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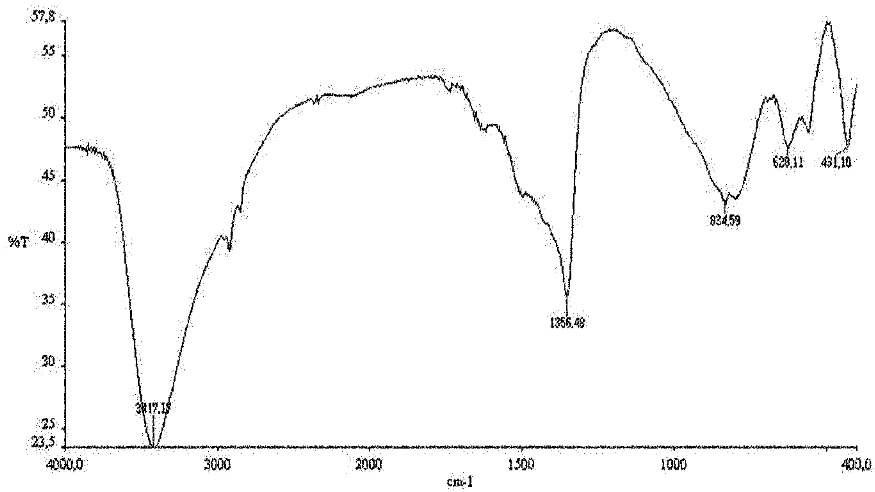


Fig. 3

(57) Abstract: A deodorant composition comprising: at least one anionic clay; silver nanoparticles and at least one excipient which is acceptable for cosmetic use.

DEODORANT COMPOSITION

The present invention relates to a deodorant composition comprising a substance of the anionic clay type and silver nanoparticles, to a process for preparing a composition comprising a substance of the hydrotalcite type and silver nanoparticles, to a deodorant composition comprising a substance of the hydrotalcite type and silver nanoparticles and to the use of these compositions as a deodorant or antimicrobial agent.

Hydrotalcites (HT) fall within the category of anionic clays, compounds which are widespread in nature but can also be synthesized in a laboratory and are constituted by a structure with superimposed and parallel charged layers, mutually bonded by weak electrostatic attractions. The size of the interlayer, also known as basal space, depends on various factors, such as the degree of hydration of the clay and the size of the ion interposed between the layers. One of the main characteristics of clays is the ability to exchange interlayer ions: this is the reason for their extensive use in the industry as adsorbent materials, as supports for catalysts, ion exchangers.

It is possible to synthesize a large number of so-called compounds of the hydrotalcite (HT) type, which can be represented by the following general formula:

$$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}{}_{x/n})\ mS$$

The main composition variables are:

– divalent ion M(II), which can also be of two different metals (Mg, Zn, Co, Ni, Mn, et cetera);

– trivalent ion M(III), in this case also of a metal or of two different metals (Al, Cr, Fe, V, Co, et cetera);

– the value 'x', i.e., the stoichiometric ratio between the two metallic ions;

– intercalated anion A^{n-}, which can have variable dimensions, charge and properties (CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-, halides, silicates, et cetera);

– number m of water molecules;

– morphology and dimensions of the crystal.

In order to better understand the structure of hydrotalcite, it can be useful to start from brucite $Mg(OH)_2$, in which the magnesium ions are bonded to 6 hydroxide ions with octahedral coordination. The various octahedra share an edge, forming layers which are mutually stacked and bonded by hydrogen bonds. If part of the magnesium ions is substituted with trivalent ions such as aluminum ions, the layers become positively charged and this charge excess must be balanced by anions, the most common of which is carbonate, which are intercalated between the hydroxide layers. Water molecules are also present in these interlayers and bond with the hydroxide layers and with the anions by means of hydrogen bonds.

There are some limitations, imposed by the layered structure, in the choice of the metallic cation. This ion must have such dimensions that it can be placed in a structure with brucitic layers and must be able to assume an octahedral coordination, hexacoordinating itself with 6 hydroxyls. For this reason, it is possible to synthesize hydrotalcites only by using ions whose radius is very similar to magnesium and aluminum ions, having electronic characteristics that are compatible with octahedral symmetry, particularly with trivalent ions with a radius comprised between 0.50 and 0.80 angstrom and with divalent ions with a radius comprised between 0.65 and 0.80 angstrom.

In order to obtain a pure hydrotalcite substance, x must be comprised between 0.2 and 0.33 so that a hydroxide phase of the excess ion does not separate next to the hydrotalcite phase. For higher values, $M(III)(OH)_3$ can form, whereas for lower values segregation of $M(II)(OH)_2$ can occur.

Various examples are reported of compounds with a structure of the type of Zn/Al, Mg/Al hydrotalcites, with many applications in the fields of medicine (antacid and antipepsin activity) and of cosmetics, with information regarding their properties, since they improve skin trophism (eudermal action), are biocompatible and have an absorbent and refreshing action. In particular, their use has been reported for the intercalation of aromatic compounds for use as sunscreens in “containers” of the hydrotalcite type in order to obtain commercial solutions that obviate the problem of photoinstability and allergenicity of certain filters such as PABA (para-aminobenzoic acid) (*"Filtri solari: impiego di argille anioniche lamellari per migliorare l'efficacia e la stabilità"* L. Perioli, V. Ambrogi, *Kosmetica* April 2008, 64-67; *"Argille anioniche nei cosmetici: skin care e make up"* L. Perioli, E. Massetti, *Kosmetica* November 2009, 34-39; *"Sunscreen immobilization on Zn/Al hydrotalcite for new cosmetic formulations"* L. Perioli, M. Nocchetti, V. Ambrogi, L. Latterini, C. Rossi, U. Costantino, *Microporous and Mesoporous Materials* 107 (**2008**) 180-189).

There are various methods for synthesizing hydrotalcites, including: precipitation at constant pH (coprecipitation); precipitation at variable pH; urea method; ion exchange; electrochemical methods; reconstruction of the structure (reference: *Hydrotalcite-like compounds: Versatile layered hosts of molecular anions with biological activity* – U. Costantino, V. Ambrogi, M. Nocchetti, L. Perioli, *Microporous and Mesoporous Materials* 107 (**2008**) 149-160).

Carja et al. (*"Nanosized silver-anionic clay matrix as nanostructured ensembles with antimicrobial activity"*, Gabriele Carja, Yoshikazu Kameshima, Akira Nakajima, Cristian Dranca, Kiyoshi Okada, *International Journal of Antimicrobial Agents* 34 (**2009**) 534-539) describe materials with a matrix based on anionic clay comprising silver nanoparticles and report the dependency of the antimicrobial activity of said materials as a function of the time elapsed between their preparation and their use.

The antibacterial activity of silver has been known for a long time and is assisted with the amount of Ag that is present and with its release rate. Silver in its metallic state is inert but can react, for example with substances that are present on the skin or with the fluid of a wound, and is ionized. Ionized silver is highly reactive, because it binds to the proteins of tissues and causes structural changes in the cellular and nuclear membrane of bacteria, leading to cell modification and death. Silver also bonds to bacterial DNA and/or RNA, leading to denaturation, and inhibits bacterial replication (*"Silver nanoparticles as a new generation of antimicrobials"*, M. Rai, A. Yadav, A. Gade, *Biotechnology Advances* 27 (**2009**) 76-83).

The individual emission of human odors is linked to hormone control and to the bacterial population that is present on the surface of the skin, which feeds by metabolizing and transforming organic compounds absorbed from the outside environment. In the analysis of VOC, HS-SPME is a quick sampling method that ensures high sensitivity and good selectivity.

There are 4 main types of bacteria on the surface of the skin of the armpit: mainly staphylococci, aerobic coryneforms and also micrococci and proprionibacteria. These bacteria decompose long-chain molecules into shorter-chain molecules and VOC such as fatty acids, aldehydes, ketones, ester alcohols, etc. Sweat is rich in molecules of acid nature (anions) which are often malodorous. In addition to chloride, uric acid and lactic acid, other substances form in situ which are generally responsible for the acrid and pungent odor of sweat and are produced by bacteria and enzymes such as protease and lipase. Sweat is mainly constituted by lipids, proteins, nitrogenous derivatives and glucides and is therefore an excellent medium for bacterial metabolism.

Absorbents, such as zinc magnesium and calcium oxide, are already used in deodorants in powder form due to their function of absorbents of excess humidity and of malodorous volatile substances that are formed by the enzymatic degradation of sweat, contrasting its evaporation, without however blocking the physiological mechanism of perspiration and the growth of the bacterial flora.

The administration of traditional deodorants, especially in powder form, must occur on properly depilated skin so as to facilitate powder-skin contact and because the presence of hairs facilitates the nesting of bacteria and does not allow suitable cleansing. Another precaution to be followed for correct use of traditional deodorants is that they must not be applied on moist or freshly depilated skin.

The suspicion has arisen recently that the use of deodorants (antiperspirants) based on aluminum is correlated with the onset of irritations, inflammations and even breast tumors.

Although traditional antiperspirants are products which are widely appreciated and used because of their effectiveness, it has been recommended to use them with moderation, discontinuously and alternated with other simpler, more delicate and less invasive deodorant practices.

The aim of the present invention is to provide a composition for cosmetic use that is capable of contrasting effectively the forming of unpleasant odors caused by the degradation of sweat with high absorbent power, excellent tolerability and high effectiveness in a wide range of conditions of use and in low doses.

Another object of the present invention is to provide active ingredients for use as skin deodorants.

Another object of the present invention is to provide a composition comprising a substance of the hydrotalcite type and silver nanoparticles which can be used in various fields of application, including use as antimicrobial agent and as deodorant active ingredient.

Another object of the present invention is to provide a process that can be applied easily on an industrial scale, with the appropriate modifications that are known to the person skilled in the art, for the production of said composition comprising a substance of the hydrotalcite type and silver nanoparticles.

This aim and other objects that will become apparent hereinafter have been achieved by means of a deodorant composition comprising:

a) at least one anionic clay;

b) silver nanoparticles; and

c) at least one excipient which is acceptable for cosmetic use.

This aim and other objects have also been achieved by using as a skin deodorant active ingredient

a) at least one anionic clay;

b) silver nanoparticles; and

c) at least one excipient which is acceptable for cosmetic use.

This aim and other objects have also been achieved by a process for preparing a composition comprising:

a) at least one substance of the hydrotalcite type having general formula (I)

$$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}{}_{x/n}).mS \qquad (I)$$

wherein:

– M(II) is a divalent ion, which can be of one or two different metals selected from Mg, Zn, Ni, Co and Fe;

– M(III) is a trivalent ion, which can be of one or two different metals selected from Al, Cr, Fe and Mn;

– x is a number that indicates the stoichiometric ratio between divalent and trivalent metal ions and is comprised between 0.2 and 0.33;

– A^{n-} is at least one anion intercalated in the structure, wherein n is the number of negative charges, selected from CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-, ClO_4^-, F^-, Cl^-, Br^- and silicates;

– S is a water molecule;

– m is the number of water molecules; and

b) silver nanoparticles;

said process comprising:

i. calcining the substance of the hydrotalcite type having general formula (I) at a temperature comprised between 450 and 700°C and for a time comprised between 1.5 and 20 hours;

ii. preparing an aqueous suspension of silver nanoparticles with dimensions comprised between 2 and 200 nm;

iii. adding under agitation at a temperature comprised between 20 and 35°C the calcined substance obtained in step i. to the suspension obtained in step ii.;

iv. leaving the suspension obtained in step iii. under agitation at a temperature comprised between 20 and 35°C for a time comprised between 0.5 and 5 hours.

This aim and other objects have also been achieved by a composition that can be obtained by said process, by a deodorant composition comprising said composition and by its use as an active ingredient with an action as a skin deodorant or as a antimicrobial agent.

In the present invention, the term “nanoparticle” references a particle with dimensions comprised between 2 and 200 nanometers.

In the present invention, the terms “deodorant” and “antiperspirant” reference a substance that is capable of preventing or removing unpleasant odors produced at the skin level, particularly by the bacterial degradation of sweat.

In one aspect, the present invention relates to a deodorant composition comprising:

a) at least one anionic clay;

b) silver nanoparticles; and

c) at least one excipient which is acceptable for cosmetic use.

Preferably, in the composition according to the invention in which at least one anionic clay is a substance of the hydrotalcite type having the general formula (I)

$$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}_{x/n}).mS \qquad (I)$$

wherein:

– M(II) is a divalent ion, which can be of one or two different metals selected from Mg, Zn, Ni, Co and Fe;

– M(III) is a trivalent ion, which can be of one or two different metals selected from Al, Cr, Fe and Mn;

– x is a number that indicates the stoichiometric ratio between divalent and trivalent metal ions and is comprised between 0.2 and 0.33;

– A^{n-} is at least one anion intercalated in the structure, wherein n is the number of negative charges, selected from CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-, ClO_4^-, F^-, Cl^-, Br^- and silicates;

– S is a water molecule;

– m is the number of water molecules.

It has been found that the composition according to the invention comprising at least one anionic clay is capable, even in extremely low quantities, of inhibiting the proliferation of the bacteria that are responsible for the degradation of sweat with generation of the substances that are responsible for unpleasant odors.

Moreover, it has been found that it is particularly advantageous to use synthetic hydrotalcites, because they have the same properties as natural ones and have the advantage of being free from impurities and of having a known and clearly defined composition. Moreover, their degree of crystallinity can be controlled during preparation. The aspect of purity is an extremely important aspect in the prospect of using these materials in cosmetic formulations which must be hypoallergenic. Generally, HT crystals have dimensions of a few microns (microfine powders) and this is highly advantageous, since these materials are easy to incorporate in any type of formulation and never cause problems in terms of spreadability or abrasion for formulations to be applied to the skin.

HTs give semisolid preparations good rheological characteristics and allow formulations to adhere very well to the skin, thus having a protective, anti-inflammatory and also deodorant effect. Anionic clays, particularly HTs, are eudermics, excellent dermatological protectors and are used for this purpose directly as powders or introduced in emulsions and pastes. They can protect the skin against external agents or even against agents produced by the skin and excreted in liquids (epidermal debris). As a consequence of this adsorbent effect, they adhere strongly to the skin, forming a film that is capable of offering mechanical protection against chemical and/or physical external agents. Furthermore, due to the mechanism of adsorption of skin secretions, they also have a refreshing and antiseptic action. Removal of organic material, including fat and toxins, alongside the absorption of water in fact helps to create an environment which is poor in water and nutrients, which becomes unfavorable for the growth of bacteria. When HTs, containing inorganic ions between their lamellae, are used in powder form, they have excellent hydrating and remineralizing properties and can also be used in case of dry skin. When instead they are used in semisolid formulations such as gels, creams, pastes, cream-gels and suspensions, in addition to having their function as active ingredients, they are excellent rheological agents capable of modifying favorably the flow characteristics of preparations, positively affecting preservation, ductility and spreadability, which are essential for good usability. Formulations containing HTs are characterized by higher viscosity at rest, a favorable characteristic during preservation, whereas as a consequence of an increase in temperature or of mechanical stresses (massage) they tend slightly to fluidify, facilitating application.

HTs, due to the specific ion exchange mechanism and to their nanoporous structure, ensure the absorption and removal of waste, of skin exudates and of sweat, storing them within their lamellar structure.

Bacterial proteases allow the forming of ammonia, amines and sulfurated derivatives (sulfurated hydrogen and mercaptans), while bacterial lipases degrade triglycerides, forming short-chain fatty acids, such as valeric acid, caprylic acid, caproic/capronic acid, capric acid, enanthic acid, pelargonic acid, butyric acid and propionic acid. HTs are a weak base and in contact with sweat can facilitate the ionization of the carboxylic group of these fatty acids, which can be exchanged more easily with the counterions that are present between the lamellae of HT.

Moreover, the particular structure of HTs allows to absorb microorganisms, thus interacting with the supported particles. Besides, the use of HTs, even if they contain metals including aluminum, offers assurances in terms of lack of toxicity. Silver nanoparticles can be deposited on the structure of the HT or can be within the structure of the HT itself. Preferably, the nanoparticles are deposited on the structure of the HT.

In particular, the effectiveness of the composition is affected directly by the cosmetic form of the product that comprises it and specifically of the active ingredient that is used and its concentration.

The composition according to the present invention can be formulated in various forms, including the form of a water-alcohol solution, of an atomizable aqueous emulsion, of an aerosol spray, of a stick, of a spray formulation without propellant gas (“no gas” deodorant).

Preferably, the composition of the present invention is in the form of a water-alcohol solution or atomizable aqueous emulsion.

Preferably in the composition according to the invention the content of substance of the hydrotalcite type having the general formula (I) and of silver nanoparticles is comprised between 1 and 30% by weight on the total weight of the composition.

Preferably, in the composition according to the invention the content of silver nanoparticles is comprised between 0.05 and 5% by weight on the weight of the substance of the hydrotalcite type of formula (I). More preferably, the content is between 0.1 and 1% by weight on the weight of the substance of the hydrotalcite type of formula (I).

It has been found that the antibacterial activity of Ag nanoparticles is distinctly higher than that of Ag particles of micrometer size and is a function of the size of the nanoparticles. Ag nanoparticles with a size of 25 nm (within the reasonable limits of the experimental methods for these measurements) in fact have the highest antibacterial activity. These last particles are toxic against bacterial cells at concentrations of less than 1.69 μg/ml of Ag.

Moreover, it has been observed that the antibacterial activity of silver nanoparticles is correlated to their shape.

Preferably, in the composition according to the invention the silver nanoparticles have dimensions comprised between 2 and 200 nm.

More preferably, in the composition according to the invention the silver nanoparticles have a size of 25 nm.

It has been found that the compositions of the invention comprising hydrotalcites based on zinc/aluminum and magnesium/aluminum are easy to prepare by means of known and reliable methods (reference: *"Hydrotalcite-like compounds: Versatile layered hosts of molecular anions with biological activity"*, U. Costantino, V. Ambrogi, M. Nocchetti, L. Perioli, *Microporous and Mesoporous Materials* 107 (2008) 149-160 and *"Preparation and catalytic properties of cationic and anionic clays"*, Angelo Vaccari, *Catalysis Today* **1998**, 41, 53-71) with minimal modifications which are within the grasp of the person skilled in the art and demonstrate an excellent deodorant and antibacterial action. Preferably, in the composition according to the invention M(II) is Mg or Zn, M(III) is Al and A^{n-} is CO_3^{2-} or the Zn/Al ratio is 2:1. Examples of preferred formulas are $Zn_{0,68}Al_{0,32}(OH)_2(CO_3)_{0,32} \times 0,42H_2O$ or $Mg_{0,68}Al_{0,32}(OH)_2(CO_3)_{0,32} \times 0,42H_2O$.

The composition according to the invention comprises one or more excipients that are suitable for cosmetic use, in particular for the treatment of the skin in areas subjected to intense sweating. In particular, the effectiveness of the composition, as mentioned, is linked to the cosmetic form of the product that comprises it and the targeted choice of excipients can give desirable properties, for example a long duration of action. In the composition of the present invention, at least one excipient is selected from a hydrophobic polymer, a fragrance, an antimicrobial agent, an enzyme deviator, a viscosity agent, a rheological agent and essential oils. The presence of a hydrophobic polymer, particularly hydrophobically modified acrylates, is preferable for products in the form of an atomizable fluid emulsion and the presence of fragrances (particularly geraniol, citronellol et cetera), even at a minimal concentration, is preferred for products intended for wide consumption.

Modern products for body deodorization comprise 5 different paths for performing a satisfactory deodorant action:

1. Antiperspirant astringents: with these substances, one works at the level of secretions. By reducing the extent, stagnant moisture is reduced and the quantity of material that can be metabolized by the microbial flora is also reduced;

2. Antimicrobial agents: with these, one works at the level of bacteria, the colonies of which are reduced, so as to reduce the potential of intervention on glandular secretions;

3. Bacteriostatic agents: with this means, excessive microbial proliferation is prevented and the forming of odorous catabolites is reduced accordingly;

4. Enzyme deviators: these substances block the hydrolytic activity of bacteria, reducing the forming of odorous volatile fractions;

5. Absorbent agents: these are substances that intercept odorous bodies by means of a chemical-physical capture process. These agents retain within their structure the odorous molecules that originate from the degradation of secretions.

Actually, a combination of these paths is often used in order to have maximum performance.

Triclosan, triclocarban, chlorhexidine, oxyglycerol etc. are among the most widely used antimicrobial agents.

Since an entirely antimicrobial action is not desirable, these antiseptic substances are used at a concentration that is sufficient to ensure a bacteriostatic action. The component that is most widely used is in any case triclosan. Moreover, mixtures have been devised which are constituted by 50% aromatic bodies having an antimicrobial action and a harmonious fragranced composition for the remaining part.

Enzyme deviators are compounds that act on the bacterial enzymes that are responsible for the degradation of glandular products. Triethyl citrate is the main representative of this category of compounds.

Absorbents are substances that act as chelating agents of short-chain fatty acids, reducing their vapor pressure and therefore making them non-volatile and consequently non-odorous. The substance most used so far is zinc ricinoleate. Every formulation seeks a good compromise between good tolerability and effectiveness in a very significant percentage of users.

Preferably, the composition according to the invention comprises at least one additional active ingredient selected among an antimicrobial agent, an enzyme deviator, an absorbent agent, a rheological agent, an essential oil and a propellant.

More preferably, in the composition according to the invention the antimicrobial agent is triclosan and the enzyme deviator is triethyl citrate.

In another aspect, the present invention relates to use as active ingredient with skin deodorant action of a composition comprising:

a) at least one anionic clay;

b) silver nanoparticles;

c) at least one excipient which is acceptable for cosmetic use.

Preferably, in this substance at least one anionic clay is a substance of the hydrotalcite type comprising silver nanoparticles and having the general formula (I)

$$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}{}_{x/n}).mS \qquad (I)$$

wherein:

– M(II) is a divalent ion, which can be of one or two different metals selected from Mg, Zn, Ni, Co and Fe;

– M(III) is a trivalent ion, which can be of one or two different metals selected from Al, Cr, Fe and Mn;

– x is a number that indicates the stoichiometric ratio between divalent and trivalent metal ions and is comprised between 0.2 and 0.33;

– A^{n-} is at least one anion intercalated in the structure, wherein n is the number of negative charges, selected from CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-, ClO_4^-, F^-, Cl^-, Br^- and silicates;

– S is a water molecule;

– m is the number of water molecules.

Preferably, in the use according to the invention in the active ingredient the concentration of silver nanoparticles is comprised between 0.1 and 1% by weight on the total weight of the substance of the hydrotalcite type having formula (I) and of the silver nanoparticles.

Preferably, in the use according to the invention in the active ingredient the silver nanoparticles have dimensions comprised between 2 and 200 nm.

Preferably, in the use according to the invention in the active ingredient the silver nanoparticles have dimensions equal to 25 nm.

Preferably, in the use according to the invention in the active ingredient M(II) is Mg or Zn, M(III) is Al and A^{n-} is CO_3^{2-}. Preferably, the active ingredient is $Zn_{0.68}Al_{0.32}(OH)_2(CO_3)_{0.32}$ x $0.42H_2O$ or $Mg_{0.68}Al_{0.32}(OH)_2(CO_3)_{0.32}$ x $0.42H_2O$.

In another aspect, the present invention relates to a process for the preparation of a composition comprising:

a) at least one substance of the hydrotalcite type having general formula (I)

$$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}_{x/n}).mS \qquad (I)$$

wherein:

– M(II) is a divalent ion, which can be of one or two different metals selected from Mg, Zn, Ni, Co and Fe;

– M(III) is a trivalent ion, which can be of one or two different metals selected from Al, Cr, Fe and Mn;

– x is a number that indicates the stoichiometric ratio between divalent and trivalent metal ions and is comprised between 0.2 and 0.33;

– A^{n-} is at least one anion intercalated in the structure, wherein n is the number of negative charges, selected from CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-, ClO_4^-, F^-, Cl^-, $Br^-$and silicates;

– S is a water molecule;

– m is the number of water molecules; and

b) silver nanoparticles;

the process comprising:

i. calcining the substance of the hydrotalcite type having general formula (I) at a temperature comprised between 450 and 700°C and for a time comprised between 1.5 and 20 hours;

ii. preparing an aqueous suspension of silver nanoparticles with dimensions comprised between 2 and 200 nm;

iii. adding under agitation at a temperature comprised between 20 and 35°C the calcined substance obtained in step i. to the suspension obtained in step ii.;

iv. leaving the suspension obtained in step iii. under agitation at a temperature comprised between 20 and 35°C for a time comprised between 0.5 and 5 hours.

It has been found surprisingly that this process, particularly suitable for production even on an industrial scale, allows to prepare a composition that has excellent properties, for example as an antimicrobial agent, is stable and lends itself to inclusion in various types of formulations, for example cosmetic or pharmaceutical ones.

In another aspect, the present invention relates to a composition that can be obtained by such process.

Preferably, in the composition obtainable by this process the silver nanoparticles have dimensions comprised between 2 and 200 nm.

In another aspect, the present invention relates to a deodorant composition comprising the composition that can be obtained by this process.

In another aspect, the present invention relates to the use of the composition as an active ingredient with an action as skin deodorant and/or as antimicrobial agent.

Some embodiments of the invention are described hereafter by way of non-limiting example.

In particular, 3 synthesis procedures are reported: the first one (example 1) related to a common Zn/Al 2:1 hydrotalcite by co-precipitation, the second one (example 2) related to a common Mg/Al 2:1 hydrotalcite, the third one (example 3, 4) related to the preparation of the nanoparticles from sugars and to the reconstruction of calcined HT with the nanoparticles.

EXAMPLE 1

Synthesis of Zn/Al 2:1 HT with the co-precipitation method.

A synthesis is performed in which the total concentration of the metals is 1.5 M and the ratio between the moles of the salts of Zn and Al is 2:1.

Starting materials:

$Zn(NO_3)*6H_2O$ M = 297.49 g/mol Titer = 98%

$Al(NO_3)*9H_2O$ M = 375.14 g/mol Titer = 98%

100 mL of a solution of 1 M in $Zn(NO_3)*6H_2O$ (m=30.049 g) and 0.5 M in $Al(NO_3)*9H_2O$ (m=19.139 g) are prepared and placed in a 250 mL separator funnel.

A 0.25M solution of Na_2CO_3 is prepared and 300 mL of this solution are placed in a 2L beaker. A 1M NaOH solution is prepared.

The beaker is placed on a heating plate with magnetic agitation.

The pH-meter is immersed in the solution.

The solution of the salts of the metals is dripped into the beaker very slowly (2 hours) at 21°C and simultaneously pH = 9 is maintained by adding 1M NaOH with a pipette.

Once synthesis has ended, agitation is continued for a further 30 minutes.

The beaker is then covered with parafilm and is left to age at 21°C for 24 hours.

Filtration is then performed with a Büchner filter, making sure to wash well the precipitate with at least 2 L of water in order to eliminate the nitrates: long times (approximately 5.5 hours) are needed and increase as the layer of precipitate on the filter increases. Indeed, in case of large quantities it is convenient to use at least 2 Büchner filters. Attention must be paid continuously to ensure that the precipitate remains at all times wetted with a thin layer of liquid, in order to avoid the forming of cracks and therefore of preferential paths that would lead to incomplete washes.

The precipitate is then placed to dry for 24 h in a stove at 110°C. The dried product is milled in a mortar and placed in an adapted labeled sample holder. Weight of the resulting product = 14 g (ZnAl21 hydrotalcite).

EXAMPLE 2

Synthesis of MgAl 2:1 HT

A synthesis is reported in which the total concentration of the metals is 1.5 M and the ratio between the moles of the salts of Mg and Al is 2:1.

$Mg(NO_3)*6H_2O$ M = 256.41 g/mol Titer = 99%

$Al(NO_3)*9H_2O$ M = 375.14 g/mol Titer = 98%

100 mL of a solution of 1 M in $Mg(NO_3)*6H_2O$ (m=25.90 g) and 0.5 M in $Al(NO_3)*9H_2O$ (m=19.14 g) are prepared and placed in a 250 mL separator funnel.

A 0.25M solution of Na_2CO_3 is prepared and 300 mL of this solution are placed in a 2L beaker. A 1M NaOH solution is prepared.

The beaker is placed on a heating plate with magnetic agitation.

The pH-meter is immersed in this solution.

The solution of the salts of the metals is dripped into the beaker very slowly (2 hours) and simultaneously pH = 9.5 is maintained by adding 1M NaOH with a pipette.

Once synthesis has ended, agitation is continued for a further 30 minutes.

The beaker is then covered with parafilm and is left to age at 21°C for 24 hours. Filtration is then performed with a Büchner filter, making sure to wash well the precipitate with at least 2 L of water in order to eliminate the nitrates: long times (approximately 6 hours) are needed and increase as the layer of precipitate on the filter increases. Indeed, in case of large quantities it is convenient to use at least 2 Büchner filters. Attention must be paid continuously to ensure that the precipitate remains at all times wetted with a thin layer of liquid, in order to avoid the forming of cracks and therefore of preferential paths that would lead to incomplete washes.

The precipitate is then placed to dry for 24 h in a stove at 110°C. The dried product is milled in a mortar and placed in an adapted labeled sample holder. Weight of the resulting product = 11 g (MgAl21 hydrotalcite).

EXAMPLE 3

Ag nanoparticles from sodium citrate (Ag3)

Draw 20 mL of 10^(-3)M $AgNO_3$ and place them in a 50 mL beaker, add a magnetic stir bar, leave the solution to heat under agitation on a heating plate.

As soon as the solution boils, add 2 mL of the 38.8 mM $Na_3C_6H_5O_7$ solution.

Continue heating until the solution acquires an intense yellow color (approximately 10 minutes), then leave to cool to 20-25°C in an adapted sample holder wrapped with silver-coated paper.

EXAMPLE 4

Preparation of Ag nanoparticles from glucose (Ag1) and reconstruction of a Zn/Al 2:1 HT calcined with the nanoparticles

0.4 g of glucose are weighed in a 25 mL beaker and are dissolved with 7.8 mL of H_2O UPP; then 200 μL of 0.01 M $AgNO_3$ are added and the system is placed to heat in a water bath at 100-150°C, under agitation for approximately 2 hours.

The system is then allowed to cool to 20-25°C in an adapted sample holder wrapped with silver-coated paper (clear yellow solution).

The preparation of nanoparticles is rather delicate: it is important that the glassware is perfectly clean and that the solutions used are fresh. If the solutions are stored in a refrigerator, allow them to stabilize at ambient temperature. As an alternative to dissolving 0.4 g of glucose in 7.8 mL of UPP H_2O, it is possible to prepare 50 mL of a solution at the same glucose concentration by weighing 2.564 g and dissolving them in a 50 mL flat-bottom flask, bringing to volume with UPP H_2O and then draw from there the 7.8 mL cited above (in this manner the preparation times are speeded up experimentally).

5 mL of Ag1 nanoparticles are then drawn, placed in a 10 mL beaker, 0.1 g of calcined ZnAl 2:1 hydrotalcite are added, agitation is performed for 2 h, then filtration is performed and the filtered fraction (filtrate) is kept. Washing with 5 mL of boiled UPP water is performed and this (washing) fraction also is kept. The solid is dried for one day in a stove at 110°C.

All these operations have been performed and repeated for each type of hydrotalcite and nanoparticles until more than 1 g of each hydrotalcite was obtained: ZnAlAg1, ZnAlAg3, MgAlAg1, MgAlAg3 with the following compositions and starting from the following materials:

1) ZnAlAg1 from ZnAl21 hydrotalcites and Ag 1 nanoparticles (from glucose)
2) ZnAlAg3 from ZnAl21 hydrotalcites and Ag 3 nanoparticles (from sodium citrate)
3) MgAlAg1 from MgAl21 hydrotalcites and Ag 1 nanoparticles (from glucose)
4) MgAlAg3 from MgAl21 hydrotalcites and Ag 3 nanoparticles (from sodium citrate)

The AAS technique (atomic absorption spectroscopy) has been used to determine the content of Zn, Mg respectively in ZnAl and MgAl hydrotalcites.

Before performing the actual analyses, it is necessary to generate calibration curves (see for example http://www.carloerbareagenti.com/Repository/Download/pdf/Catalogue/IT/catchem100_sez2_anatra.pdf; and http://www.iza-online.org/synthesis/VS_2ndEd/ElementComp.htm).

It is necessary to calculate an approximate concentration of the metals (Zn, Mg) in the various samples to be analyzed and then generate a calibration curve with four solutions at different concentrations of the metals, using as initial material standard solutions with a concentration equal to 1000 ppm.

The formulas of the synthesized hydrotalcites are hypothesized and the mass percentage of the elements in which one is interested is calculated. As regards determining Zn, the following specifications occur:

λ (nm)	Slit width (mm)	Optimum Working Range (μg/mL)
213.9	1.0	0.01-2
307.6	1.0	100-14000
Air Acetylene flame		
Flame Stoichiometry: Oxidizing		

In order to perform analyses with the first line, the samples must therefore be prepared so as to remain in the range 0.01-2 ppm (mg/L or μg/mL).

4 standards are prepared in order to determine the Zn having Zn concentrations equal to:

0.5 ppm;

1 ppm;

1.5 ppm;

2 ppm.

As regards the samples, amounts of around 1.25 mg to be dissolved in 250 mL are used:

0.394*1.25 mg/ 0.250 L = 1.95 ppm

A mixture of HNO_3/H_2O 13.6:100 (10 mL HNO_3 68% + 40 mL distilled H_2O) is used as diluent to make the solutions and dissolve the samples.

The flows used for the flame are:

– air 3.5 L/min;

– acetylene 1.5 L/min.

The four solutions at the above cited concentrations were prepared starting from a solution with a concentration of 1000 ppm in Zn.

Moreover, the solutions of the following samples were prepared (the actual weighed amounts of each sample, brought to volume in a 250 mL flat-bottom flask using the above cited solution as diluent, are also reported):

ZnAl 2:1 1.4 mg;

ZnAlAg1 1.3 mg;

ZnAlAg3 1.3 mg.

The following table lists the results related to these tests.

	Weighing (mg)	Volume (L)	HT Conc. (ppm)	Zn Conc. (ppm)	Zn mass %
ZnAl 2:1	1.4	0.25	5.6	1.7	30.4
ZnAlAg1	1.3	0.25	5.2	2.4	46.2
ZnAlAg3	1.3	0.25	5.2	2.4	46.2

The HT concentrations (ppm) are obtained by dividing the weighing by the volume.

The Zn concentrations are derived from the analyses.

The Zn mass % is calculated by multiplying by 100 the value of the ratio between Zn Conc and HT Conc.

DETERMINATION OF Mg

The determination of Mg is similar to that of Zn; it is only necessary to observe the analysis specifications and prepare the 4 standards and the samples to be analyzed in the concentration range for the wavelength that is chosen.

The results obtained for Mg are listed hereafter in the table and are expressed clearly and concisely.

	Weighing (mg)	Volume (L)	HT Conc. (ppm)	Mg Conc. (ppm)	Mg mass %
MgAl 2:1	1.0	0.05	20	4.7	23.5
MgAlAg1	1.2	0.05	24	6.7	27.9
MgAlAg3	0.9	0.05	18	5.1	28.3

With the AAS technique it has thus been possible to characterize hydrotalcites, making it possible to determine the mass percentage of Zn and Mg.

Determination by XRF analysis of the percentage by weight of Ag on Zn/Al, Mg/Al hydrotalcite samples on which Ag nanoparticles have been deposited.

The analyzed samples are:

- Zn/Al Ag1;
- Zn/Al Ag3;
- Mg/Al Ag1;
- Mg/Al Ag3.

2 calibration curves are required, one for Zn/Al, one for Mg/Al at different percentages of Ag w/w.

The EDS data on these samples show that the point percentages found vary in the range 0.1-1% w/w.

It was thus decided to prepare 4 standards for each hydrotalcite at a mass percentage of Ag equal to:

1) 0.05
2) 0.1
3) 0.5
4) 1

$AgNO_3$ is used as an Ag source.

$AgNO_3$ MW = 169.87 g/mol

Ag MW = 107.868 g/mol

Ag mass % in $AgNO_3$ = 107.868/169.87 = 0.635

It was decided to prepare the standards in the form of pellets with a diameter of 12 mm, with a total weight of 0.5 g.

The standards for Zn/Al are prepared as described hereafter.

STANDARD 1: 0.05 % w/w Ag

0.0787 % w/w $AgNO_3$

Pellet with overall mass of 0.5 g.

The $AgNO_3$ weighing to be performed is calculated as follows:

$$(0.0787/100)*0.5 = 0.0004 \text{ g}$$

The actual weighing was exactly 0.0004 g, which correspond to a % w/w of Ag of 0.05%.

ZnAl216P is added until 0.5 g is reached, then the system is ground well and placed in a pelletizer for approximately 10 minutes.

STANDARD 2: 0.1 % w/w Ag

0.1575 % w/w $AgNO_3$

Pellet with overall mass of 0.5 g.

The $AgNO_3$ weighing to be performed is calculated as follows:

$$(0.1575/100)*0.5 = 0.0008 \text{ g}$$

The actual weighing was 0.0010 g, which correspond to a % w/w of Ag of 0.125%.

ZnAl216P is added until 0.5 g is reached, then the system is ground well and placed in a pelletizer for approximately 10 minutes.

STANDARD 3: 0.5 % w/w Ag

0.7874 % w/w $AgNO_3$

Pellet with overall mass of 0.5 g.

The $AgNO_3$ weighing to be performed is calculated as follows:

$$(0.7874/100)*0.5 = 0.004\ g$$

The actual weighing was exactly 0.004 g, which correspond to a % w/w of Ag of 0.5%.

ZnAl216P is added until 0.5 g is reached, then the system is ground well and placed in a pelletizer for approximately 10 minutes.

STANDARD 4: 1 % w/w Ag

1.5748 % w/w $AgNO_3$

Pellet with overall mass of 0.5 g.

The $AgNO_3$ weighing to be performed is calculated as follows:

$$(1.5748/100)*0.5 = 0.008\ g$$

The actual weighing was 0.009 g, which correspond to a % w/w of Ag of 1.125%.

ZnAl216P is added until 0.5 g is reached, then the system is ground well and placed in a pelletizer for approximately 10 minutes.

The calculations for making the standards for Mg/Al hydrotalcite are similar.

The exact concentrations of the 8 standards, 4 for Zn/Al, 4 for Mg/Al, are listed hereafter.

Zn/Al

STANDARD 1 0.050 % w/w
STANDARD 2 0.125 % w/w
STANDARD 3 0.500 % w/w
STANDARD 4 1.125 % w/w

Mg/Al

STANDARD 1 0.0625 % w/w
STANDARD 2 0.1000 % w/w
STANDARD 3 0.5625 % w/w

STANDARD 4 1.0750 % w/w

These 2 series of standards were analyzed first in order to have the 2 calibration curves.

Then the following samples were analyzed: Zn/Al Ag1, Zn/Al Ag3, Mg/Al Ag1, Mg/Al Ag3.

The Zn/Al Ag1, Zn/Al Ag3 pellets flaked and therefore it was decided to prepare them again in order to perform analysis.

A PX-10 crystal is used for analysis in order to have as much transmission as possible.

Analysis time is divided as follows:

– 200 s to measure the peak;

– 20 s to measure the first background point;

– 20 s to measure the second background point.

A calibration curve (Figure 1) and a picture (Figure 3) in which there are the two samples with Zn/Al hydrotalcite matrix are provided as attachments.

As regards the calibrations:

RMS, root mean square: the lower it is, the smaller the spread of the data, and the calibration approaches the model chosen for regression, in the specific case a line of the type C= D + E x RM. The values of D (intercept) and E (slope) are found on the charts.

The mass % of Ag of the analyzed samples has thus been determined. The results are given hereafter:

Sample	[Ag] (%, w/w)
Zn/Al Ag1	0.13
Zn/Al Ag3	0.57
Mg/Al Ag1	0.12
Mg/Al Ag3	0.44

The FT-IR spectra of the selected obtained materials are shown hereafter: ZnAl21, MgAl21, ZnAlAg1, ZnAlAg3, MgAlAg1, MgAlAg3.

The ZnAlAg1, ZnAlAg3 samples have IR spectra that are practically identical and the MgAlAg1, MgAlAg3 samples also have practically identical IR spectra. For this reason, only the following IR spectra are given in Figures 3-6: ZnAl212P; ZnAlAg1; MgAl21; MgAlAg1.

On the basis of the articles *"Effects of γ radiation on chromate immobilization by calcined hydrotalcites"*, (Sonia Martinez- Gallegos, Silvia Bulbulian, *Clays and Clay Minerals*, **2004**, Vol. 52, No. 5, 650-656) and *"Influence of calcination on the adsorptive removal of phosphate by Zn-Al layered double hydroxides from excess sludge liquor"* (X. Cheng, X. Huang, X. Wang, D. Sun, *Journal of Hazardous Materials,* **2010**, 17 (1-3), 516) it is possible to identify the typical peaks of Mg/Al 2:1 and Zn/Al 2:1 hydrotalcites in the form with interlamellar carbonate anion.

In particular, the widened peak that is present at approximately 3420 cm^{-1} is due to the stretching of the hydroxyl groups ($\nu_{O\text{-}H}$), both of the layers of the hydrotalcite and of the interlamellar water molecules. The low-intensity peak that is present at 1637-1648 cm^{-1} is assigned to the bending vibrations of highly absorbed water molecules.

The peak at 1356 cm^{-1} is assigned to the asymmetric stretching of the carbonate anions (ν_3) and the shoulder around 1500 cm-1 is attributed to the splitting of the vibration ν_3 of the carbonate.

The interlamellar carbonate ions of the HT can also be observed at ν_2 (795-880 cm^{-1}) and ν_4 (603-636 cm^{-1}), both being bending vibrations.

Figure 7 plots the UV spectrum of the silver nanoparticles obtained with 3 different methods (1 glucose, 3 sodium citrate, 2 fructose for comparison).

With reference to the UV-VIS spectrum of the nanoparticles, it can be observed that from the shape of the peaks one obtains a nanoparticle distribution that is centered on dimensions comprised between 20 and 50 nm (approximate information taken from the article *Morphology and size-controlled synthesis of Silver nanoparticles in aqueous surfactant polymer solutions* – Z. Shervani, Y. Ikushima, M. Sato, H. Kawanami, Y. Hakuta, T. Yokoyama, T. Nagase, H. Kuneida, K. Aramaki, *Colloid Polym Science* **2008**, 286:403-410).

Figures 8-10 are SEM images of the most representative samples. In particular:

Figure 8: -ZnAl21 Mag = 40000 KX SIGNAL A = SE1;
Figure 9: -MgAlAg3 Mag = 20000 KX SIGNAL A = QBSD;
Figure 10: -ZnAlAg3 20000 QBSD.

The presence of small luminous spots which can be attributed to the nanoparticles is noticed more or less clearly depending on the type of HT. The presence of Ag is confirmed also by EDS.

Figure 11 lists the results of the antibacterial tests performed in the following manner.

One wishes to test the following samples:

- ZnAl 2:1;
- ZnAlAg1;
- ZnAlAg3;
- MgAl 2:1;
- MgAlAg1;
- MgAlAg3.

A liquid culture medium heated to 120°C for 20 min, constituted by a triptone concentration equal to 10 g/L (chemically hydrolyzed casein) is prepared.

Parts of the samples of around 25 mg, to be introduced in 25 mL of solution of culture medium (1:1000 ratio) and 50 μL of an inoculum of a bacterial suspension of Escherichia Coli (balance 1 to 500 because 50 μL in

25 mL), are used.

The actual weightings are:

No.	SAMPLE	ACTUAL WEIGHING (mg)
1	ZnAl 2:1	29.1
2	ZnAlAg1	24.5
3	ZnAlAg3	24.1
4	MgAl 2:1	26
5	MgAlAg1	17.5
6	MgAlAg3	26.3

Adapted sterile flasks are used with a lateral attached portion which allows to read the transmittance with a turbidimeter. The flasks are placed under agitation at 37°C.

Bacterial growth is evaluated by measuring transmittance every hour, making sure to perform the analysis well (same position of the lateral attached part).

The transmittance values are all converted into absorbance values.

The following values are all related to transmittance % measurements.

Sample No.	Start T %	Cult/ with HT	With inoculum t=0	t= 1h	t= 2h	t= 3h
1	100	85	81.5	81.5	72	58
2	97	35	34.5	34.5	33.5	32.5
3	98.75	30	27.75	26	25.5	25
4	98.5	85.25	82.75	84.5	79.5	69.5
5	100	57.5	54.5	57.5	54.5	42.5

6	89.75	59.75	58.25	57.5	56.5	56.5

No.	t= 4h	t= 5h	t= 6h	t= 7h	t= 8h	t= 9h	t= 10h
1	37	20	8.5	5	4	3	2.5
2	33.5	33	32.5	32	32	32	31.5
3	25	24.5	24.5	24.5	24.5	24.5	24
4	49.5	28.5	13	6.5	5	4.5	3.5
5	26	13	6	4	3	2.5	2.5
6	56	54	56	53	51.5	42	28.5

The following are all absorbance values.

N.	Initial absorbance	Cult/ with HT	with inoculum t=0	t= 1h	t= 2h
1	0	0.070581074	0.088842391	0.088842	0.142668
2	0.01322827	0.455931956	0.462180905	0.462181	0.474955
3	0.005462896	0.522878745	0.556737013	0.585027	0.59346
4	0.00656377	0.069305612	0.082231998	0.073143	0.099633
5	0	0.240332155	0.263603498	0.240332	0.263603
6	0.046965543	0.22366209	0.23470407	0.240332	0.247952

N.	t= 3h	t= 4h	t= 5h	t= 6h	t= 7h	t= 8h
1	0.236572	0.431798	0.69897	1.070581	1.30103	1.39794
2	0.488117	0.474955	0.481486	0.488117	0.49485	0.49485
3	0.60206	0.60206	0.610834	0.610834	0.610834	0.610834

4	0.158015	0.305395	0.545155	0.886057	1.187087	1.30103
5	0.371611	0.585027	0.886057	1.221849	1.39794	1.522879
6	0.247952	0.251812	0.267606	0.251812	0.275724	0.288193

N.	t= 9h	t= 10h
1	1.522879	1.60206
2	0.49485	0.501689
3	0.610834	0.619789
4	1.346787	1.455932
5	1.60206	1.60206
6	0.376751	0.545155

The values of absorbance for each flask (a sample plus inoculum and bacterial suspension) are then plotted on a chart as a function of the elapsed time. A bacterial growth curve is thus traced. The assumption on which one interprets this chart is that if there is bacterial growth there is an increase in turbidity, a reduction in transmittance and accordingly an increase in absorbance (which is inversely proportional to transmittance). From this chart it can be seen that hydrotalcites as such, without nanoparticles, i.e., ZnAl 2:1, MgAl 2:1 have no antibacterial power. The ZnAlAg1, ZnAlAg3 hydrotalcites have an antimicrobial effect. MgAlAg3 hydrotalcite has a bacteriostatic effect (bacterial growth is stopped for 8 hours and then resumes). As regards MgAlAg1 hydrotalcite, the test is not significant, since a smaller amount than the others has been drawn and evidently it was not sufficient to provide a bacteriostatic or antimicrobial power. It is believed that by repeating the test with a larger amount (higher concentration) an effect similar to that of MgAlAg3 would be obtained. It is important to specify this because hydrotalcites assuredly will be used in larger quantities in order to ensure the adsorbent effect.

The materials obtained have excellent antibacterial properties.

Figures 12-17 show the exemplifying chromatographs related to the adsorption tests on the part of substances of the hydrotalcite type which comprise silver nanoparticles of a mixture of fatty acids (mixture 16) intended to simulate the components of the odor produced by the bacterial decomposition of sweat.

In particular, Figure 12 relates to the control, Figure 13 relates to ZnAl21, Figure 14 to ZnAlAg1, Figure 15 to MgAl21, figure 16 to MgAlAg1, Figure 17 to zinc ricinoleate.

The following methodology is used: a MIXTURE 16 is always used:

- 2.5 mM in hexanoic acid;
- 1.25 mM in heptanoic, 2-ethylhexanoic, octanoic acid;
- 0.625 mM in 4-ethyloctanoic acid.

20 mg of HT to be tested are weighed in a 10 mL vial, 5 mL of mixture 16 are added, the fiber is introduced in the vial and adsorption is allowed for 30 minutes at 40°C (1.4 cm height).

In the meantime, 5 mL of 1mM solution of standard are drawn and placed in a 10 mL vial. Once the 30 minutes have elapsed, the fiber is allowed to adsorb for 15 minutes in this last vial which contains the standard (always at 40°C and with a fiber height of 1.4 cm).

Analysis is performed by introducing the fiber in the GC with a holder height of 3.6 cm.

Three identical tests are repeated for each hydrotalcite type (as well as for the control and the zinc ricinoleate, which will be used as comparison).

The GC analysis method with HS-SPME-GC-FID methodology (reference *"HS-SPME-GC-MS analysis of body odor to test the efficacy of* *foot deodorant formulations"* – A. Caroprese, S. Gabbanini, C. Beltramini, E. Lucchi, L. Valgimigli, *Skin Research and Technology* **2009**, *15*, 503-510; *"Head-space analysis in modern gas chromatography"*, Nicholas H. Snow, *Trends in analytical chemistry*, Vol. 21, nos. 9+10, **2002**) is as follows:

"Mixture 16" is prepared:

2.5 mM in hexanoic acid;

1.25 mM in heptanoic, 2-ethylhexanoic, octanoic acid;

0.625 mM in 4-ethyloctanoic acid.

Moreover, a 1mM solution of standard (undecylenic acid) is prepared.

5 mL of mixture 16 are drawn and placed in a 10 mL vial, the fiber (CAR/PDMS) is allowed to absorb for 30 min. at a height of 1.4 cm of the holder at a temperature of 40°C.

5 mL of 1 mM solution of standard are drawn and placed in a 10 mL vial. Once the 30 minutes have ended, the fiber is extracted from the vial with the analytes and is placed to absorb for 15 minutes in the vial with the standard always at 40°C.

GC analysis with the following conditions is then carried out:

Injector: 275°C for CAR/PDMS fiber

Pressure: 19.135 psi

Total flow: 17.653 mL/mis

Septum Purge Flow: 3 mL/min

Split: 25 to 1 156 mL/min

Temperature program of furnace:

– 180°C for 2 minutes;

– increase by 20°C/min to 230°C

– increase by 1°C/min to 231°C

– holding at 231°C for 1 minute

The following results were obtained with ZnAlAg1 hydrotalcite

(normalized areas)

	TEST 23	TEST 24	TEST 25	AVERAGE ZnAl21- Ag1
	Area	Area	Area	Average area
Hexanoic acid	4.94	5.25	5.69	5.29
Heptanoic acid	1.65	1.69	1.15	1.50
2-ethylhexanoic acid	2.71	2.88	2.00	2.53
Octanoic acid	1.65	1.88	1.23	1.59
4-ethyloctanoic acid	2.35	2.31	1.85	2.17

Similar tests are performed for ZnAlAg3 hydrotalcite (i.e., ZnAl hydrotalcite with deposited nanoparticles pre-synthesized from glucose).

The following results were obtained with ZnAlAg3 hydrotalcite (normalized areas).

	TEST 26	TEST 28	TEST 30	AVERAGE ZnAl21- Ag3
	Area	Area	Area	Average area
Hexanoic acid	4.4	4.44	4.11	4.32
Heptanoic acid	0.94	0.89	1.11	0.98
2-ethylhexanoic acid	1.47	1.5	2.39	1.79
Octanoic acid	0.94	0.89	1.11	0.98
4-ethyloctanoic	1.41	1.33	1.39	1.38

acid				

Similar tests are performed for ZnAl21 and MgAl21 hydrotalcites.

Summarizing the tests for ZnAl21 hydrotalcite (normalized areas).

	TEST 31	TEST 32	TEST 33	AVERAGE ZnAl21
	Area	Area	Area	Average area
Hexanoic acid	14.22	14	12.88	13.7
Heptanoic acid	11.44	10.5	9.81	10.58
2-ethylhexanoic acid	17.67	15.71	14.50	15.96
Octanoic acid	14.83	13.79	12.19	13.60
4-ethyloctanoic acid	8.5	8.57	7.62	8.23

Summarizing the tests for MgAl21 hydrotalcite (normalized areas).

	TEST 36	TEST 37	TEST 38	AVERAGE MgAl21
	Area	Area	Area	Average area
Hexanoic acid	17.47	18.73	17.09	17.76
Heptanoic acid	13.59	14.13	12.48	13.40
2-ethylhexanoic acid	18.00	20.5	16.24	18.25
Octanoic acid	15.35	16.3	12.55	14.73
4-ethyloctanoic acid	9.12	11.1	7.76	9.33

Similar tests are performed for the primary component in non-antiperspirant deodorations, zinc ricinoleate.

Summarizing the tests for Zn RIC (normalized areas).

	TEST 39	TEST 40	TEST 41	AVERAGE Zn RIC
	Area	Area	Area	Average area
Hexanoic acid	19.07	22	18.1	19.72
Heptanoic acid	16.2	19	16.1	17.10
2-ethylhexanoic acid	28.0	32.7	27.1	29.27
Octanoic acid	20.8	24.4	21.5	22.23
4-ethyloctanoic acid	11.3	12.1	10.4	11.27

Three control tests, i.e., in the absence of hydrotalcite, are then performed and will be used to understand which areas of the analytes are in the absence of hydrotalcites in order to make a comparison with the areas of the analytes with the various hydrotalcites and establish the extent to which the analyte areas decrease and therefore evaluate the effectiveness of adsorption of each hydrotalcite.

Summarizing the tests for Control (normalized areas).

	TEST 43	TEST 44	TEST 45	AVERAGE CONTROL
	Area	Area	Area	Area
Hexanoic acid	29	27.78	31.29	29.36
Heptanoic acid	36.8	33.56	39.12	36.49
2-ethylhexanoic acid	43.56	40.39	45.82	43.26
Octanoic acid	68.39	63.28	72.71	68.13
4-ethyloctanoic	37.39	37.39	40.94	38.57

acid				

Similar tests are performed for MgAlAg3 hydrotalcite.

Summarizing the tests for MgAlAg3 (normalized areas).

	TEST 49	TEST 49C	TEST 49D	AVERAGE MgAlAg3
	Area	Area	Area	Area
Hexanoic acid	15.58	14.59	14.11	14.76
Heptanoic acid	11.9	11.76	11.22	11.63
2-ethylhexanoic acid	17.8	19.88	18.89	18.86
Octanoic acid	15.32	15.12	13.44	14.63
4-ethyloctanoic acid	10.16	13.35	11.11	11.54

Similar tests are performed for MgAlAg1 hydrotalcite.

Summarizing the tests for MgAlAg1 (normalized areas).

	TEST 54	TEST 55	TEST 56	AVERAGE MgAlAg1
	Area	Area	Area	Area
Hexanoic acid	14.63	14.45	15.2	14.76
Heptanoic acid	10.89	11.45	11.7	11.35
2-ethylhexanoic acid	17.95	18.95	19.1	18.67
Octanoic acid	11.11	12.6	12.4	12.04
4-ethyloctanoic acid	9.32	10.85	10.35	10.17

FINAL SUMMARY

The values of the average normalized areas (on 3 tests) are given below for each HT or control (Cntr)/comparison.

	Cntr	ZnAl 2:1	ZnAl Ag1	ZnAlAg3	MgAl 2:1
Hexanoic acid	29.36	13.7	5.29	4.32	17.76
Heptanoic acid	36.49	10.58	1.50	0.98	13.40
2-ethyloctanoic acid	43.26	15.96	2.53	1.79	18.25
Octanoic acid	68.13	13.60	1.59	0.98	14.73
4-ethyloctanoic acid	38.57	8.23	2.17	1.38	9.33

	MgAl Ag1	MgAl Ag3	Zn RIC
Hexanoic acid	14.76	14.76	19.72
Heptanoic acid	11.35	11.63	17.10
2-ethylhexanoic acid	18.67	18.86	29.27
Octanoic acid	12.04	14.63	22.23
4-ethyloctanoic acid	10.17	11.54	11.27

Control is the reference required to understand how much each sample adsorbs. The smaller the normalized areas for the analytes and therefore the smaller the signals that reach the detector, the more that sample absorbs that analyte. All samples adsorb.

Zinc ricinoleate (Zn RIC) is the main constituent of non--antiperspirant deodorants and therefore acts as a commercial reference.

It is noted that all the samples lead to a good adsorption, which can be compared with, and is even greater than, that of the commercial reference.

The samples that lead to the highest adsorptions are, in absolute terms, ZnAlAg3 and ZnAlAg1, followed by ZnAl 2:1.

The MgAl2:1, MgAlAg1, MgAlAg3 samples lead to similar adsorptions (slightly higher in some acids, lower in others, but these differences are small and may also fall within the errors of the determination).

As regards the Zn RIC, it has a lower adsorbent effect than ZnAl hydrotalcite samples, comparable with that of MgAl hydrotalcite samples, albeit clearly lower as regards 2-ethylhexanoic, octanoic and heptanoic acids.

The disclosures in Italian Patent Application No. BO2011A000034 from which this application claims priority are incorporated herein by reference.

CLAIMS

1. A deodorant composition comprising:

a) at least one anionic clay;

b) silver nanoparticles; and

c) at least one excipient which is acceptable for cosmetic use.

2. The composition according to claim 1, wherein at least one anionic clay is

a substance of the hydrotalcite type having general formula (I)

$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}{}_{x/n}).mS$ (I)

wherein:

– M(II) is a divalent ion, which can be of one or two different metals selected from Mg, Zn, Ni, Co and Fe;

– M(III) is a trivalent ion, which can be of one or two different metals selected from Al, Cr, Fe and Mn;

– x is a number that indicates the stoichiometric ratio between divalent and trivalent metal ions and is comprised between 0.2 and 0.33;

– A^{n-} is at least one anion intercalated in the structure, wherein n is the number of negative charges, selected from CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-, ClO_4^-, F^-, Cl^-, Br^- and silicates;

– S is a water molecule;

– m is the number of water molecules.

3. The composition according to claims 1-2, wherein the content of substance of the hydrotalcite type having general formula (I) and of silver nanoparticles is comprised between 1 and 30% by weight on the total weight of the composition.

4. The composition according to one of the preceding claims, wherein the content of silver nanoparticles is comprised between 0.05 and 5% by weight on the weight of the substance of the hydrotalcite type having

formula (I).

5. The composition according to one of the preceding claims, wherein the silver nanoparticles have dimensions comprised between 2 and 200 nm.

6. The composition according to one of the preceding claims, wherein M(II) is Mg or Zn, M(III) is Al, A^{n-} is CO_3^{2-}, or the Zn/Al ratio is 2:1, or the compound is $Zn_{0.68}Al_{0.32}(OH)_2(CO_3)_{0.32}$ x $0.42H_2O$ or $Mg_{0.68}Al_{0.32}(OH)_2(CO_3)_{0.32}$ x $0.42H_2O$.

7. The composition according to one or more of the preceding claims, wherein at least one excipient is selected from a hydrophobic polymer, a fragrance, an antimicrobial agent, a viscosity agent, a rheological agent and an essential oil.

8. The composition according to one of the preceding claims, comprising at least one additional active ingredient selected from an antimicrobial agent, an enzyme deviator, an absorbent agent, a viscosity agent, a rheological agent, an essential oil and a propellant.

9. A process for the preparation of a composition comprising:

a) at least one substance of the hydrotalcite type having general formula (I)

$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}_{x/n}).mS$ (I)

wherein:

– M(II) is a divalent ion, which can be of one or two different metals selected from Mg, Zn, Ni, Co and Fe;

– M(III) is a trivalent ion, which can be of one or two different metals selected from Al, Cr, Fe and Mn;

– x is a number that indicates the stoichiometric ratio between divalent and trivalent metal ions and is comprised between 0.2 and 0.33;

– A^{n-} is at least one anion intercalated in the structure, wherein n is the number of negative charges, selected from CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-, ClO_4^-, F^-, Cl^-, Br^-;

– S is a water molecule;

– m is the number of water molecules; and

b) silver nanoparticles;

said process comprising:

i. calcining the substance of the hydrotalcite type having general formula (I) at a temperature comprised between 450 and 700°C and for a time comprised between 1.5 and 20 hours;

ii. preparing an aqueous suspension of silver nanoparticles with dimensions comprised between 2 and 200 nm;

iii. adding under agitation at a temperature comprised between 20 and 35°C the calcined substance obtained in step i. to the suspension obtained in step ii.;

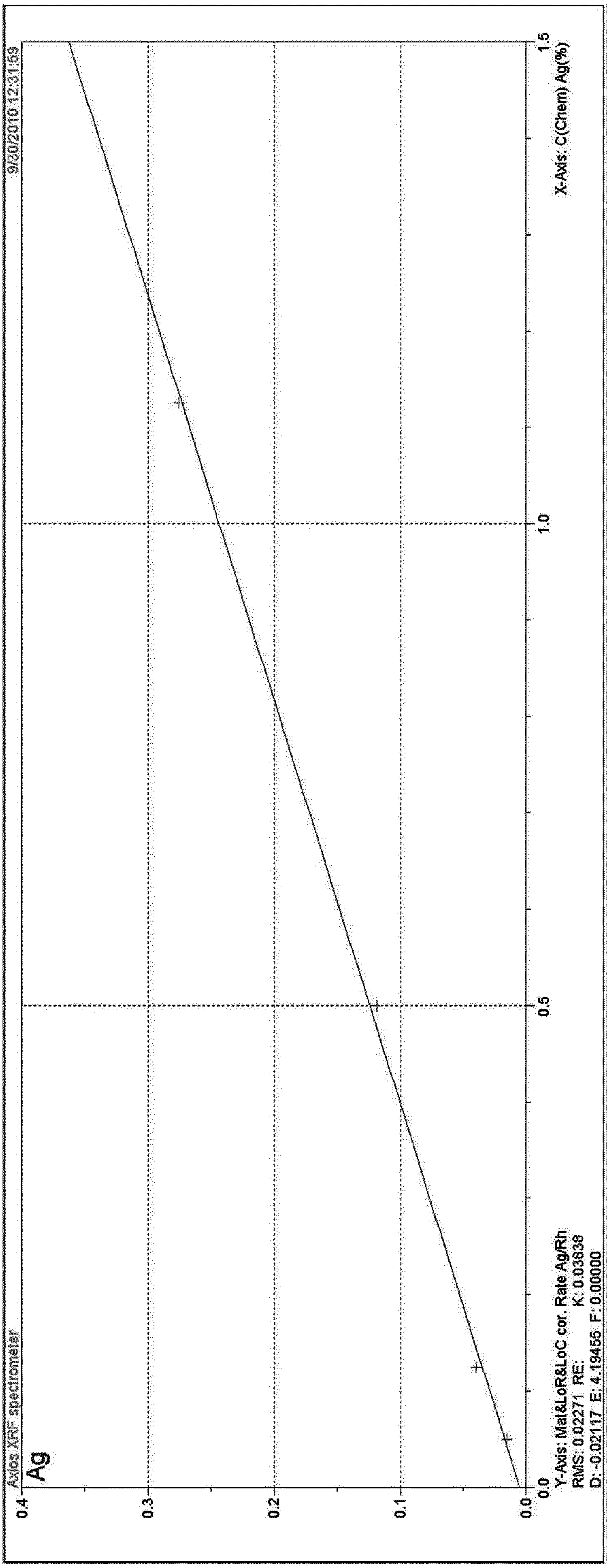
iv. leaving the suspension obtained in step iii. under agitation at a temperature comprised between 20 and 35°C for a time comprised between 0.5 and 5 hours.

10. A composition obtainable by the process according to claim 9.

11. The composition according to claim 10, wherein the silver nanoparticles have dimensions comprised between 2 and 200 nm.

12. Use of the composition according to claims 1-8 or 10-11 as a skin deodorant.

13. Use of the composition according to claims 1-8 or 10-11 as an antimicrobial agent.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1.0
1.5
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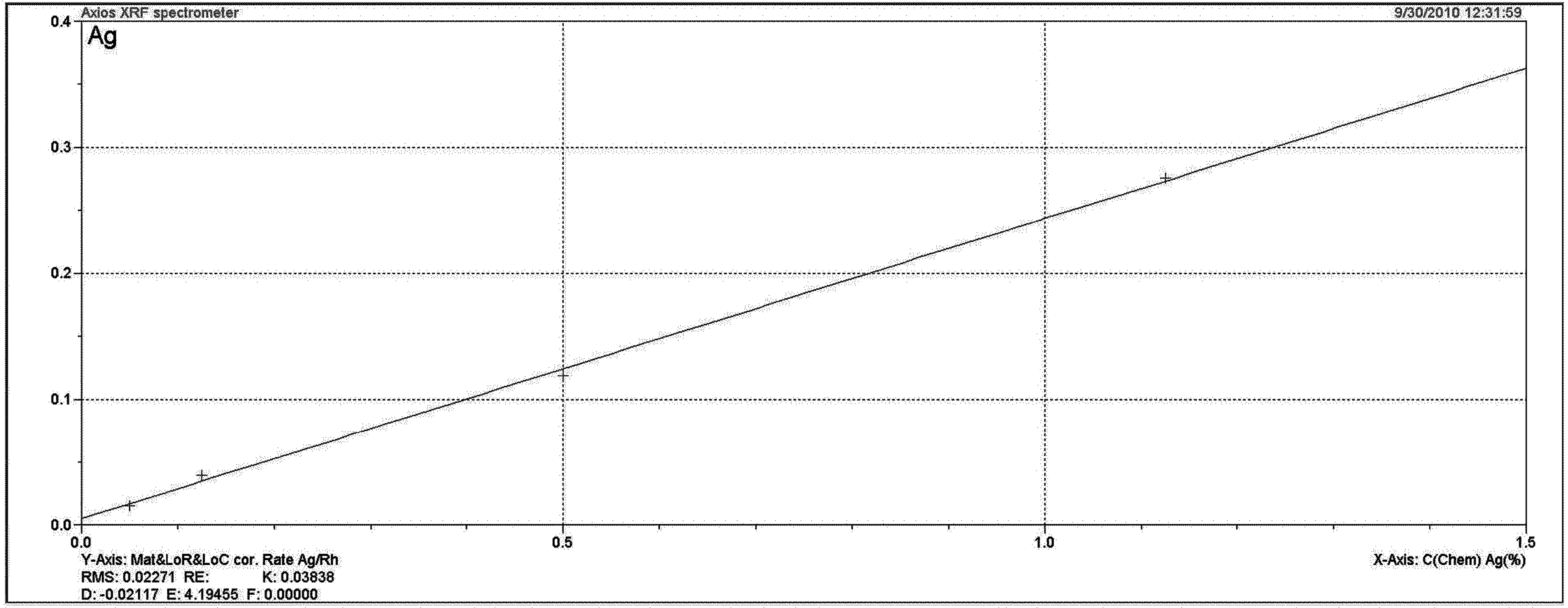
Y-Axis: Mat&LoR&LoC cor. Rate Ag/Rh
RMS: 0.02271 RE: K: 0.03838
D: -0.02117 E: 4.19455 F: 0.00000

Fig.1


Axios XRF spectrometer
9/30/2010 12:31:59
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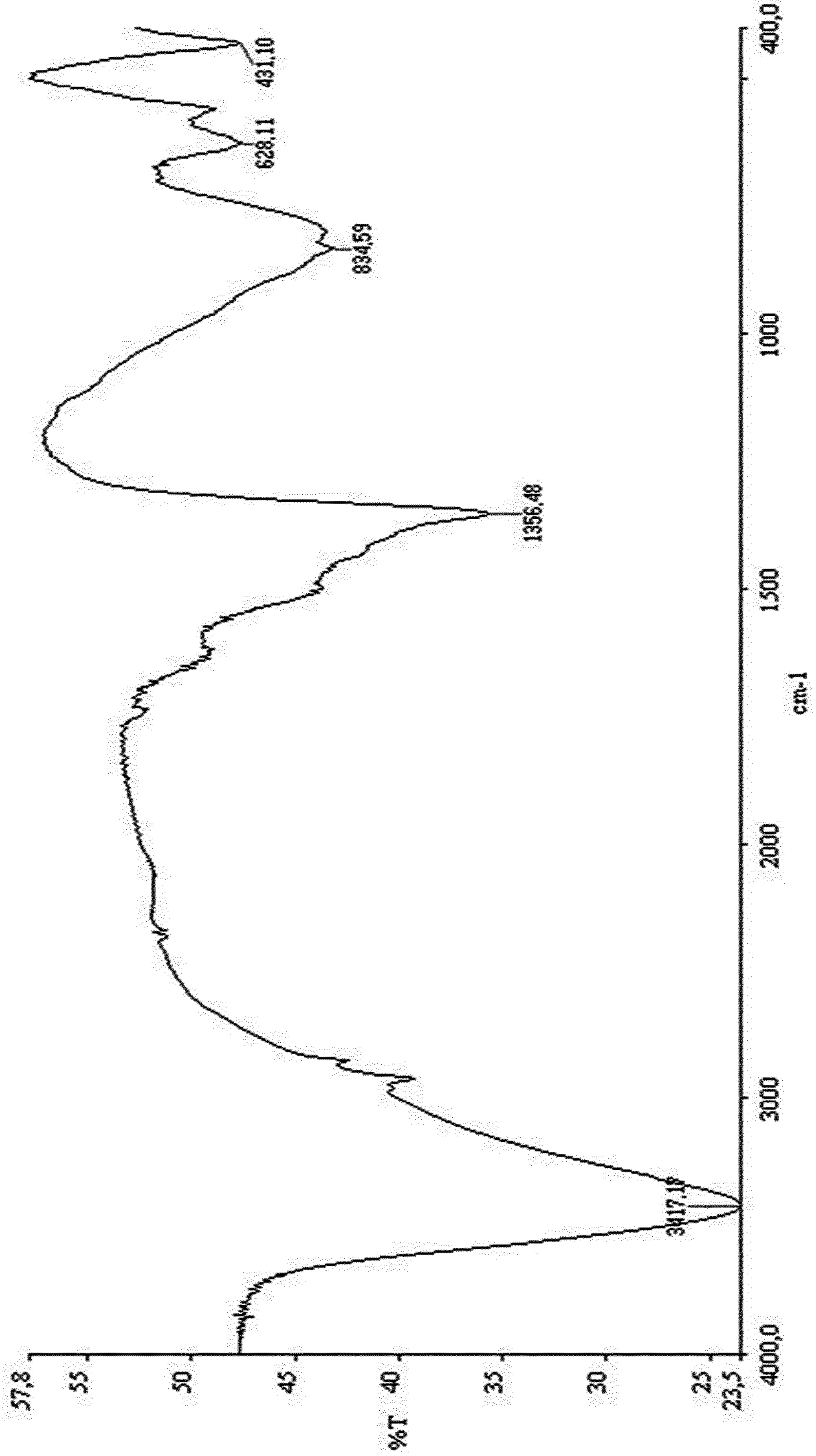
0.2
0.1
0.0
0.0
0.5
1.0
1.5
Y-Axis: Mat&LoR&LoC cor. Rate Ag/Rh
RMS: 0.02271 RE: K: 0.03838
D: -0.02117 E: 4.19455 F: 0.00000
X-Axis: C(Chem) Ag(%)

Fig. 2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45
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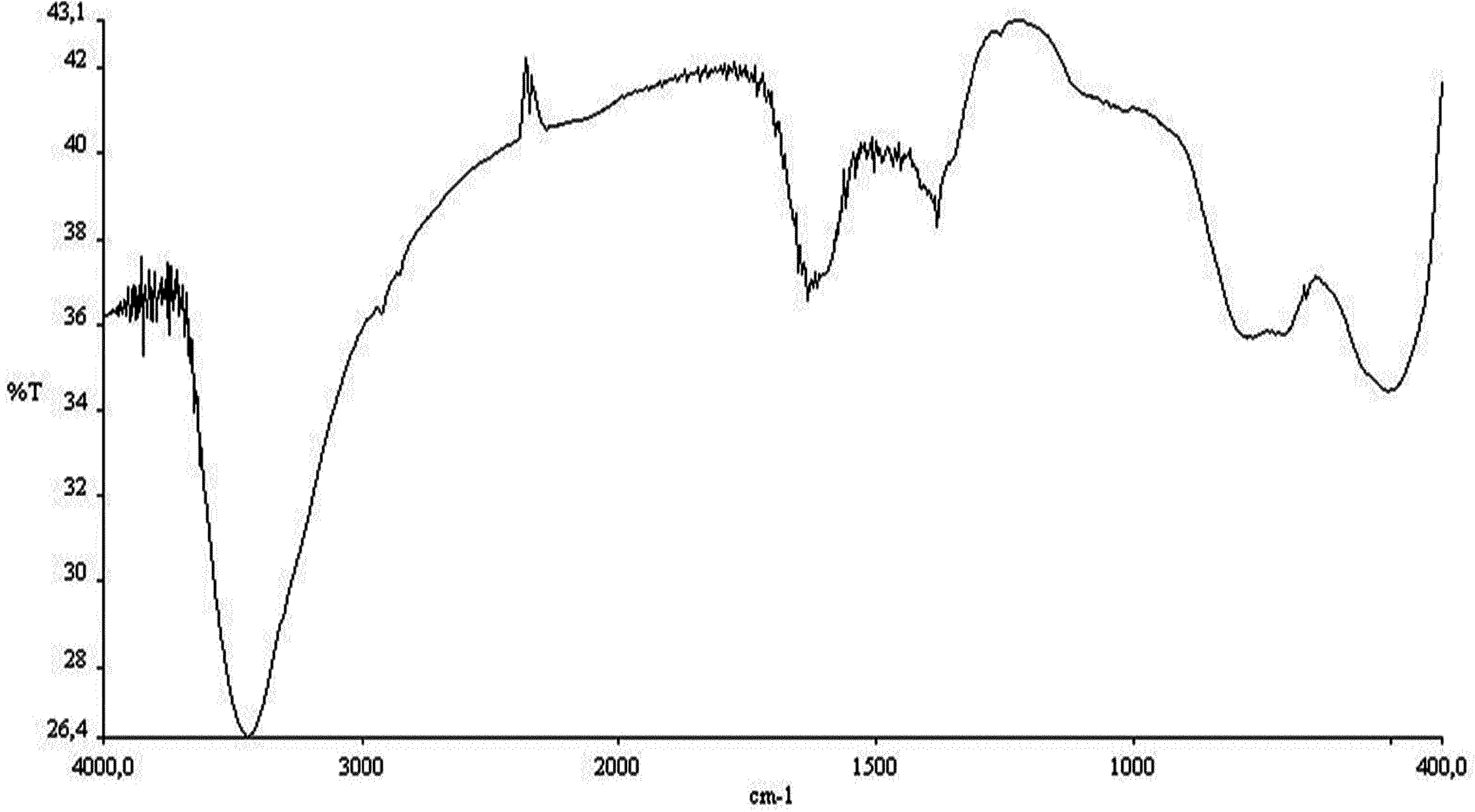
1356,48
834,59
628,11
431,10

Fig. 3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36
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32
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28
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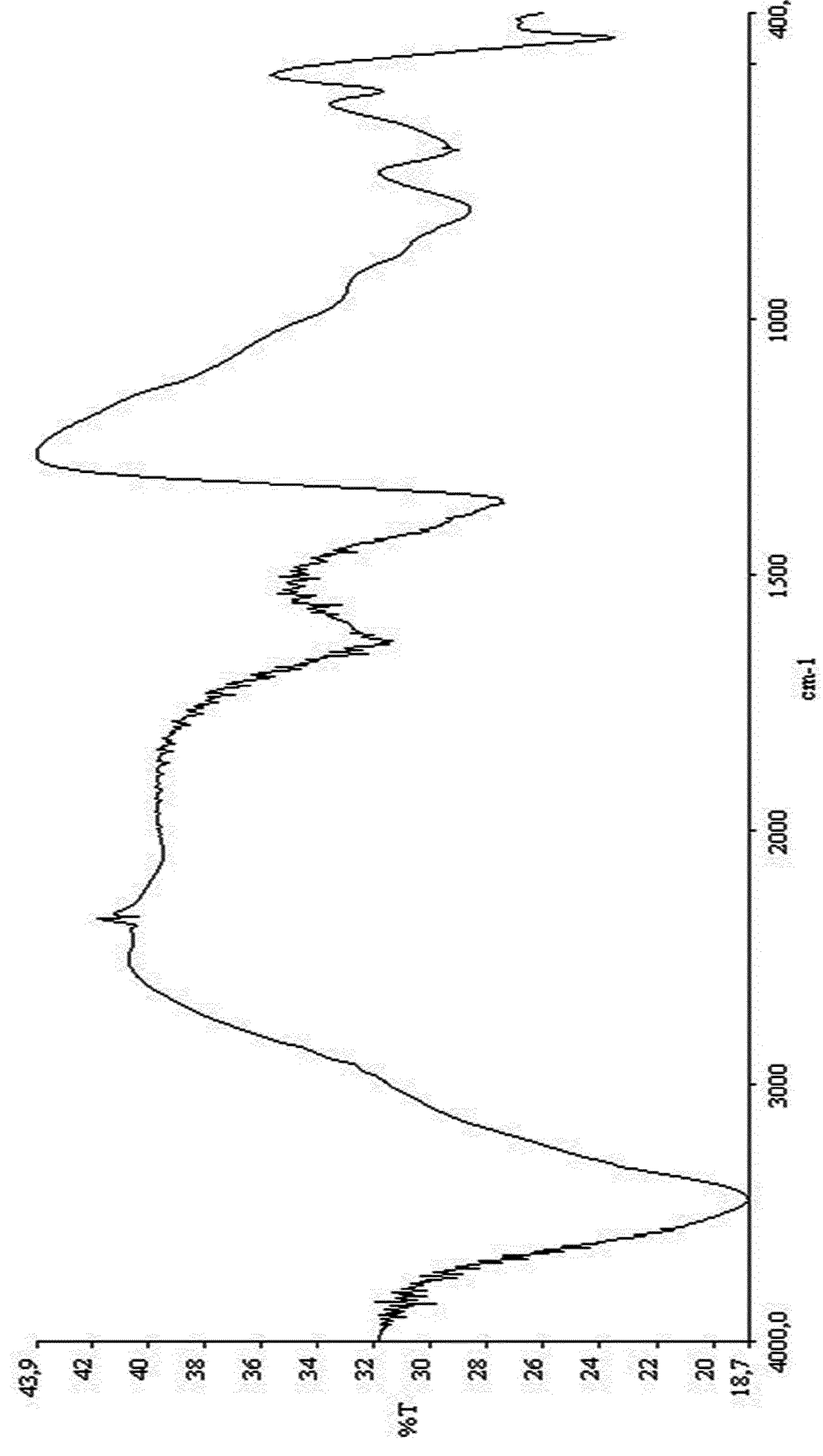
1000
400,0
cm-1

Fig. 4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40
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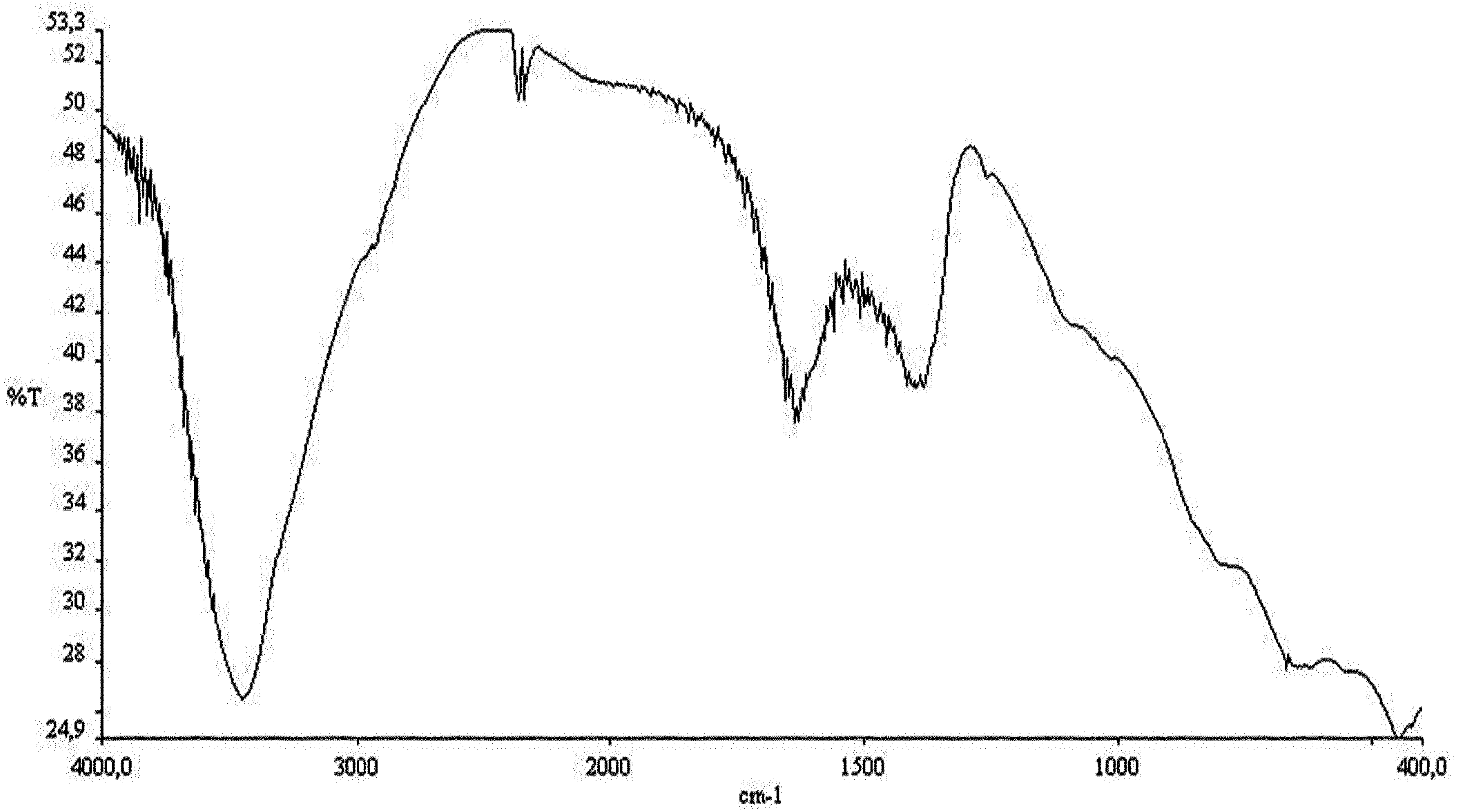
400,0
cm-1

Fig. 5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42
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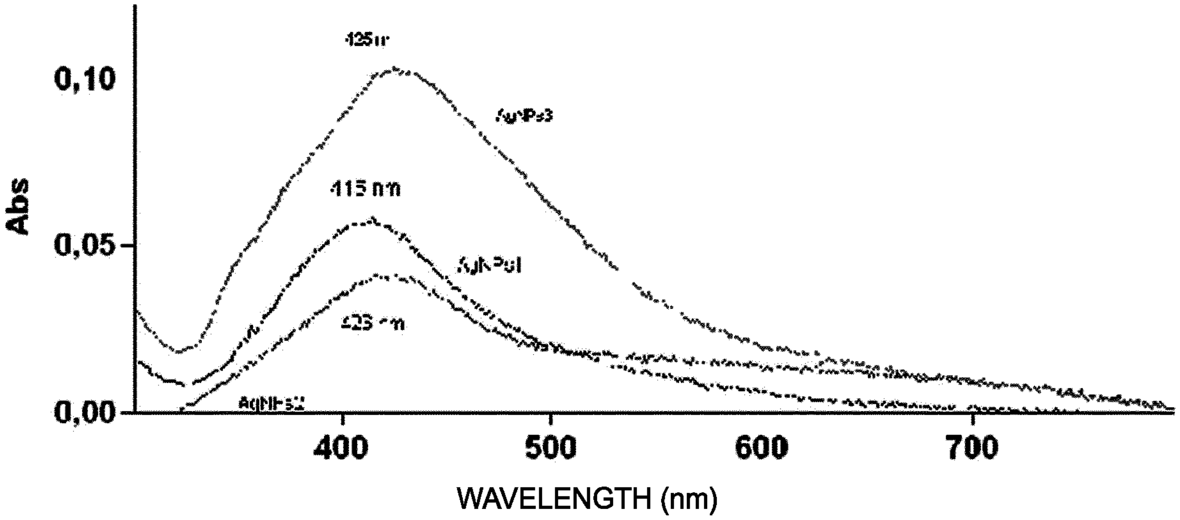
1500
1000
400,0
cm-1

Fig. 6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AgNPs3
415 nm
AgNPs1
423 nm
AgNPs2
Abs
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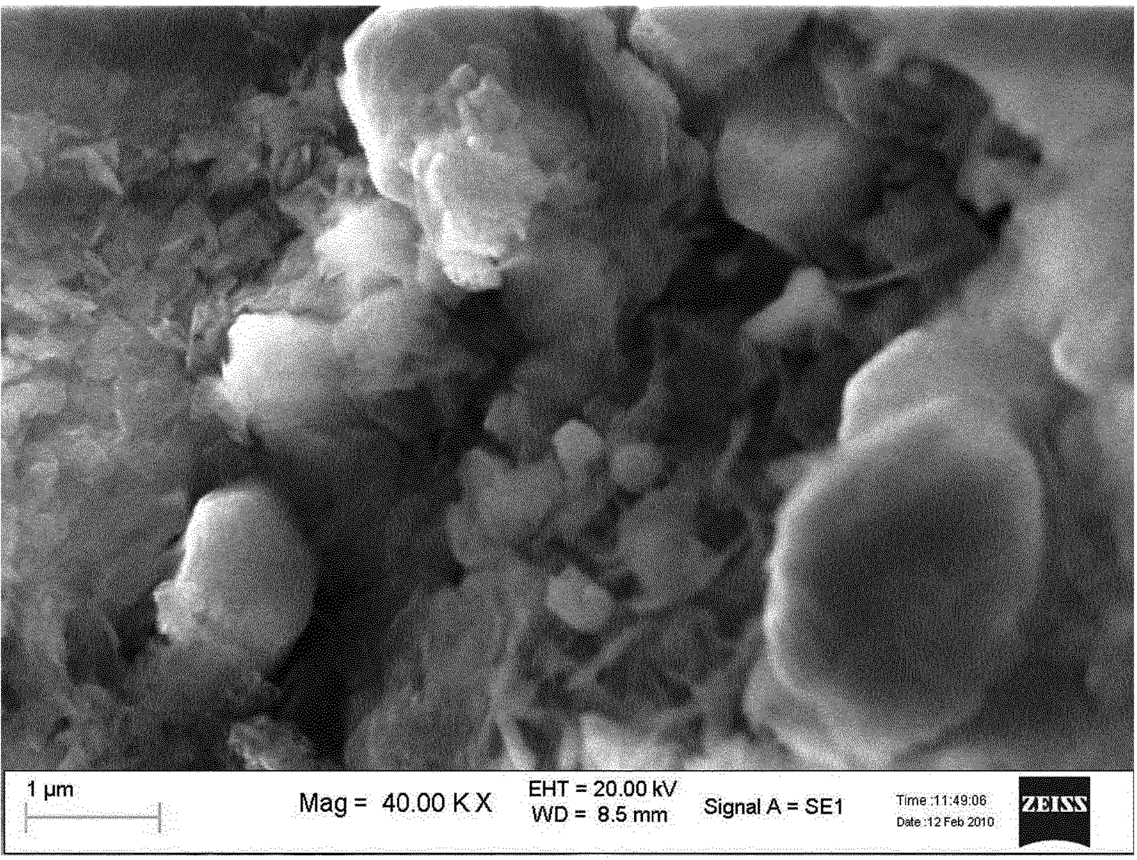
0,05
0,00
400
500
600
700
WAVELENGTH (nm)

Fig. 7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WD = 8.5 mm
Signal A = SE1
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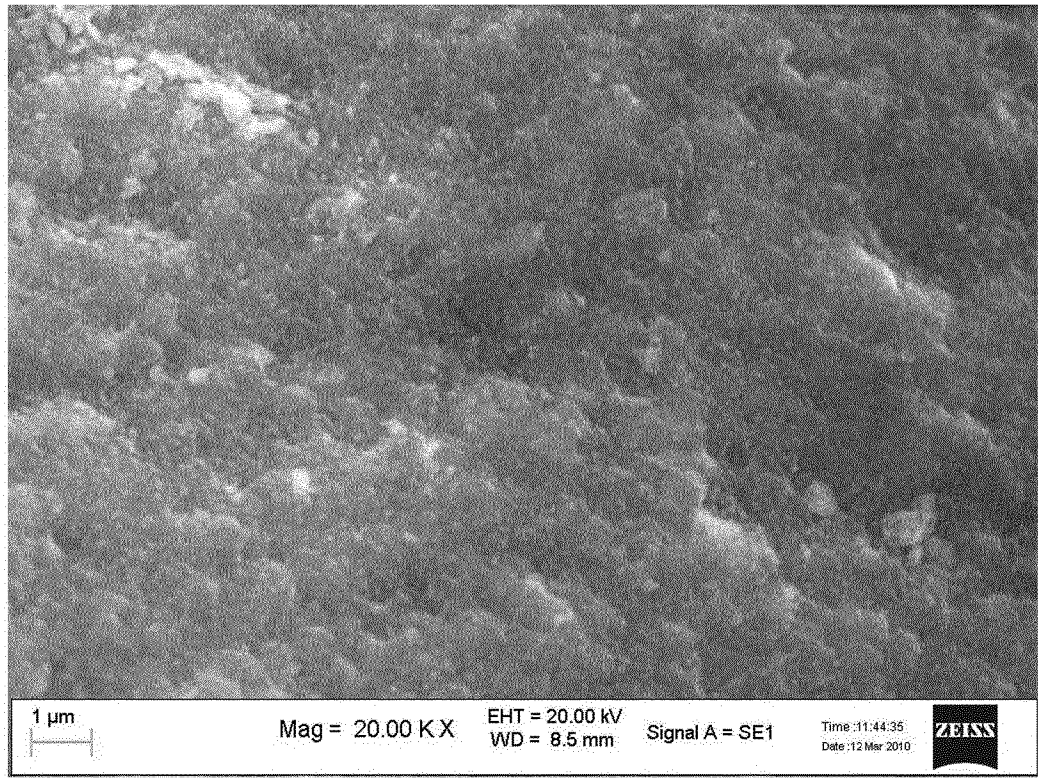
Date :12 Feb 2010
ZEISS

Fig. 8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EHT = 20.00 kV
WD = 8.5 mm
Signal A = SE1
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Date :12 Mar 2010
ZEISS

Fig. 9

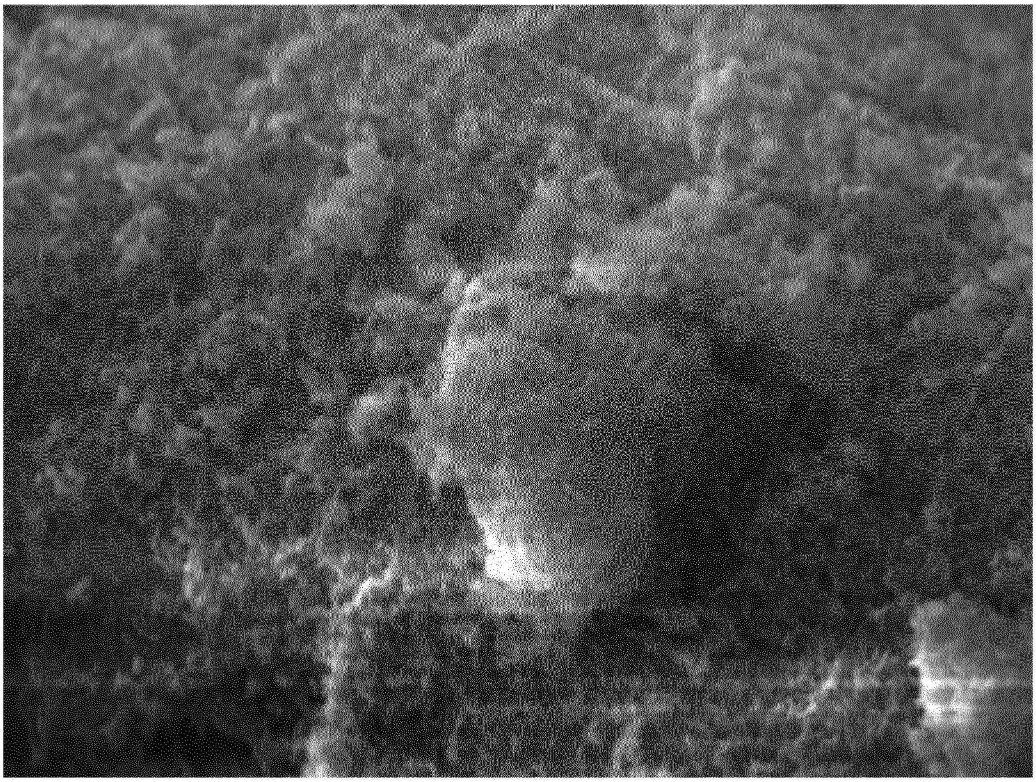
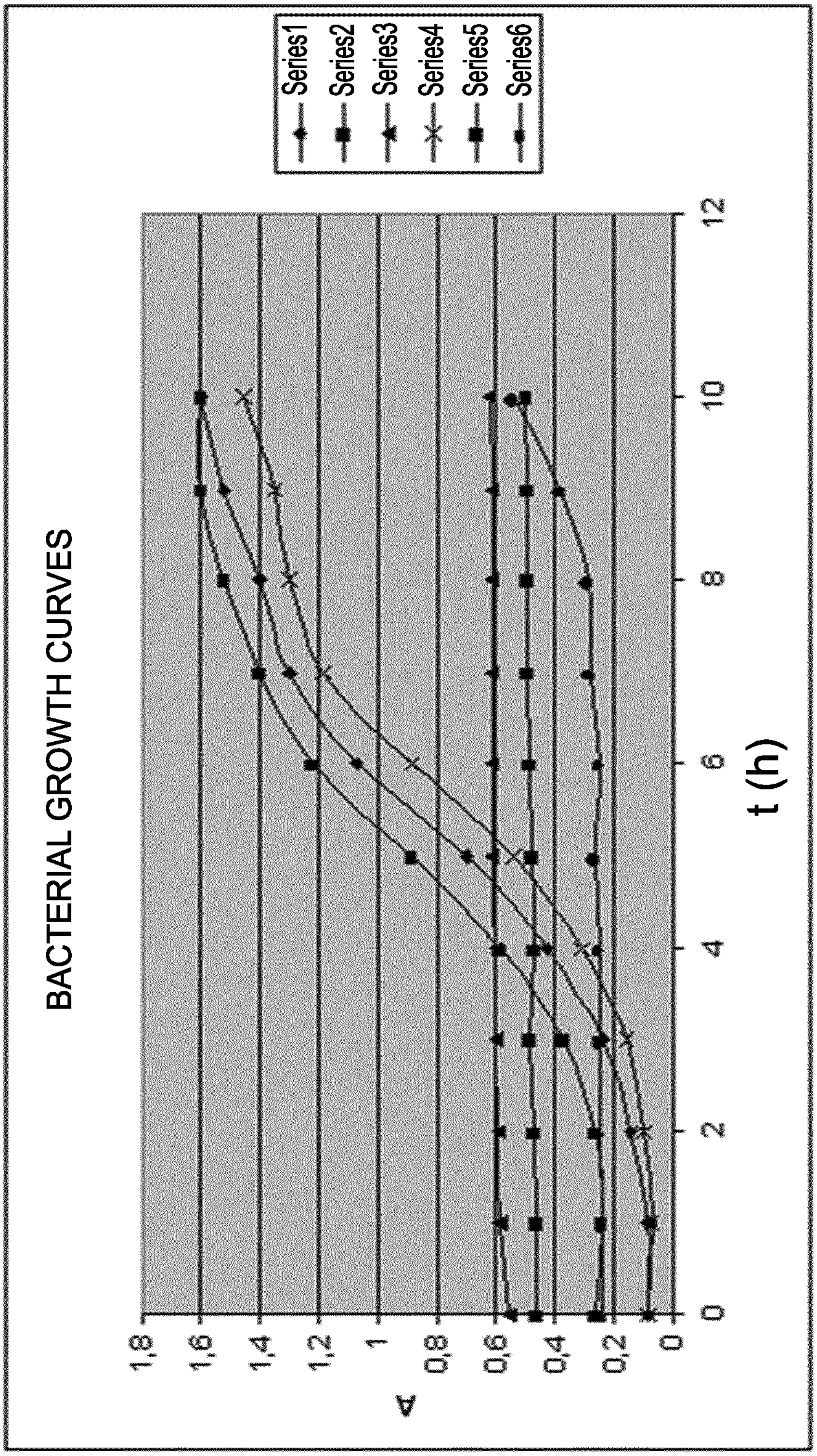


Fig. 10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0,2
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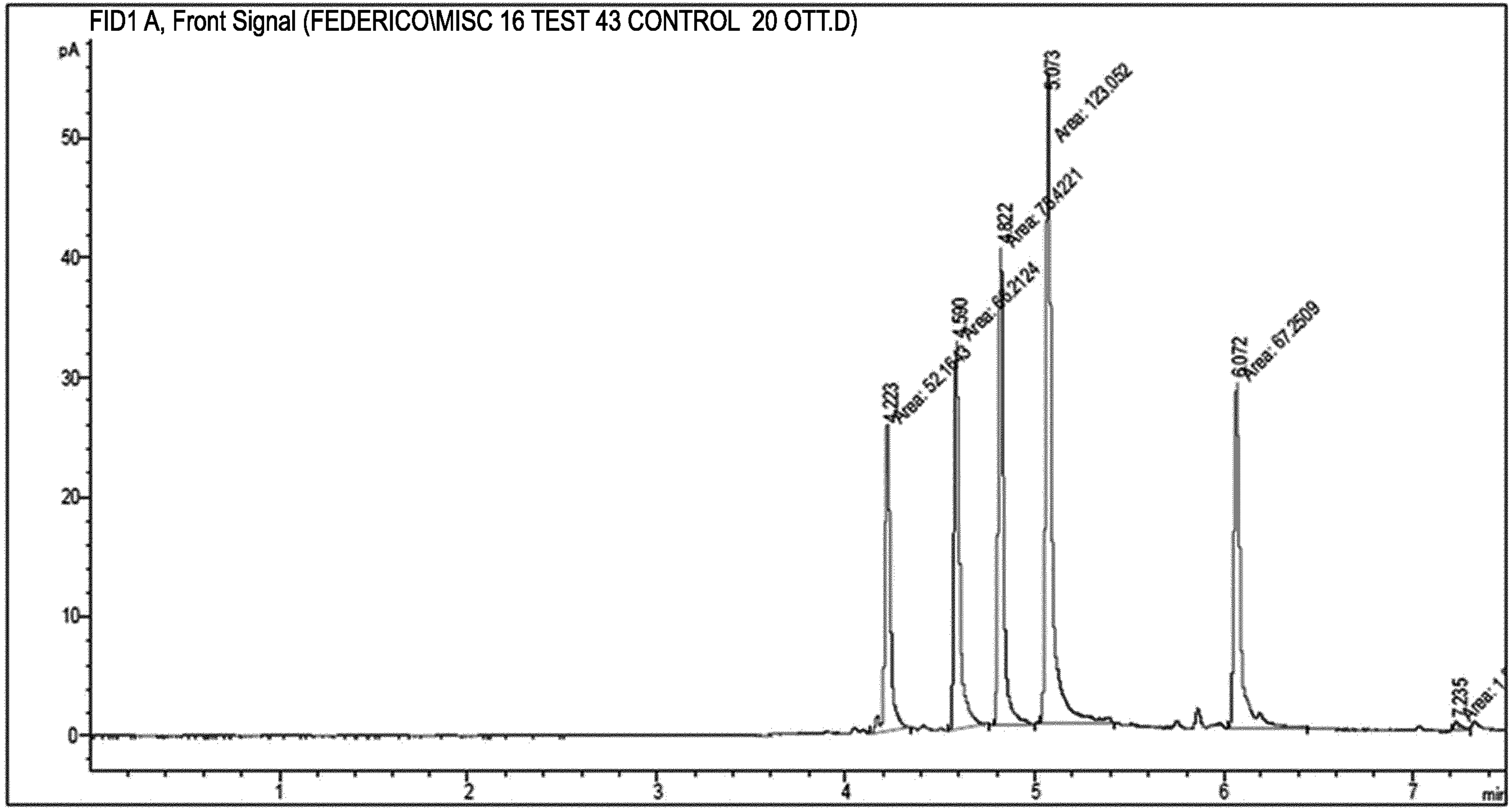
0
2
4
6
8
10
12
t (h)
Series1
Series2
Series3
Series4
Series5
Series6

Fig. 11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40
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20
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2
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4
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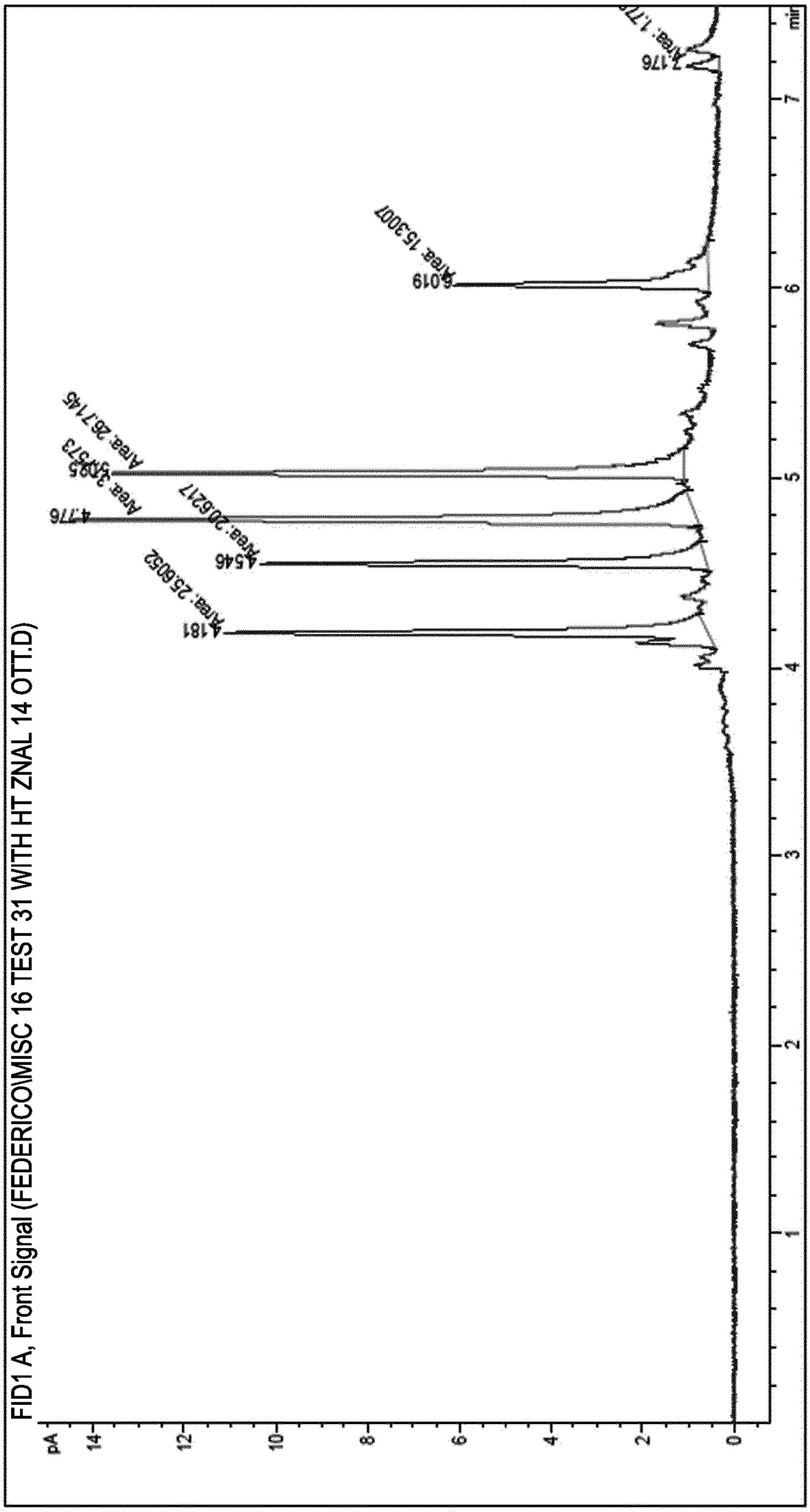
6
7
min
4.223
Area: 52.1643
4.590
Area: 66.2124
4.822
Area: 78.4221
5.073
Area: 123.052
6.072
Area: 67.2509
7.235
Area: 1

Fig. 12


FID1 A, Front Signal (FEDERICOMISC 16 TEST 31 WITH HT ZNAL 14 OTT.D)
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8
6
4
2
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1
2
3
4
5
6
7
min
4.181
Area: 25.6052
4.546
Area: 20.6217
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6.019
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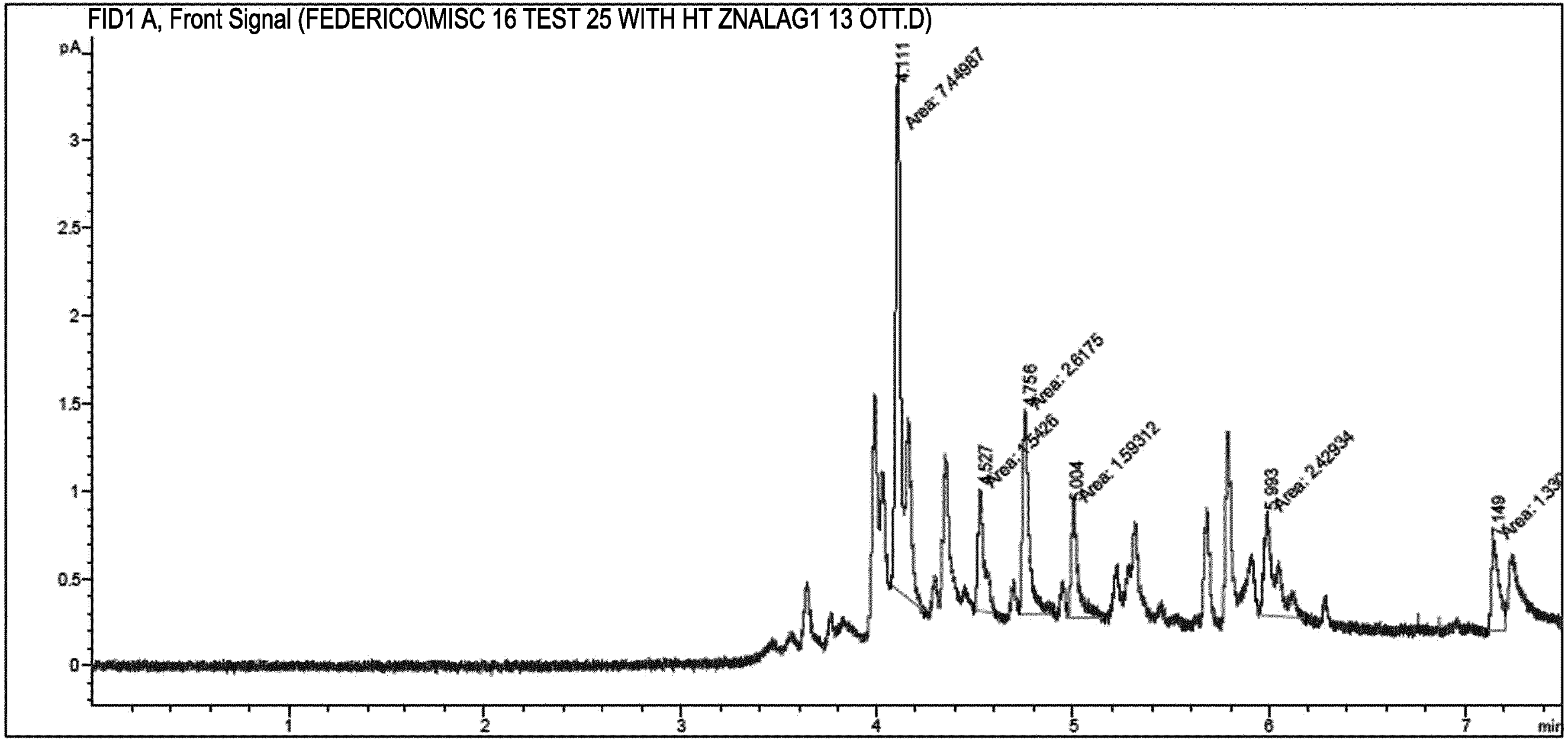
7.176
Area: 1.77

Fig. 13


FID1 A, Front Signal (FEDERICO\MISC 16 TEST 25 WITH HT ZNALAG1 13 OTT.D)
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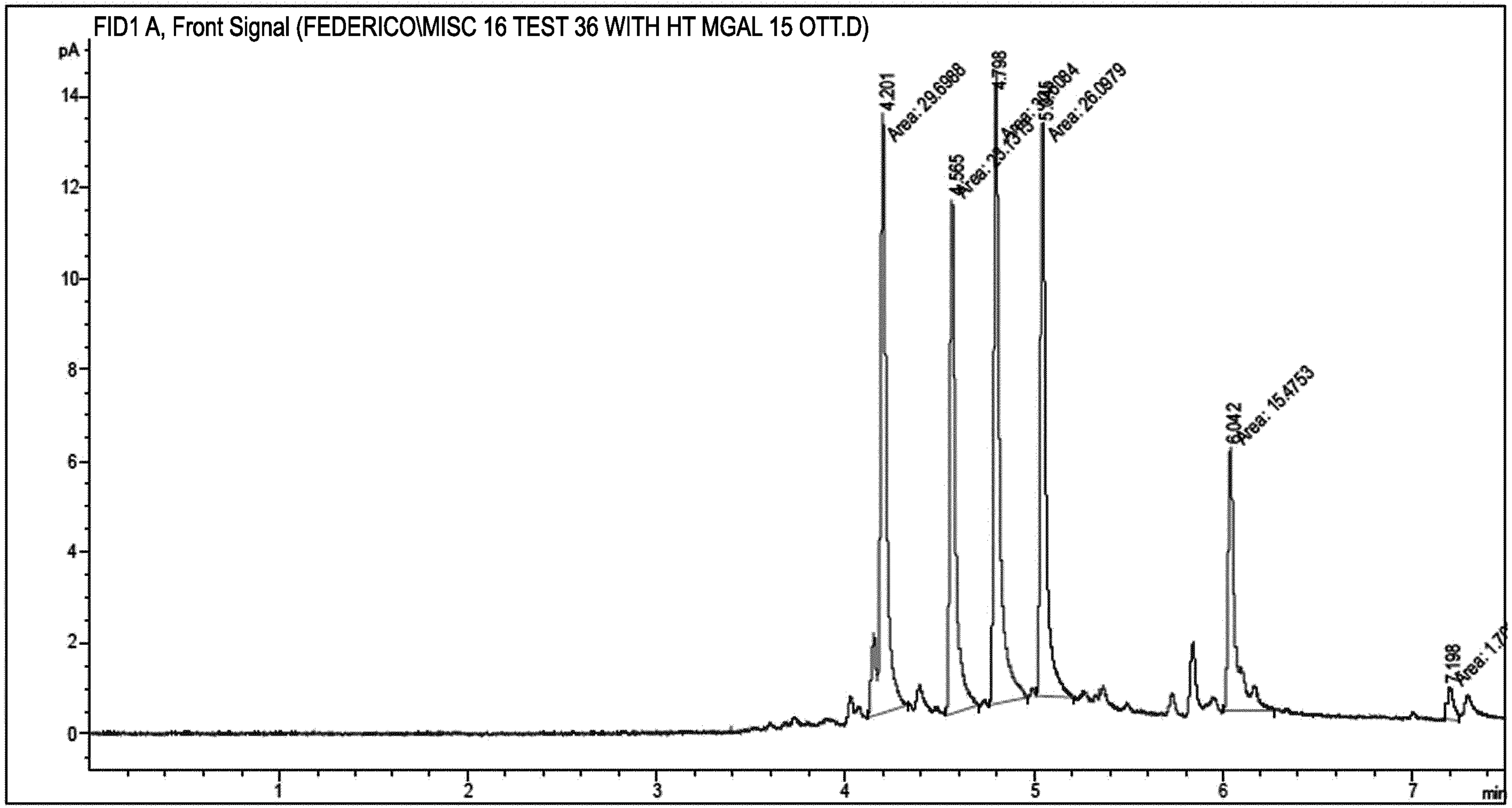
1
1.5
2
2.5
3
1
2
3
4
5
6
7
min
4.111
Area: 7.44987
4.527
Area: 1.5426
4.756
Area: 2.6175
5.004
Area: 1.59312
5.993
Area: 2.42934
7.149
Area: 1.330

Fig. 14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12
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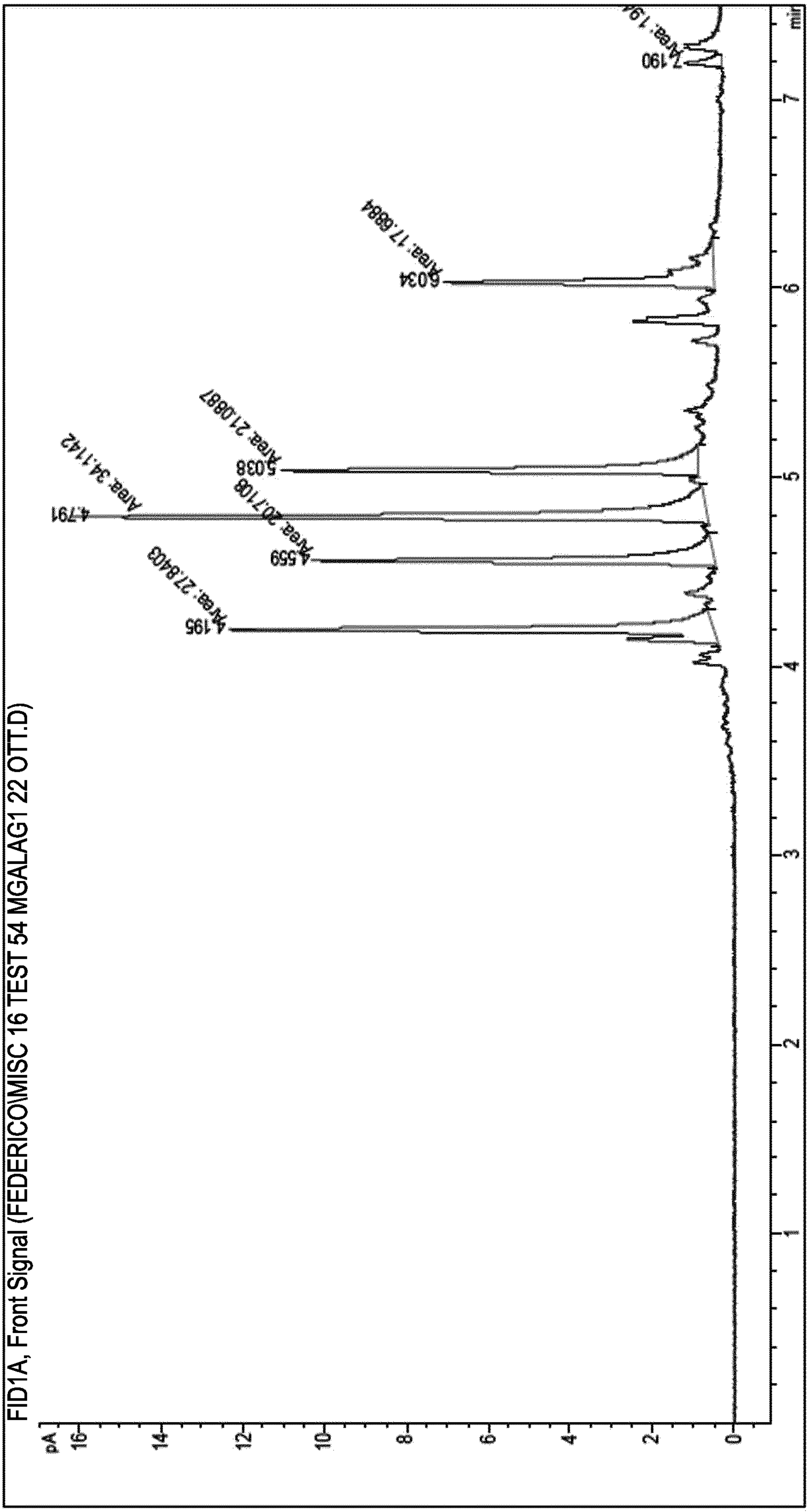
8
6
4
2
0
1
2
3
4
5
6
7
min
4.201
Area: 29.6988
4.565
Area: 23.1319
4.798
Area: 30.8084
5.045
Area: 26.0979
6.042
Area: 15.4753
7.198
Area: 1.7

Fig. 15


FID1A, Front Signal (FEDERICO\MISC 16 TEST 54 MGALAG1 22 OTT.D)
pA
16
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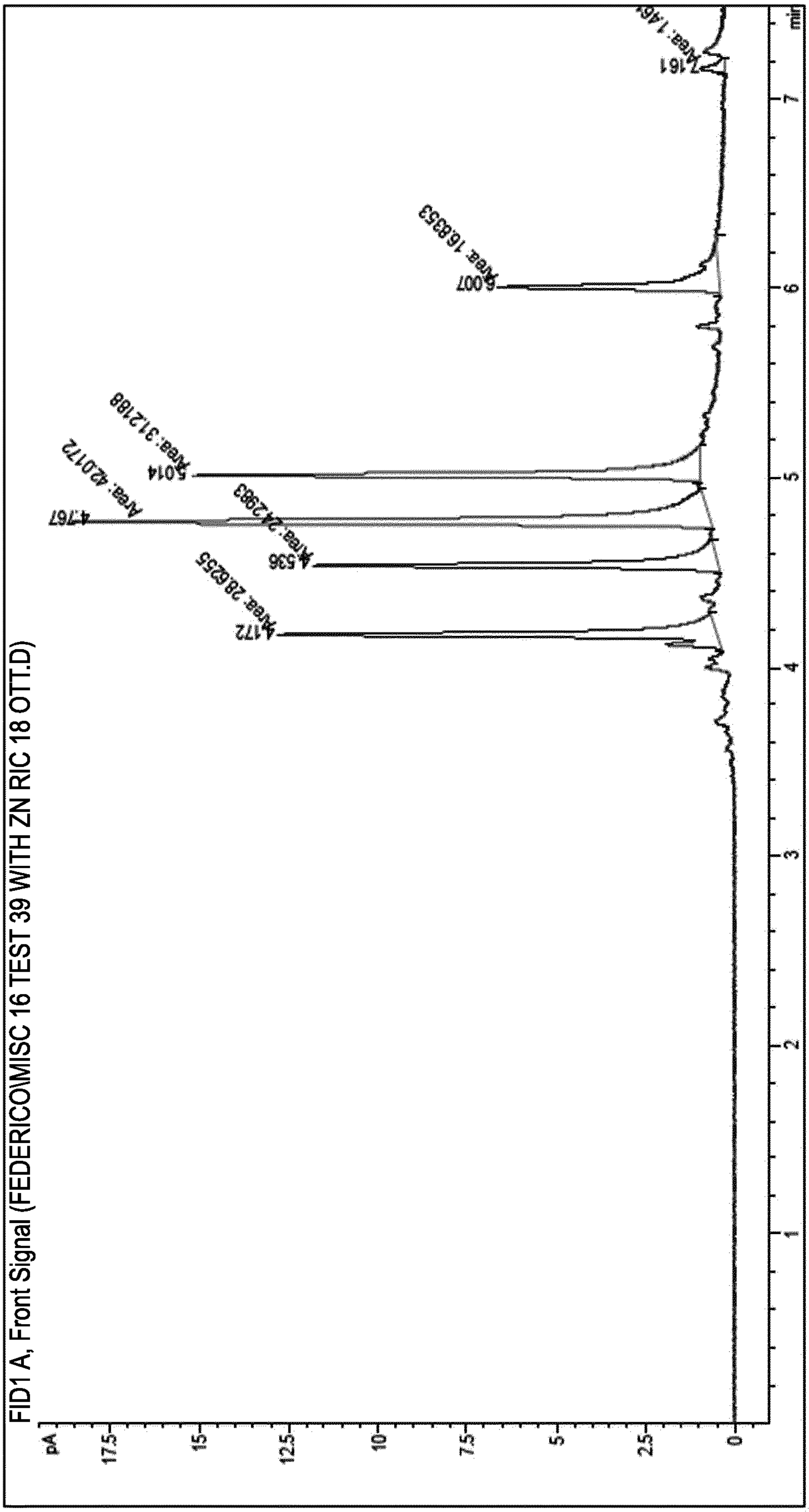
12
10
8
6
4
2
0
1
2
3
4
5
6
7
min
4.195
Area: 27.8403
4.559
Area: 20.7108
4.791
Area: 34.1142
5.038
Area: 21.0887
6.034
Area: 17.6884
7.190
Area: 1.94

Fig. 16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15
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2.5
0
1
2
3
4
5
6
7
min
4.172
Area: 28.6255
4.536
Area: 24.2983
4.767
Area: 42.0172
5.014
Area: 31.2188
6.007
Area: 16.8353
7.161
Area: 1.46

Fig. 17

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/051248

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61Q15/00 A61K8/19 A61K8/26 A61K8/02 A61Q17/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61Q A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 066 825 A1 (PROCTER & GAMBLE [US]) 10 January 2001 (2001-01-10) claims 1, 17, 18	1-13
Y	WO 94/14409 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; FRANKLIN KEVIN RONALD [GB]; WIGHT) 7 July 1994 (1994-07-07) claims examples	1-13

-/--

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search
22 February 2012

Date of mailing of the international search report
02/03/2012

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer
Hauss, Regina

International application No
PCT/EP2012/051248

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 11 January 1992 (1992-01-11), NAKANE, TOSHIHIKO ET AL: "Skin and hair cosmetics containing hydrotalcite", XP002659148, retrieved from STN Database accession no. 1992:11037 abstract -& JP 3 190811 A (SHISEIDO CO., LTD., JAPAN) 20 August 1991 (1991-08-20) -----	1-13
Y	EP 0 737 711 A1 (KYOWA CHEM IND CO LTD [JP]) 16 October 1996 (1996-10-16) page 5, line 36 - line 49 claim 1 -----	1-13
A	EP 1 840 113 A1 (TAYCA CORP [JP]) 3 October 2007 (2007-10-03) the whole document -----	9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/051248

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		WO 2006068118 A1	29-06-2006