examples, the quantity of nitric acid in the nitric aqueous phase can be about 1 mol.L^{-1} (i.e. $1 \text{ mol.L}^{-1} \pm 0.50 \text{ mol.L}^{-1}$), about 2 mol.L^{-1} (i.e. $2 \text{ mol.L}^{-1} \pm 0.50 \text{ mol.L}^{-1}$), about 3 mol.L^{-1} (i.e. $3 \text{ mol.L}^{-1} \pm 0.50 \text{ mol.L}^{-1}$), about 4 mol.L^{-1} (i.e. $4 \text{ mol.L}^{-1} \pm 0.50 \text{ mol.L}^{-1}$) or even about 5 mol.L^{-1} (i.e. $5 \text{ mol.L}^{-1} \pm 0.50 \text{ mol.L}^{-1}$). The quantities of nitric acid given hereinabove
15 are intended prior to the putting into contact with the organic phase. Indeed, a certain quantity of nitric acid can be extracted in the organic phase by the extractant malonamide.

 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
20 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 [7], 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
25 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 possibly be present partially in the form of a complex by the nitrate or chloride anions present in the solution.

 The nitric aqueous phase implemented in the method according to the present invention may contain, as acid, only nitric acid. Alternatively, this nitric aqueous
30 phase can contain, in addition to nitric acid, at least one other acid notably 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 peroxider (or H_2O_2).

Within the framework of the method for separating according to the present invention, the extractant contained in the organic phase immiscible with water has the form of a malonamide free of sulphur atoms of formula (I) or of several different malonamides free of sulphur atoms of which at least one and advantageously all have the formula (I). The latter are able to form 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 dithiodiglycolamides. 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 of formula (I).

In formula (I) of the malonamides implemented within the framework of the present invention, "alkyl group" means an alkyl group, linear, branched or cyclic, comprising from 5 to 20 carbon atoms, notably from 5 to 15 carbon atoms, in particular, from 5 to 12 carbon atoms and, more particularly, from 5 to 10 carbon atoms.

Within the framework of the present invention, "heteroalkyl group" means a heteroalkyl group, linear, branched or cyclic, comprising from 5 to 20 carbon atoms, notably from 5 to 15 carbon atoms, in particular, from 5 to 12 carbon atoms and, more particularly, from 5 to 10 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. It is obvious that, within the framework of the present invention, no heteroatom present in a heteroalkyl group is a sulphur 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.

Within the framework of the present invention, "arylalkyl group" means an alkyl group, linear, branched or cyclic, comprising from 1 to 20 carbon atoms, notably

from 1 to 15 carbon atoms, in particular, from 1 to 12 carbon atoms and, more particularly, from 1 to 10 carbon atoms, said alkyl group being substituted by an aryl group. "Aryl group" means an aromatic mono- or polycyclic group having from 4 to 10 carbon atoms and, notably, from 6 to 8 carbon atoms. Within the framework of the present invention, when
 5 at least one group among the R^1 , R^2 , R^3 and R^4 groups is an arylalkyl group, this group is fixed to the nitrogen of the malonamide via the alkyl group thereof.

In accordance with the invention, the malonamide free of sulphur atoms of formula (I) implemented is, preferably, selected from among the malonamides in which the R^1 , R^2 , R^3 and R^4 groups, identical or different each have at least 5 carbon atoms and
 10 advantageously at least 6 carbon atoms. Typically, the total number of carbon atoms that all the R^1 , R^2 , R^3 and R^4 groups have is greater than or equal to 20, notably greater than or equal to 22 and, in particular greater than or equal to 24. Indeed, such malonamides have a hydrophobic nature that is sufficient to be used in the organic phase immiscible with water.

15 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 R^1 and R^4 groups are identical and the R^2 and R^3 groups are identical, the R^1 and R^3 groups able to be identical or different.

In particular, the malonamide free of sulphur atoms of formula (I)
 20 implemented within the framework of the present invention is selected from the group consisting of *N,N,N',N'*-tetrahexylmalonamide (or THEMA), *N,N,N',N'*-tetraoctylmalonamide (or TOMA), *N,N,N',N'*-tetra(2-ethylhexyl)malonamide (or T2EMA), *N,N'*-dihexyl-*N,N'*-dibenzylmalonamide, *N,N,N',N'*-tetra(2-phenylethyl)malonamide and *N,N'*-dihexyl-*N,N'*-dicyclohexylmalonamide.

25 Even more particularly, the malonamide free of sulphur atoms of formula (I) implemented within the framework of the present invention is THEMA or TOMA.

Within the framework of the method of separating of the invention, the malonamide free of sulphur atoms of formula (I) is present in the organic phase in a quantity greater than or equal to 10 mM, notably in a quantity greater than or equal to
 30 40 mM, in particular, in a quantity greater than or equal to 60 mM, more particularly in a

quantity comprised between 80 mM and 2 M and, even more particularly, in a quantity comprised between 100 mM and 1 M. When the organic phase comprises several different malonamides and in particular several different malonamides free of sulphur atoms of formula (I), the total quantity of malonamides in the organic phase is greater than or equal to 10 mM, notably in a quantity greater than or equal to 25 mM, in particular, in a quantity comprised between 50 mM and 1.5 M and, more particularly, in a quantity comprised between 100 mM and 0.5 M.

Finally, the organic phase immiscible with water used within the framework of the present invention contains at least one malonamide free of sulphur atoms of formula (I) 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. By way of illustrative and non-limiting examples of molten salts that can be used as a solvent of the organic phase implemented during the method of separating 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'-dialkylimidazoliniums, and of a hexafluorophosphate or bis(trifluoromethanesulfonyl)imide anion.

In the method for separating according to the invention, those skilled in the art will know how to determine, without inventive effort, the O/A ratio that is best suited according to the nitric aqueous phase implemented. Typically, the volume ratio between the organic phase and the nitric aqueous phase is comprised between 1/10 and 10, notably between 1/5 and 2, in particular between 1/3 and 1 and, more particularly, about 0.5 (i.e. 0.5 ± 0.2). In addition, during this method, the putting into contact between the nitric aqueous phase and the organic phase lasts between 5 min and 2 h, notably between 10 min and 90 min and, in particular, about 30 min (i.e. $30 \text{ min} \pm 10 \text{ min}$).

The method of separating 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. "Ambient temperature" means a temperature of $20^{\circ}\text{C} \pm 5^{\circ}\text{C}$.

The present invention relates to a method for the selective recovery of palladium from a nitric aqueous phase that contains, in addition to palladium, at least one other metal cation the valence of which is greater than or equal to 2, said method comprising the implementation of a method for separating such as defined hereinabove.

More particularly, the method for recovering according to the invention comprises the following steps:

a) extracting palladium from a nitric aqueous phase that contains, in addition to palladium, at least one other metal cation the valence of which is greater than or equal to 2, which extracting comprises at least one operation in which said nitric aqueous phase is put into contact with an organic phase that is immiscible with it, containing, as an extractant, at least one malonamide free of sulphur atoms of formula (I) such as defined hereinabove, then separated from this organic phase;

b) optionally 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 (a), which back-extracting comprises at least one operation in which the organic phase coming 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 and

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

All that has been described hereinabove for the method for separating applies *mutatis mutandis* to step (a) of the method for recovering according to the invention. Thus, during this step, the nitric aqueous phase containing palladium and at least one other metal cation the valence of which is greater than or equal to 2 is such as defined hereinabove, in particular in terms of concentration in nitric acid.

Within the framework of the method for recovering according to the present invention, step (b) is an optional washing step of the organic phase obtained following step (a). It makes it possible to further improve the selectivity of the recovery of palladium by extracting, from the organic phase obtained following step (a), other metal cations the valence of which is greater than or equal to 2 which may have been driven in this phase.

In certain cases, the organic phase obtained following step (a) contains at least one malonamide free of sulphur such as defined hereinabove, palladium and at least one other metal cation the valence of which 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 (b) of the method for recovering according to the invention is either water, or an aqueous solution of nitric acid. The nitric aqueous solution implemented during step (b) 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 (b) of the method for recovering according to the invention, the operation of putting into contact of the organic phase with an aqueous phase such as defined hereinabove is not repeated. Alternatively, during step (b) of the method for recovering 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.

Advantageously, when step (b) 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.

In a 1st embodiment of step (b) 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, when step (b) 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 (b) 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 (b), 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. $60 \text{ min} \pm 10 \text{ min}$).

5 Step (b) 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 (b) is the ambient temperature.

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

10 In a 1st embodiment of this back-extraction step, the aqueous phase implemented during step (c) 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 phase put into the presence of the organic phase containing the palladium initially
15 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 (a) and optionally following step (b).

In a 2nd embodiment of this back-extraction step, the aqueous phase used
20 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 (a) and optionally following step (b).

Advantageously, this complexing agent is selected from the agents the use of which has already been proposed for the realisation of liquid-liquid extractions. Such
25 an agent is typically capable of complexing the palladium contained in the organic phase obtained following step (a) or optionally following step (b) 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
30 such as lithium 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 back-extraction step can contain hydrochloric acid at a concentration comprised between 1 mol.L⁻¹ and 8 mol.L⁻¹ of aqueous phase, and/or thiourea in a quantity comprised between 0.1 mol.L⁻¹ and 2 mol.L⁻¹ of aqueous phase and/or thiosulphate in a quantity comprised between 0.1 mol.L⁻¹ and 2 mol.L⁻¹ of aqueous phase. Therefore, an aqueous ammonia based phase can be used, at a content comprised between 1 and 4% (example ammonia 1 M).

In a 3rd embodiment of this back-extraction step and according to the nature (chemical composition) of the aqueous flow used in step (a) or optionally after step (b), the organic phase obtained after this step (a) or optionally (b) can be of a purity that is sufficient for carrying out a direct recovery of the metal palladium during step (c). 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 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 non-limiting and illustrative 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 mol.L⁻¹ or a solution of sodium or potassium formate.

In step (c) of the method according to the invention, the volume ratio between the organic phase and the aqueous phase containing the palladium is comprised between 1/10 and 10, notably between 1/8 and 8 and, in particular between 1/6 and 6 and, very particularly, between 1/2 and 2. In addition, the putting into contact of the aqueous phase and the organic phase containing the palladium lasts between 5 min and 90 min, notably between 10 min and 60 min and, in particular, about 30 min (i.e. 30 min $\pm$ 10 min).

Step (c) 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 this method of separating is the ambient temperature.

Following step (c) of the method according to the invention and notably following the 1st and the 2nd embodiment, 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 Pd²⁺ present in the aqueous phase obtained following step (c) to a reduction. This reduction can be carried out according to the many known techniques available. As non-limiting and illustrative 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 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 (c)). As non-limiting and illustrative examples, it is possible to recover the palladium in the form of a precipitate of palladium(II) hydroxide, of ammonium and palladium(II) chloride, of palladium(II) sulphite, of palladium(II) and sodium or potassium disulphite. In this latter case, a precipitation will advantageously be carried out using ammonium chloride.

In addition, following step (c) of the method according to the invention, the organic phase containing at least one malonamide free of sulphur atoms of formula (I) can be recovered and reused and this, notably 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 illustration and in a non-limiting way.

DETAILED DISCLOSURE OF PARTICULAR EMBODIMENTS

I. Synthesis and purification of the malonamides used

I.1. *N,N,N',N'*-tetrahexylmalonamide (THEMA – batch A)

A mixture of diethyl malonate (2.0 g) and of *N,N*-dihexylamine (4.9 g) in an autoclave is heated to 150°C for 16 h. The ethanol formed is eliminated from the product of the reaction via evaporation, then the compound obtained is purified by chromatography on silica gel (eluent gradient: pure cyclohexane with cyclohexane/ethyl acetate – 60/40). The THEMA is obtained in the form of a colourless oil (4.4 g).

Analyses: NMR ¹H: δ(ppm) 3.37 (s, 2H), 3.21-3.29 (m, 8H), 1.48-1.53 (m, 8H), 1.17-1.25 (m, 24H), 0.79 (t, J = 7.2 Hz, 12H). NMR ¹³C: δ(ppm) 166.6, 48.4, 46.0, 40.8, 31.5, 31.5, 28.9, 27.5, 26.6, 26.6, 22.5, 13.9, 13.9.

I.2. *N,N,N',N'*-tetrahexylmalonamide (THEMA - batch B)

A mixture of diethyl malonate (2.0 g) and of *N,N*-dihexylamine (4.9 g) in a flask provided with an air condenser is heated to 180°C for 4 h. The ethanol formed is eliminated from the reaction product via evaporation, then the crude of the reaction is included in 4 mL of a ethyl acetate/cyclohexane 50/50 mixture. 1.2 g of active charcoal is added, then the suspension obtained is stirred for 30 min. The residual mixture is filtered over celite (rinsing by an ethyl acetate/cyclohexane 50/50 mixture), then vacuum concentrated. The THEMA is obtained in the form of a pale yellow oil (5.2 g).

The analysis by NMR ¹H is similar to that of the pure product (point I.1 hereinabove).

I.3. *N,N,N',N'*-tetraoctylmalonamide (TOMA)

A mixture of diethyl malonate (1.0 g) and of *N,N*-dioctylamine (3.3 g) in an autoclave is heated to 160°C for 16 h. The ethanol formed is eliminated from the reaction product via evaporation, then the compound obtained is purified by chromatography on silica gel (eluent: cyclohexane/ethyl acetate – 80/20). The TOMA is obtained in the form of a colourless oil (3.1 g).

Analyses: NMR ¹H: δ(ppm) 3.47 (s, 2H), 3.29-3.36 (m, 8H), 1.51-1.58 (m, 8H), 1.22-1.29 (m, 40H), 0.82 (t, J = 7.3 Hz, 12H).

II. Extraction of metals

II.1. Protocol

An aqueous stock solution in nitric medium 5 M containing 2,000 mg/L of Pd, 2,000 mg/L of Nd and 20 g/L of Fe is prepared from salts $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, purchased from the companies STREM or ALDRICH.

Different organic solutions are prepared. Each one of them contains a certain quantity of THEMA or of TOMA in toluene, in various concentrations.

The organic phases are pre-balanced with the corresponding aqueous phases without metal. For this, each organic phase is put into contact 1 h with an aqueous phase of desired acidity for the extraction. The aqueous volume is at least five times higher than the organic volume.

The extractions are carried out by putting into contact the pre-balanced organic phases with the aqueous phases containing 200 mg/L of Pd and of Nd, and 2,000 mg/L of Fe (dilution 10 of the aqueous stock phase) and by adjusting the concentration in nitric acid to each operating condition. The volumes of the 2 phases are equal. The extraction lasts 1 h.

The phases are then separated. The organic phases are counter-extracted using an aqueous solution of thiourea at 0.2 M. The volume of the aqueous phase is four times that of the organic phase. Each counter-extraction lasts 30 minutes.

The concentrations in metals of the different aqueous phases (of extraction or of counter-extraction) are dosed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

II.2 Results

The results with the THEMA – batch A and the purified TOMA are provided in the following Table 1:

[THEMA] (mol/L)	[HNO ₃] (mol/L)	DPd	DFe	DNd
0.5	2.0	> 34	0.004	0.017
	2.5	> 34	0.014	0.026
	3.0	> 34	0.050	0.038

0.6	2.0	> 34	0.007	0.028
	2.5	> 34	0.028	0.051
	3.0	> 34	0.091	0.069

[TOMA] (mol/L)	[HNO ₃] (mol/L)	DPd	DFe	DNd
0.6	3.0	> 34	0.053	0.037

Table 1

5 The value of 34 corresponds to the maximum value of D that can be determined by this protocol because in any case the quantity of Pd in the aqueous phase after extraction is less than the quantification limit (2.8 mg/L).

The results with the THEMA – batch B are provided in the following Table 2:

[THEMA] (mol/L)	[HNO ₃] (mol/L)	DPd	DFe
0.3	1.6	> 70	< QL
	2.0	> 70	0.0003
0.2	2.0	34	< QL
	3.0	38	0.015
0.1	3.0	9	0.0025
	5.0	7	0.023

10

Table 2

The value of 70 corresponds to the maximum value of D that can be determined taking account of the quantification limit (QL) of the Pd.

15 Even when not using a purified THEMA, remarkable effectiveness and selectivity is obtained for the extraction of palladium.

II.3. Comparison of the THEMA – DMDBTDMA performance

20 The results with the THEMA – batch B and the N,N'-dimethyl-N,N'-dibutyltetradecylmalonamide (DMDBTDMA) purchased from the company Pharmasynthèse are provided in the following Table 3:

Concentration en extractant (mol/L)	[HNO ₃] (mol/L)	DPd with THEMA	DPd with DMDBDMA
0.1	3.0	9	0.3
0.3	2.0	> 70	0.8
0.3	1.0	4.5	0.1

Table 3

5 The malonamides of formula (I) implemented within the framework of the present invention and in particular the THEMA make it possible to obtain an effectiveness for the extraction of palladium that is improved compared to that obtained with the malonamides of formula (F) such as used in **[3]** and notably DMDBDMA.

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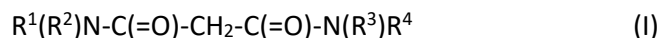
CLAIMS

1) Method for separating palladium from the other metal elements contained in a nitric aqueous phase comprising:

5 – putting into contact a nitric aqueous phase containing, in addition to palladium, at least one other metal cation the valence of which is greater than or equal to 2 with an organic phase mmiscible with water then

 – separating the nitric aqueous phase and the organic phase wherein the palladium has been extracted,

10 said organic phase containing, as an extractant, at least one malonamide free of sulphur atoms of formula (I):



in which the R^1 , R^2 , R^3 and R^4 groups, identical or different, represent an alkyl, an heteroalkyl or an arylalkyl, said alkyl, heteroalkyl and arylalkyl being free of sulphur atoms and each
15 having at least 5 carbon atoms.

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

20 3) Method according to claim 1 or 2, characterised in that said nitric aqueous phase contains, in addition to nitric acid, at least one other acid notably selected from the group consisting of hydrochloric acid, bromhydric acid, fluorhydric acid and sulphuric acid.

25 4) Method according to any of claims 1 to 3, characterised in that said R^1 , R^2 , R^3 and R^4 groups, identical or different, each have at least 6 carbon atoms.

5) Method according to any of claims 1 to 4, characterised in that said malonamide free of sulphur atoms of formula (I) is selected from the group consisting of

N,N,N',N'-tetrahexylmalonamide, *N,N,N',N'*-tetraoctylmalonamide, *N,N,N',N'*-tetra(2-ethylhexyl)malonamide, *N,N'*-dihexyl-*N,N'*-dibenzylmalonamide, *N,N,N',N'*-tetra(2-phenylethyl)malonamide and *N,N'*-dihexyl-*N,N'*-dicyclohexylmalonamide.

5 6) Method according to any of claims 1 to 5, characterised in that said malonamide free of sulphur atoms of formula (I) is present in said organic phase in an quantity greater than or equal to 10 mM, notably in a quantity greater than or equal to 25 mM, in particular, in a quantity comprised between 50 mM and 1.5 M and, more particularly, in a quantity comprised between 100 mM and 0.5 M.

10

7) Method for the selective recovering of palladium from a nitric aqueous phase that contains, in addition to palladium, at least one other metal cation the valence of which is greater than or equal to 2, said method comprising the implementing of a method for separating such as defined in any of claims 1 to 6.

15

8) Method according to claim 7, characterised in that said method comprises the following steps:

a) extracting palladium from a nitric aqueous phase that contains, in addition to palladium, at least one other metal cation the valence of which is greater than or equal to 2, which extracting comprises at least one operation in which said nitric aqueous phase is put into contact with an organic phase that is immiscible with it, containing, as an extractant, at least one malonamide free of sulphur atoms of formula (I) such as defined hereinabove, then separated from this organic phase;

20

b) optionally 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 (a), 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 and

25

c) selectively back-extracting the palladium present in the organic phase stemming from step (a) or optionally stemming from step (b), which back-extracting

30

comprises at least one operation in which the organic phase stemming from step (a) or optionally stemming from step (b) is put into contact with an aqueous phase, then separated from this aqueous phase.

5 9) Method according to claim 8, characterised in that the aqueous phase implemented during said step (b) is either water, or an aqueous solution of nitric acid.

10 10) Method according to claim 8 or 9, characterised in that, during said step (b), said O/A ratio is less than 7 and notably less than 6 and, in particular, less than 5.

15 11) Method according to claim 8 or 9, characterised in that, during said step (b), 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.

15 12) Method according to any of claims 8 to 11, characterised in that said aqueous phase implemented during said step (c) is a diluted solution of acid with a pH greater than 1.

20 13) Method according to any of claims 8 to 11, characterised in that said aqueous phase implemented during said step (b) contains a complexing agent of the palladium 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
25 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.

30 14) Method according to any of claims 8 to 11, characterised in that said aqueous phase implemented during said step (b) comprises a palladium reducer.