



## Method and device for detecting metal ion release

Jellesen, Morten S.; Thyssen, Jacob Pontoppidan; Olsen , Christian Bang

*Publication date:*  
2016

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Jellesen, M. S., Thyssen, J. P., & Olsen , C. B. (2016). Method and device for detecting metal ion release. (Patent No. WO2016207361).

---

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



- (51) International Patent Classification:  
*G01N 31/22* (2006.01) *G01N 27/42* (2006.01)
- (21) International Application Number:  
PCT/EP2016/064686
- (22) International Filing Date:  
24 June 2016 (24.06.2016)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
15173995.0 26 June 2015 (26.06.2015) EP
- (71) Applicants: **DANMARKS TEKNISKE UNIVERSITET** [DK/DK]; Anker Engelunds Vej 101 A, 2800 Kgs. Lyngby (DK). **HERLEV OG GENTOFTE HOSPITAL** [DK/DK]; Arkaden, Herlev Ringvej 75, 2730 Herlev (DK).
- (72) Inventors: **JELLESEN, Morten, S.**; Aprilvej 9, 2860 Søborg (DK). **THYSSEN, Jacob, Pontoppidan**; Lindevangen 81, 2830 Virum (DK). **OLSEN, Christian, Bang**; Nybrovej 304 F-58, 2800 Kgs. Lyngby (DK).
- (74) Agent: **GUARDIAN IP CONSULTING I/S**; Diplomvej, Building 381, 2800 Kgs. Lyngby (DK).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: METHOD AND DEVICE FOR DETECTING METAL ION RELEASE

(57) Abstract: The present invention relates to a method and a device for colorimetric detection of metal ion release from a metallic item.

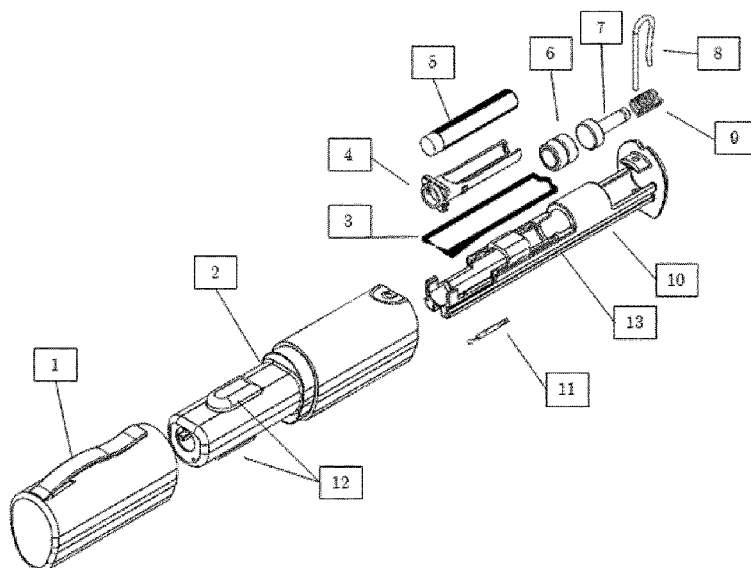


Figure 5.1

## METHOD AND DEVICE FOR DETECTING METAL ION RELEASE

### FIELD OF THE INVENTION

- 5     The present invention relates to a method and a device for colorimetric detection of metal ion release from a metallic item.

### BACKGROUND

- 10    Many people suffer from metal allergy due to prolonged exposure to metal releasing devices. In particular nickel, chromium and cobalt ions result in metal allergy and dermatitis. It is imperative that allergic individuals avoid all future contact with culprit metal devices both at home and at the work place to avoid chronic dermatitis.

- 15    At present, the only easily accessible and rapid method to detect excessive release of these metal ions involves the use of cotton stick tests, which require the use of a cotton stick that is dipped in a test solution and then rubbed 20-30 seconds against a test item while observing a possible color change.

- 20    There are, however, several problems with the available spot test kits. For example the cobalt test is not always positive when using the cotton stick method although cobalt is indeed released in high amounts. Also approximately 50% of negative nickel test reactions are false when nickel is released in high amounts.

- 25    Importantly, the interpretation of these traditional colorimetric tests can be difficult as the mandatory rubbing with a cotton stick often results in dirt from the surface obscuring a possible color change and the test outcome is dependent on the individual pressure, area and time used for wiping a surface.

- 30    Pertinently, allergists and dermatologists who perform allergy testing in patients with dermatitis need a reliable tool to correlate diagnosed allergies with exposures in the patients work environment as this is essential in work compensation

insurance cases. Also patients are advised to screen their home environment for metal release, for example new devices, jewellery, watches, belts, phones and smart phones. Therefore spot tests are sold at pharmacies and on the internet.

- 5 A number of methods for detecting a specific metal ion in a metallic item exist, but none of these methods are suitable for replacing the conventional spot tests that are available on the market today.

10 JP S56 125658 A to DAIDSO STEEL CO LTD describes a method for detecting the presence or absence of cobalt. In the method an anode is abutted electricity-conductably on a metallic material, cotton is impregnated with a water-containing coloring reagent and pinched with a pincette acting as a cathode. The coloring agent is a mixed solution of a nitroso R solution, which forms orange complexes with cobalt. Prescribed current is flowed to the circuit for about 5 seconds, and if  
15 cobalt is present in the material it elutes from the material and causes a coloration reaction. The document does not discuss or mention the problems that may appear when the coloring solution is not stored inside a closed container prior to use and it is not explained how the user avoids skin contact with the coloring solution during detection. Moreover, the solution volume is not controlled. In fact,  
20 the document does not discuss any safety risks, and the method does not appear to be suitable for use as a replacement method to the conventional spot tests, since handling of the solution in a safe and controlled manner is not provided.

JP S56 125655 A and JP S56 124043 A disclose similar methods for detecting  
25 nickel and chrome, respectively.

KR 2009 0100510 discloses a method for testing stainless steel to discriminate low-nickel stainless steel and high-nickel stainless steel. In the method an acidic solution is dropped on the stainless steel where after said solution is colored as  
30 the acidic salt reacts with the metallic ion electrolyzed from the stainless steel. The color is compared with a reference color of stainless steel. The test does not appear to be suitable for use when testing valuable items such as for example jewelries, because the test leaves a mark.

**SUMMARY OF THE INVENTION**

The inventors of the present invention have developed a novel method and device for detecting metal ion release. The method is reliable, fast and inexpensive as compared with the known spot test and it can be used on complex geometries and surfaces. It applies a voltage that will dramatically accelerate metal release for faster and better detection when compared to standard colorimetric identification methods. The novel method does not display the inherent problem of discoloration and the test is less dependent on the individual pressure, area and time used for wiping a surface, which is often observed with conventional colorimetric spot tests, which may lead to unreliable results. The novel method and device is more reliable and it is expected that the device will be important for consumers with metal allergy so that they easily may screen their working and home environment.

A broad aspect of the present invention pertains to a method for colorimetric detection of metal ion release from a metallic sample, said method comprises the steps of:

- 1) providing a voltage via a power supply,
- 2) providing an electrically conducting mounting unit,
- 3) providing a pad comprising an electrically conducting colorimetric solution,
- 4) building an electrochemical circuit comprising the direct voltage from the power supply, the mounting unit acting as cathode, the pad comprising an electrically conducting colorimetric solution acting as electrolyte and the metallic sample acting as anode,
- 5) applying a direct voltage to said electrochemical circuit for a period of at least 0.1 second, and
- 6) detecting the presence of metal ion release by inspecting the color of the pad.

Another broad aspect of the present invention pertains to a kit adapted for use in the above mentioned method for colorimetric detection of metal ion release from a metallic sample, said kit comprising:

- an electrically conducting mounting unit,
- a pad, and
- an electrically conducting colorimetric solution.

In a first aspect the present invention pertains to a method for colorimetric detection of metal ion release from a metallic item, said method comprising the steps of:

- a. providing a voltage via a power supply,
- 5 b. providing a cathode part,
- c. providing an electrically conducting colorimetric solution inside a closed container,
- d. providing a swab,
- e. puncturing the closed container,
- 10 f. wetting the swab with the electrically conducting colorimetric solution,
- g. building an electrochemical circuit comprising
  - the power supply,
  - the cathode part,
  - the swab wetted with electrically conducting colorimetric solution acting as
  - 15 electrolyte and
  - the metallic item acting as anode,
- h. applying a voltage to said electrochemical circuit for a period of at least 0.1 second, and
- i. detecting the presence of metal ion release by inspecting the color of the
- 20 swab.

In a second aspect the present invention pertains to a device adapted for use in the method for colorimetric detection of metal ion release from a metallic item, said device comprising:

- 25 • a cathode part,
- a swab, and
- an electrically conducting colorimetric solution stored inside a closed container.

## 30 BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a schematic drawing of the electrochemical circuit which is built in order to detect metal ion release in the method according to the present invention. The electrochemical circuit comprises a power supply [a], a metal plate

35 acting as the cathode [b], a metallic sample acting as the anode [c] and a pad

comprising an electrically conducting colorimetric solution acting as the electrolyte [d]. If metal ion is released when the voltage is applied a change in color will appear at the spot [e] where the metallic sample has been in contact with the pad.

5

Figure 2a, 2b and 2c shows a schematic drawing of the embodiment where the voltage is provided by a battery inside of a handheld computer, electrical device or smart phone and where the pad comprising an electrically conducting colorimetric solution is formed as a patch. In the embodiment the power supply [a] is connected to the cathode [b] by use of a wire [h]. The pad [d] is mounted on the cathode [b]. The pad also forms part of a patch comprising an adhesive [f] for attachment to the metallic sample [c]. The metallic sample [c] is connected to the power supply by use of a clip [g]. If metal ion is released when the voltage is applied a change in color will appear at the spot [e] where the metallic sample has been in contact with the pad.

15

Figure 3 shows a side view of the patch used in the embodiment shown in Figure 2a, 2b and 2c. The patch comprises a wire for cathode connection [h], a metal plate acting as cathode [b], a pad comprising an electrically conducting colorimetric solution acting as electrolyte [d], patch adhesive [f] and a polymer film for protection of electrolyte oxidation and liquid evaporation [i]. The polymer film is removed prior to use.

20

Figure 4 shows a schematic drawing of the device formed as a pen.

25

Figure 5 is a drawing of a prototype, which has been designed, manufactured and tested.

## DETAILED DESCRIPTION OF THE INVENTION

30

Accordingly, in a broad aspect the present invention relates to a method for colorimetric detection of metal ion release from a metallic sample, said method comprises the steps of:

- 1) providing a voltage via a power supply,
- 35 2) providing an electrically conducting mounting unit,

- 3) providing a pad comprising an electrically conducting colorimetric solution,
  - 4) building an electrochemical circuit comprising the power supply, the mounting unit acting as cathode, the pad comprising an electrically conducting colorimetric solution acting as electrolyte and the metallic sample acting as
  - 5 anode,
  - 5) applying a direct voltage to said electrochemical circuit for a period of at least 0.1 second, and
  - 6) detecting the presence of metal ion release by inspecting the color of the pad.
- 10 In one aspect the present invention pertains to a method for colorimetric detection of metal ion release from a metallic item, said method comprising the steps of:
- a. providing a voltage via a power supply,
  - b. providing a cathode part,
  - 15 c. providing an electrically conducting colorimetric solution inside a closed container,
  - d. providing a swab,
  - e. puncturing the closed container,
  - f. wetting the swab with the electrically conducting colorimetric solution,
  - 20 g. building an electrochemical circuit comprising
    - the power supply,
    - the cathode part,
    - the swab wetted with electrically conducting colorimetric solution acting as electrolyte and
    - 25 - the metallic item acting as anode,
  - h. applying a voltage to said electrochemical circuit for a period of at least 0.1 second, and
  - i. detecting the presence of metal ion release by inspecting the color of the swab.

30

The method is directed to detection of metal ion release from a metallic item or a metallic sample. The metal ion is released in an accelerated manner by building an electrochemical circuit in which the metallic item or metallic sample acts as an anode so that anodic oxidation of metals in the metallic item or metallic sample

35 will occur when a voltage is applied.



The method is designed to replace the conventional spot tests that presently are available on the market.

In the context of the present invention the term "colorimetric determination" or  
5 "colorimetric determination of metal ion release" pertains to an analysis in which the concentration of a metal ion is determined with the aid of a coloring agent, also referred to herein as the "colorimetric agent". The concentration is determined by analyzing the intensity of the color which appears when a metal ion chemically reacts with the coloring agent thereby forming a chemical compound  
10 having another color than unreacted metal ion and coloring agent.

The metal ions which can be detected in the method of the present invention include cobalt ions, chromium ions, nickel ions, iron ions, lead ions, aluminium ions, mercury ions, copper ions, tin ions, molybdenum ions, cadmium ions and  
15 palladium ions. The preferred metal ions to be detected include cobalt ions, chromium ions and nickel ions.

The metallic item may in principle be any kind of metallic item. By the term "metallic item" or "metallic sample" as used herein is meant an item or a sample  
20 made up entirely or partly of metal. Patients suffering from metal allergy are usually advised to screen items from their home environment in order to reduce any further exposure to the specific metal. Such items may include jewellery, watches, belts, phones and smart phones. Other samples that could be interesting to test include massive metals and alloys and electrically conductive surfaces.  
25 Also, patients are occupationally exposed to metals and here the testing can benefit the prognosis as well.

In step a, a voltage from a power supply is provided. Said power supply is typically a battery and also includes a battery in a phone or smart phone or in a  
30 computer, iPad or solar cell panel. The voltage applied may also be from a direct current provided by converting alternating current from an electric socket to direct current by use of an ac-dc converter. In a specific embodiment the direct current may be one or more pulse(s) of the alternating current.

35 In step b, a cathode part is provided. The cathode part acts as the cathode in the electrochemical circuit and is adapted for mounting the swab wetted with the

electrically conducting colorimetric solution. The cathode part is referred to as the "electrically conducting mounting unit" in the broad aspect of the present invention. Another purpose of the presence of the cathode part is to keep the swab in position in the electrochemical circuit when the voltage is applied and to  
5 make sure that the swab is electrically connected to the power supply. The cathode part may be formed as a plate, a grid or a clip.

In step c, an electrically conducting colorimetric solution is provided. The electrically conducting colorimetric solution acts as the electrolyte in the  
10 electrochemical circuit and therefore the solution must be electrically conductive or else the current cannot flow in the circuit. In some embodiments the ionic conductivity of the solution is ranging from 1-50 mS/m. In other embodiments the ionic conductivity of the solution is ranging from 1-40 mS/m, such as for example 1-30 mS/m, such as for example 1-20 mS/m, such as for example 1-10 mS/m. In  
15 other embodiments the ionic conductivity of the solution is ranging from 5-50 mS/m, such as for example 10-50 mS/m, such as for example 20-50 mS/m, such as for example 30-50 mS/m.

In step d a swab is provided. In the broad aspect the swab is referred to as "a  
20 pad". The swab may be made of any kind of material that is capable of being wetted with the electrically conducting colorimetric solution. Hence, the wetted swab may be made of woven or non-woven fabric, which has been wetted or immersed in the colorimetric solution, or the wetted swab may be made of a gelling material in which the colorimetric solution has been dissolved or  
25 incorporated. Examples of fabrics include cotton and rayon and examples of gelling materials include agar gel, gelatine, silicone, starch, conductive adhesive, aloe vera gel and electrode gel. Examples of commercial available gelling materials include Tensive® Conductive Adhesive from Parker Laboratories, Inc.

30 The colorimetric solution comprises a colorimetric agent. By the term "colorimetric agent" as used herein is meant the coloring agent which is capable of reacting with the metal ion to be detected and forming a chemical compound having another color than non-reacted metal ion and the colorimetric agent. Preferred examples of colorimetric agents include 1-nitroso-2-naphthol-3,6-disulfonic acid  
35 disodium salt (NRS) for detection of cobalt ions, diphenylcarbazide for detection of chromium ions and dimethylglyoxime (DMG) for detection of nickel ions.

Other examples of useful colorimetric agents include sodium rhodizonate or diphenylthiocarbazone for detection of lead ions, eriochromcyanin R or catechol violet for detection of aluminium ions, 3-methoxysalicylaldehyde-4-

5 hydroxybenzoylhydrazone for detection of palladium ions catechol violet for detection of tin ions, gold nanoparticles for detection of mercury, lead and copper ions and a mixture of potassium ferricyanide and phenolphthalein for detection of iron ions.

10 The electrically conducting colorimetric solution is kept inside a closed container during storage in order to minimize, or even avoid, evaporation of the liquid. Preferably the container is hermetically sealed. Another beneficial effect of storing the solution inside a closed container is that the user's skin is protected from any contact with the solution, which may be chemically aggressive or even toxic. Also  
15 the user's cloth will be protected from the solution.

Yet another advantage of storing the solution inside a closed container is that the volume of the solution remains constant during storage and the colorimetric properties of the solution are also preserved when the solution is stored inside a  
20 closed container.

Hence, for methods which are designed to replace the conventional spot tests that are available on the market it is essential that the electrically conducting colorimetric solution is stored inside a closed container.

25

In a preferred embodiment, the solution is stored inside the closed container in an inert atmosphere in order to prevent undesirable chemical reactions in the solution that may affect the colorimetric properties of the solution e.g. caused by oxidation. By the term "inert atmosphere" is meant a non-reactive gas  
30 atmosphere, such as for example nitrogen or helium.

In step e the closed container is punctured. In some embodiments the closed container is made of glass, and in such cases the pressure needed for puncturing the closed container can be ranging from 0.01 to 10 N/mm<sup>2</sup>.

35

In step f the swab is wetted with the electrically conducting colorimetric solution. When the closed container is punctured the electrically conducting solution is not anymore trapped inside the container and is therefore free to be brought in contact with the swab, which accordingly is then wetted.

5

In other embodiments the swab is stored together with the electrically conducting colorimetric solution inside the closed container and in such cases the wetting of the swab with the electrically conducting colorimetric solution occurs when the closed container is produced.

10

In step g, the electrochemical circuit is built by connecting the power supply, the cathode part, the swab wetted with the electrically conducting colorimetric solution and the metallic item. In some embodiments said connections are formed by use of wires, spring loaded pins, pogo pins and/or clips, preferably pogo pins.

15

In step h, the voltage is applied for a period of at least 0.1 second. In this step the metal ion release is accelerated by applying the voltage, because the metallic item is acting as the anode in the electrochemical circuit, whereby anodic oxidation of the metals in the item will occur. This accelerated release makes the method fast and reliable. Hence, a color change may be detected also when the voltage has only been applied for a very short period of time. It may actually be the case that applying an alternating current instead of a direct current may also provide a reliable test result because anodic oxidation will also occur during single anodic pulses in the alternating current.

20

The applied voltage typically ranges from 1.5-9V. In some embodiments the applied voltage ranges from 3-9 V, such as 4.5-9 V, for example 6-9 V. In other embodiments the applied voltage ranges from 1.5-6V, such as 1.5-4.5 V, for example 1.5-3V. In a preferred embodiment the applied voltage range from 3-6V, and more preferred from 3-4.5V. The applied voltage is most preferably 3V.

25

In some embodiments the voltage is applied for a period of at least 0.1 second and at most 5 minutes. In other embodiments the voltage is applied for a period of 0.1-60 seconds, such as for example 0.1-30 seconds, such as for example 0.1-10 seconds, such as for example 0.1-5 seconds, such as for example 0.1-2 seconds. In other embodiments the voltage is applied for a period of 0.5-60

30

seconds, such as 5 to 40 seconds. In preferred embodiments the voltage is applied for a period of 10-30 seconds, more preferred 15-25 seconds, most preferred 20 seconds.

- 5 In step i, the presence of metal ion release is detected by inspecting the color of the pad. As disclosed above the present method is a colorimetric detection method in which a colorimetric agent will react with a specific metal ion, if said metal ion is released from the metallic item, and thereby cause a color change. The chemical reaction will occur in the colorimetric solution which is comprised in  
10 the swab, and therefore the color change will occur in the swab. Hence, the presence of release of a specific metal ion can be detected by inspecting the color (or color change) of the swab.

- 15 In another broad aspect the present invention relates to a kit, which is adapted for use in the method for colorimetric detection of metal ion release from a metallic sample as described in the broad aspect of the method above. The kit comprises an electrically conducting mounting unit, a pad and an electrically conducting colorimetric solution.

- 20 In a preferred embodiment the kit is a device.

Accordingly, in another aspect the present invention relates a device, which is adapted for use in the method for colorimetric detection of metal ion release from a metallic item as described above.

- 25 The different parts of the device may be found in the device as separate units or some of the parts may be found as a combined unit. By the term "separate units" as used herein is meant that the different parts of the device are not connected during storage. By the term "combined unit" as used herein is meant that the  
30 different parts comprised in the device are unreleasably connected.

- In one embodiment the cathode part, the swab and the electrically conducting colorimetric solution stored inside a closed container are found in the device as separate units. In another embodiment the cathode part, the swab and the  
35 electrically conducting colorimetric solution are found in the device as a combined unit. In such embodiment, both the swab and the electrically conducting

colorimetric solution are found inside the closed container and the swab is wetted with the solution. The closed container is preferably hermetically sealed in order to minimize, or even avoided, evaporation of the liquid solution and in order to preserve the colorimetric properties of the solution, e.g. caused by oxidation.

5

In a preferred embodiment the cathode part, the swab and the electrically conducting colorimetric solution stored inside a closed container are found in the device as separate units.

10 In another preferred embodiment the cathode part, the swab and the electrically conducting colorimetric solution are found in the device as a combined unit which has been formed as a patch. In such cases the patch is stored inside the closed container.

15 In one embodiment the cathode part and the swab are found in the device as separate units. In another embodiment the cathode part and the swab are found in the device as a combined unit.

In cases where the cathode part and the swab are found in the device as a  
20 combined unit, the swab is preferably mounted on cathode part by use of electric conductive glue or electric conductive adhesive.

In one embodiment the swab and the electrically conducting colorimetric solution stored inside the closed container are found in the device as separate units. In  
25 another embodiment the swab and the electrically conducting colorimetric solution are found in the device as a combined unit where the swab is wetted with the colorimetric solution and stored inside the closed container. The closed container is preferably hermetically sealed in order to minimize, or even avoid, evaporation of the liquid solution and in order to preserve the colorimetric properties of the  
30 solution. In a preferred embodiment the swab and the electrically conducting colorimetric solution stored inside the closed container are found in the device as separate units.

In cases where the swab and the electrically conducting colorimetric solution are  
35 found in the device as separate units, at least the solution is stored in a closed container which can be hermetically sealed so that evaporation is minimized, or

even avoided, and in order to preserve the colorimetric properties of the solution against oxidation.

5 When the swab and the electrically conducting colorimetric solution are found in the device as separate units said swab must be wetted with the solution before use. If the swab is made of fabric said fabric swab could be wetted with the solution by dipping the swab into the solution before the electrochemical circuit is built.

10 In one embodiment the device comprises only one type of electrically conducting colorimetric solution for the determination of release of one specific type of metal ion. In other embodiments the device comprises two or more electrically conducting colorimetric solutions so that two or more metal ion releases can be detected by use of the same device. Hence, in one embodiment the device  
15 comprises one colorimetric solution for detecting cobalt ions and one colorimetric solution for detecting chromium ions. In another embodiment the device comprises one colorimetric solution for detecting cobalt ions and one colorimetric solution for detecting nickel ions. In yet another embodiment the device comprises one colorimetric solution for detecting chromium ions and one  
20 colorimetric solution for detecting nickel ions. In still another embodiment the device comprises one colorimetric solution for detecting cobalt ions and one colorimetric solution for detecting chromium ions and one colorimetric solution for detecting nickel ions.

25 In the device the two or more electrically conducting colorimetric solutions can be found as two or more separate units, where each solution is found inside a closed container, which can be hermetically sealed so that evaporation is minimized, or even avoided. Alternatively, the two or more electrically conducting colorimetric solutions each can be found as combined units together with a swab, i.e. where  
30 one swab is wetted with one colorimetric solution and another swab is wetted with another colorimetric solution. Each combined unit is stored inside a closed container, which preferably is hermetically sealed in order to minimize, or even avoid, evaporation of the liquid solution and in order to preserve the colorimetric properties of the solution.

35

In other embodiments the device comprises a swab, which has been divided into two or more compartments, where each compartment comprises different types of electrically conducting colorimetric solutions so that two or more metal ion releases can be detected by use of the same swab. Hence, in one embodiment the

5 swab comprises at least two compartments, where one compartment comprises a colorimetric solution for detecting cobalt ions and another compartment comprises colorimetric solution for detecting chromium ions. In another embodiment the swab comprises at least two compartments, where one compartment comprises a colorimetric solution for detecting cobalt ions and another compartment comprises

10 colorimetric solution for detecting nickel ions. In yet another embodiment the swab comprises at least two compartments, where one compartment comprises a colorimetric solution for detecting chromium ions and another compartment comprises colorimetric solution for detecting nickel ions. In still another embodiment the swab comprises at least three compartments, where one

15 compartment comprises a colorimetric solution for detecting cobalt ions and another compartment comprises a colorimetric solution for detecting chromium ions and yet another compartment comprises colorimetric solution for detecting nickel ions.

20 In yet other embodiments the cathode part, the swab and the electrically conducting colorimetric solution are found in the device as a combined unit which has been formed as a patch, in which the swab has been divided into two or more compartments, where each compartment comprises different types of electrically conducting colorimetric solutions so that two or more metal ion releases can be

25 detected by use of the same swab. Hence, in one embodiment the swab comprises at least two compartments, where one compartment comprises a colorimetric solution for detecting cobalt ions and another compartment comprises colorimetric solution for detecting chromium ions. In another embodiment the swab comprises at least two compartments, where one compartment comprises a

30 colorimetric solution for detecting cobalt ions and another compartment comprises colorimetric solution for detecting nickel ions. In yet another embodiment the swab comprises at least two compartments, where one compartment comprises a colorimetric solution for detecting chromium ions and another compartment comprises colorimetric solution for detecting nickel ions. In still another

35 embodiment the swab comprises at least three compartments, where one compartment comprises a colorimetric solution for detecting cobalt ions and



another compartment comprises a colorimetric solution for detecting chromium ions and yet another compartment comprises colorimetric solution for detecting nickel ions.

- 5 In some embodiments the device further comprises a power supply. In a preferred embodiment the power supply is a battery. In some embodiments the battery is a 9V battery. In other embodiments the battery is a 3V battery. In yet other embodiments the battery is a 1.5V battery. In cases where the device does not  
10 comprise a power supply the method for detecting metal ion release is performed by using the battery for example inside of a phone, a smart phone, an iPad, a computer or the like.

- The device may further comprise one or more connecting unit(s). By the term "connecting unit" as used herein is meant a device which electrically connects the  
15 units in the electrochemical circuit so that electrons can flow. The one or more connecting unit(s) may take the form of wires, spring loaded pins, pogo pins and/or clips.

- In one embodiment the device comprises one connecting unit for electrically  
20 connecting the cathode part with the power supply. In another embodiment the device comprises one connecting unit for electrically connecting the cathode part with the swab. In yet another embodiment the device comprises one connecting unit for electrically connecting the metallic item with the power supply.

- 25 In another embodiment the device comprises two connecting units for electrically connecting the cathode part with the power supply and for electrically connecting the cathode part with the swab. In still another embodiment the device comprises two connecting units for electrically connecting the cathode part with the swab and for electrically connecting the metallic item with the power supply. In yet  
30 another embodiment the device comprises two connecting units for electrically connecting the cathode part with the swab and for electrically connecting the metallic item with the power supply.

- In yet another embodiment, which is also a preferred embodiment, the device  
35 comprises three connecting units for electrically connecting the cathode part with

the power supply and for electrically connecting the cathode part with the swab and for electrically connecting the metallic item with the power supply.

5 The device may further comprise one or more color chart(s) for reading the concentration of the released metal ions. By the term "color chart" as used herein is meant a color reference chart which is used for color comparison and measurements. Typically, the intensity (or darkness) of the color increases with increased concentration of released metal ion, because the concentration of the chemical compound which causes the color formation is related to the  
10 concentration of released metal ion.

In cases where the device does not comprise a color chart, the concentration of metal ion release may be read by using a color chart which has been downloaded on the user's smart phone. In other cases the color chart may be bought as a  
15 separate item, because the color chart is not consumed during the method for colorimetric detection of metal ion release in the same manner as the swab and the colorimetric solution, which must be discarded after one use.

In a particular embodiment the voltage is provided by a battery inside of an  
20 electrical device, such as for example a handheld computer or smart phone. This device will have a program or application that can be used to verify whether a reaction is positive or negative. Also, photographs can be taken with the device and these can be stored on the device and shared with other users via an online access and stored in a database. Also, information about the product scanned can  
25 be stored and shared.

A preferred embodiment of the device is shown in Figure 4. The device is formed as a pen which consists of a housing (shown in Figure 4a) and an insert part (shown in Figure 4b). The housing (a) contains a power supply (b) e.g. in the  
30 form of a series of batteries resulting in a total voltage from 1.5-9V. A press button (c) is a part of the housing allowing for puncturing of the glass container (h) of the insert part. Via electrical connections (d) a cathode part (e), which can be made of stainless steel, is connected to the power supply. The cathode part is flexible and allows for the insert part to be inserted. The anode connection (f) has  
35 a flexible connection (e.g. pogo pin) so that the pen can be pressed against the item to be tested (i). The insert part consists of an insert housing (g) and a glass

container (h) with the electrically conducting colorimetric solution (i) in a controlled atmosphere (for example inert gas). The glass container (h) is placed inside the housing and a wettable swab (k) is attached with an adhesive (j). Before use, the insert part is placed inside the housing (a) and the cathode part  
5 intrudes the swab (shown in Figure 4c). The glass container of the insert part is then punctured by the press button and the swab is wetted by the electrically conducting colorimetric solution (i) (see Figure 4d). As the swab is pressed against the metal item to be tested (l) the pogo pin establishes electrical contact to the anode part of the power supply.

10

The most preferred embodiment of the device is shown in Figure 5. This figure is a drawing of a prototype which has been manufactured and tested for use in the method for colorimetric detection of metal ion release according to the present invention. The prototype consists of a housing (2), an insert part (4+5) and a cap  
15 (1) which protects the tip of the prototype when not in use. The housing (2) contains a drawer (10) in which the cathode (3), the insert part (4+5) and batteries (6) acting as the power supply are inserted. The cathode (3) is connected to (-) at the batteries (6) via the load caused by the spring (9). The anodic part of the batteries (+) are connected to the pogo pin (11) via a contact  
20 pin (7), a spring (9), a locking clip (8) and a conducting wire (13). The insert part contains a cartridge holder (4) and an ampoule (5). The ampoule (5) is made of a plastic container (5.1) and a closed glass container (5.2) containing the colorimetric solution and a swab (5.3). The swab is preferably mounted on the inside of the plastic container by use of an adhesive. The house (2) further  
25 contains press buttons (12).

In use the ampoule (5) is inserted in the cartridge holder (4) and then the cathode (3) is mounted so that the tips of the cathode are inserted in the swab (5.3) of the ampoule (5). The ampoule (5), the cartridge holder (4) and the  
30 cathode (3) are then placed inside the drawer (10) and connected with the batteries (6), the pin (7), the locking clip (8), the spring (9) and the pogo pin (11). There after the drawer (10) is inserted into the house (2) and the cap (1) is removed. The press buttons are pressed so that the glass container (5.2) inside the plastic container (5.1) is broken resulting in wetting of the swab (5.3). The  
35 swab is then pressed against the metallic item to be tested for a specified period of time. The swab and the metallic item is then disconnected and the color of the

swab is inspected and optionally compared with a color charge to determine the concentration of metal ion release.

## EXAMPLES

5

### Example 1. Nickel release from pure nickel sample

A titanium plate (size 4·1 cm, thickness 1 mm) with a 90 degrees angle bending at the one end was placed in a glass beaker (radius 10 cm) and a crocodile clip was mounted at the bended titanium end enabling wire assembling to a 9V battery cathode part (marked -). On top of the titanium a piece of cotton (approximately 2cm·2cm) was placed and 5 droplets of a 1 wt% dimethylglyoxime (DMG) solution was added to the cotton. A crocodile clip held a pure nickel sample with a wire connected to a 9V battery anode (marked +). As the pure nickel sample came in contact with the DMG wetted cotton, the pure nickel sample acted as anode and the titanium plate as cathode with the wetted cotton in between acting as electrolyte. Since the nickel sample acted as anode the imposed electrochemical potential caused increased nickel ion release due to the 9V voltage supply from the battery and the DMG solution instantly caused coloration due to complex formation. The red coloration was easily seen when the nickel sample was removed from the cotton. When the nickel sample was removed from the cotton the electrochemical circuit was stopped.

### 25 Example 2. Cobalt release from a CoCr laser fused layer on steel

A steel sample with a surface layer of laser fused CoCr was placed on a piece of cotton (2cm·2cm) wetted with 5 drops of 1 wt% solution of 1-nitroso-2-naphthol-3,6-disulfonic acid disodium salt (NRS) on top of a titanium plate (5cm·1cm·1mm). As the CoCr is in contact with the NRS wetted cotton no color change appeared until a 3V battery was connected via wires to the titanium plate acting as cathode and the steel sample with CoCr layer acting as anode.

35

### Example 3. Effect of applied voltage

A swab was wetted with 0.5 ml of a solution containing 0.9 wt% NaCl, 3.8 wt.% DMG in a 25/75 vol.% mixture of water/ethanol and pressed against a nickel plated stainless steel plate placed on a laboratory scale until the load measured was 700 g. The nickel plated stainless steel specimen was connected to a power supply as anode (+) using a wire and a pogo pin for connection. Two stainless steel clips were pressed 1 mm into the swab 4 mm above the interface with the nickel plated stainless steel plate and were connected as cathode (-) to the power supply by using a wire. Various voltage levels were applied for 120 seconds and the resulting color of the swab surface was photographed. The results (shown in Table 1) show clear coloration at voltages above 3 V.

Table 1: The effect of voltage on coloration of swab surface when using a swab wetted with 0.5 ml 0.9 wt% NaCl, 3.8 wt.% DMG in a 25/75 vol.% mixture of water/ethanol and pressed against a nickel plated stainless steel plate with a load of 700 g for 120 seconds.

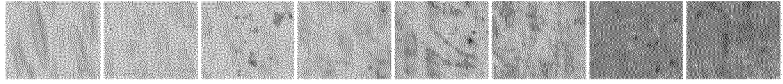



### Example 4. Effect of time

A swab was wetted with 0.5 ml of a solution containing 0.9 wt% NaCl, 3.8 wt.% DMG in a 25/75 vol.% mixture of water/ethanol and pressed against a nickel plated stainless steel plate placed on a laboratory scale until the load measured was 700 g. The nickel plated stainless steel specimen was connected to a potentiostat as anode (+) using a wire and a pogo pin for connection. Two stainless steel clips were pressed 1 mm into the swab 4 mm above the interface with the nickel plated stainless steel plate and were connected as cathode (-) to the potentiostat by using a wire. A constant voltage level of 3 V was applied and the resulting current was monitored with a potentiostat. The time duration of testing was varied from 0-120 seconds, where after the resulting color of the swab surface was photographed and light optical microscopy was performed on the metal surface in contact with the swab. The results (shown in Table 2) show clear coloration of the swab with a testing time of more than 10 seconds. Light

optical microscopy shows signs of degradation of the tested metal surface when testing time exceeds 45 seconds.

- 5 Table 2: The effect of time on coloration of swab surface when wetted with a 0.5 ml 0.9 wt% NaCl, 3.8 wt.% DMG in a 25/75 vol.% mixture of water/ethanol and pressed against a nickel plated stainless steel plate with a load of 700 g and using a voltage of 3 V.

Time [seconds]	0	10	20	30	45	60	90	120
Light optical investigation of metal surface (10* magnification)								
Coloration of swab surface								
Average current [mA]	0	1,49	1,74	1,58	1,35	1,70	1,71	1,59







10

#### Example 5. Investigation of nickel detection in various metals

- A swab was wetted with 0.5 ml of a solution containing 0.9 wt% NaCl, 3.8 wt.% DMG in a 25/75 vol.% mixture of water/ethanol and pressed against various  
 15 metallic specimen placed on a laboratory scale until the load measured was 700 g. The metallic specimen was connected to a potentiostat as anode (+) using a wire and a pogo pin for connection. Two stainless steel clips were pressed 1 mm into the swab 4 mm above the interface with the nickel plated stainless steel plate and were connected as cathode (-) to the potentiostat by using a wire. A constant  
 20 voltage level of 3 V was applied for 120 seconds and the resulting current was monitored with a potentiostat. The resulting current was measured after 120 seconds and the resulting color of the swab surface was photographed. The results (shown in Table 3) show clear coloration of the swab for metallic specimens that contain nickel whereas aluminum alloy 1050 (99.5 wt.% Al) did

not result in any color change. The current measured after 120 seconds when applying a voltage of 3V was between 1.5 and 2.9 mA for all samples.

Table 3. Investigation of various metals with a voltage of 3V for 120 seconds.

Material type	Stainless steel type AISI 316	Nickel plated guitar string	Nickel coated (Watts) stainless steel	Electroless coating of nickel on stainless steel	Electrolytic coating of nickel on stainless steel	Aluminum alloy 1050
Coloration of swab surface						
Current measured after 120 sec. (3V) [mA]	1.5	2.0	1.9	1.7	2.1	2.9

5











#### Example 6. Investigation of cobalt detection in various metals

- 10 A swab was wetted with 0.5 ml of a solution containing 0.1 wt.% oxalic acid, 0.02 wt.% nitroso-R salt in a 5/95 vol.% sodium acetate and water mixture and pressed against various metal specimens placed on a laboratory scale until the load measured was 700 g. The metallic specimen was connected to a potentiostat as anode (+) using a wire and a pogo pin for connection. Two stainless steel clips
- 15 were pressed 1 mm into the swab 4 mm above the interface with metal specimen and were connected as cathode (-) to the potentiostat by using a wire. A constant voltage level of 3 V was applied for 120 seconds and the resulting current was monitored with a potentiostat. The resulting current was measured after 120 seconds and the resulting color of the swab surface was photographed. The
- 20 results (shown in Table 4) show clear coloration of the swab for metallic specimens except sample B, G and H. Specimen H is a control disc of aluminum

alloy 1050 (99.5 wt.% Al) which did not result in any color change and thus indicates that there is no cobalt release. Samples B and G both have a surface coating consisting of  $\text{Al}_2\text{O}_3$  which has a high electrical resistance and hence limits the current and release of cobalt ions. The current measured after 120 seconds

5 when applying a voltage of 3V was between 1E-6 and 6.73 mA for all samples.

Table 4. Investigation of various metals with a voltage of 3V for 120 seconds.

Sample	A	B	C	D	E	F	G	H	I	K
Usage	Hard metal tools	Hard metal tools	Hard metal tools	Hard metal tools	Hard metal tools	Hard metal tools	Hard metal tools	Control disc	Dental Alloy	Dental alloy
Cobalt content in base alloy [wt.%]	6.0	6.0	6.0	7.5	7.5	15.0	15.0	0	64.6	33.0
Coating	None	TiCN+ $\text{Al}_2\text{O}_3$	TiN	None	TiCN+ $\text{Al}_2\text{O}_3$ + TiN	None	TiCN+ $\text{Al}_2\text{O}_3$ + TiN	None	None	None
Coloration of swab surface										
Current after 120 sec. (3V) [mA]	6,39	1E-6	0,22	6,73	0.38	5,88	0.21	0.20	5.57	3.39



**Exampel 7: Nickel detection in jewellery by using cotton stick method and a device as shown in fig. 4.**

163 pieces of jewellery was tested with 3 V for 20 seconds by wetting of a swab  
5 with 0.5 ml 0.9 wt% NaCl, 3.8 wt.% DMG in a 25/75 vol.% mixture of  
water/ethanol and pressed against various metallic jewellery placed on a  
laboratory scale until the load measured was 700 g. The results were compared to  
testing with cotton stick test [Jacob P Thyssen, Lizbet Skare, Lennart Lundgren,  
Torkil Menné, Jeanne D Johansen, Howard I Maibach, and Carola Lidén. Sensitivity  
10 and specificity of the nickel spot (dimethylglyoxime) test. Contact Dermatitis,  
62(5):279, 88, 2010]. All the tested samples were analysed with X-ray  
fluorescence for elemental composition. All tested samples contained nickel from  
0.6 wt% to 75.7wt%.

15 The metallic specimen was connected to the positive side of 2 serial connected 1.5  
V LR44 batteries as anode (+) using a wire and a pogo pin for connection. Two  
stainless steel clips were pressed 1 mm into the swab 4 mm above the interface  
with the nickel plated stainless steel plate and were connected as cathode (-) to  
the negative of the serial connected batteries by using a wire. A constant voltage  
20 of 3 V was applied for 20 seconds.

For the conventional test a cotton stick was wetted with 2 drops of 1wt% DMG  
dissolved in ethanol and 2 drops of 5M ammonia solution. The wetted cotton stick  
was rubbed against the jewellery for 20 seconds. The results given in table 5 show  
25 a higher sensitivity for the 3V biased spot test method as compared to  
conventional cotton stick test.

Table 5: Comparison of jewellery testing performed with a stick test and a 3 V voltage applied for 20 seconds by using a device as shown in figure 4.

Elemental composition as determined by XRF [wt.%]	Total number of jewellery	Cotton stick test [% positive tests]	Fig.4. device (3V, 20 sec) [% positive tests]
0-4.99	30	20	27
5-9.99	20	35	55
10-14.99	11	27	45
15-19.99	13	62	62
20-24.99	21	48	86
25-29.99	10	70	80
30-34.99	13	100	100
35-39.99	10	70	100
40-44.99	9	78	89
45-49.99	5	100	100
50-54.99	4	100	75
55-59.99	5	80	100
60-64.99	9	89	100
65-69.99	1	100	0
70-74.99	1	100	100
75-79.99	1	100	100


## 5 Example 8: Nickel detection by the use of a swab wetted by puncturing a glass ampoule

Reference is made to Figure 5, which shows the most preferred embodiment of the invention.

- 10 An ampoule (5) consisting of a closed glass tube (5.2) with 0.5 ml 1% dimethylglyoxime and 10% ammonium hydroxide solution was placed in a cartridge holder (4) and the cathode (3) was mounted so that the tips of the cathode were inserted in the swab (5.3) of the ampoule (5). The ampoule (5), the cartridge holder (4) and the cathode (3) were then placed inside the drawer (10)
- 15 in which the cathode was connected to (-) at the batteries (6) via the load caused by the spring (9). The anodic part of the batteries (+) was connected to the pogo

pin (11) via the contact pin (7), the locking clip (8) and the conducting wire (13). The drawer (10) was then inserted into the house (2) and the cap (1) was removed. The press buttons (12), which are designed to break the glass tube (5.2) inside the plastic container (5.1), were pressed with  $0.4 \text{ N/mm}^2$  resulting in breakage of the glass tube (5.2), while maintaining the shape of the plastic container (5.1), resulting in wetting of the swab (5.3). Hereafter the swab was pressed against a metal specimen placed on a laboratory scale until the load measured was 700 g. The metallic specimen was connected to a potentiostat as anode (+) using a wire and a pogo pin for connection. Two stainless steel clips were pressed 1 mm into the swab 4 mm above the interface with metal specimen and were connected as cathode (-) to the potentiostat by using a wire. A constant voltage of 3 V was applied for 120 seconds. The resulting color of the swab surface was photographed. The results (shown in Table 6) show clear coloration of the swab.

- 15 Table 6: Nickel detection by puncturing ampoule with 0.5 ml 1% dimethylglyoxime and 10% ammonium hydroxide solution is wetting a swab and tested with a voltage of 3 V for 20 seconds.

	Coloration of swab surface
Electroless nickel plated stainless steel	

**CLAIMS**

1. A method for colorimetric detection of metal ion release from a metallic item, said method comprising the steps of:
  - 5 a. providing a voltage via a power supply,
  - b. providing a cathode part,
  - c. providing an electrically conducting colorimetric solution inside a closed container,
  - d. providing a swab,
  - 10 e. puncturing the closed container,
  - f. wetting the swab with the electrically conducting colorimetric solution,
  - g. building an electrochemical circuit comprising
    - the power supply,
    - the cathode part,
    - 15 - the swab wetted with electrically conducting colorimetric solution acting as electrolyte and
    - the metallic item acting as anode,
    - h. applying a voltage to said electrochemical circuit for a period of at least 0.1 second, and
    - 20 i. detecting the presence of metal ion release by inspecting the color of the swab.
2. The method according to claim 1, wherein the method is for detecting release of a metal ion selected from the group consisting of cobalt ions, chromium ions  
25 and nickel ions.
3. The method according to any of the claims 1 or 2, wherein the metallic item is selected from the group consisting of jewellery, watches, belts, phones, smart phones, massive metals and alloys, electroplated parts and samples comprising  
30 an electrically conducting surface.
4. The method according to any of the preceding claims, wherein the electrochemical circuit in step g is built by connecting the power supply, the cathode part, the swab wetted with the electrically conducting colorimetric  
35 solution and the metallic item by use of wires, spring loaded pins, pogo pins and/or clips.

5. The method according to any of the preceding claims, wherein the power supply is a battery.

5     6. The method according to any of the preceding claims, wherein the voltage is applied in step h for a period of at least 0.1 second and at most 5 minutes.

7. The method according to any of the preceding claims, wherein the swab is stored together with the electrically conducting colorimetric solution inside the closed container and where the wetting of the swab with the electrically  
10     conducting colorimetric solution in step f is performed when the closed container is produced.

8. A device adapted for use in the method for colorimetric detection of metal ion release from a metallic item according to any of the claims 1-7, said device  
15     comprising:

- a cathode part,
- a swab, and
- an electrically conducting colorimetric solution stored inside a closed  
20     container.

9. The device according to claim 8, wherein the cathode part is formed as a plate, a grid or a clip.

25     10. The device according to any of the claims 8 or 9, wherein the swab is made of woven or non-woven fabric or gelling material.

11. The device according any of the claims 8-10, wherein the electrically conducting colorimetric solution comprises a colorimetric agent selected from the group consisting of 1-nitroso-2-naphthol-3,6-disulfonic acid disodium salt (NRS),  
30     diphenylcarbazine and dimethylglyoxime (DMG).

12. The device according any of the claims 8-11, wherein the swab and the electrically conducting colorimetric solution is found in the device as separate units or as a combined unit in which combined unit the swab is wetted with the  
35     colorimetric solution inside the closed container.

13. The device according to any of the claims 8-12, wherein the device further comprises a power supply.

- 5      14. The device according to any of the claims 8-13, wherein the device further comprises one or more connecting unit(s) for electrically connecting
- the cathode part with the power supply, and/or
  - the cathode part with the swab, and/or
  - the metallic item with the power supply.

10

15. The device according to any of the claims 8-14, wherein the device further comprises one or more color chart(s).

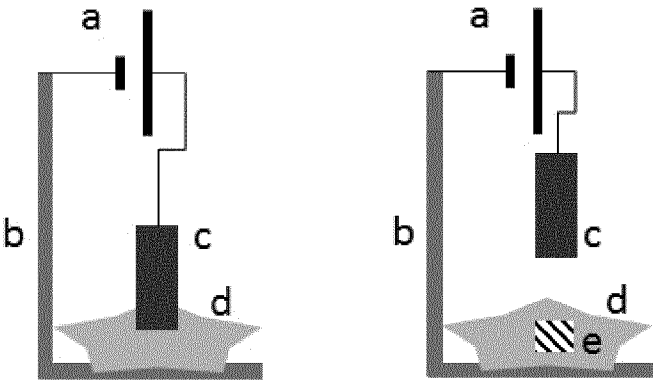


Figure 1

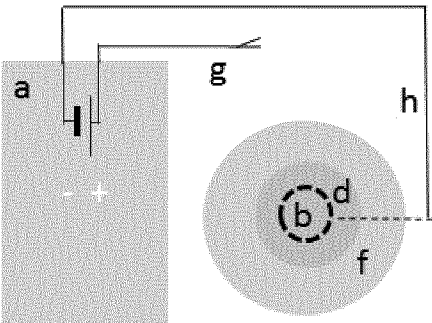


Figure 2a

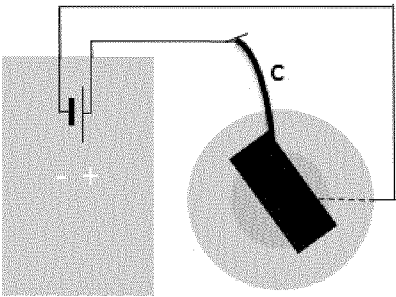


Figure 2b

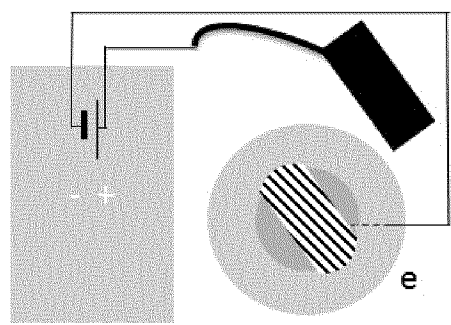


Figure 2c

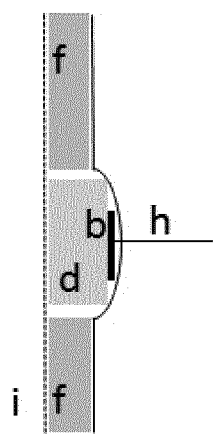


Figure 3



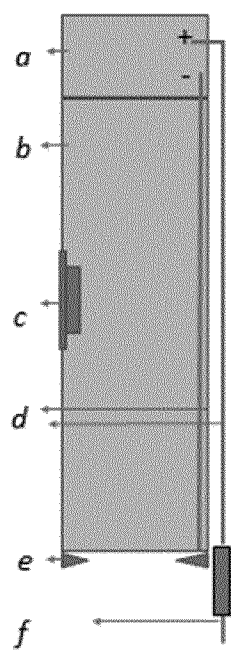


Figure 4a

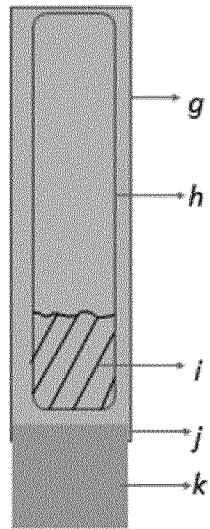
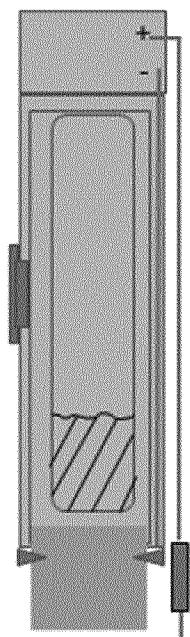
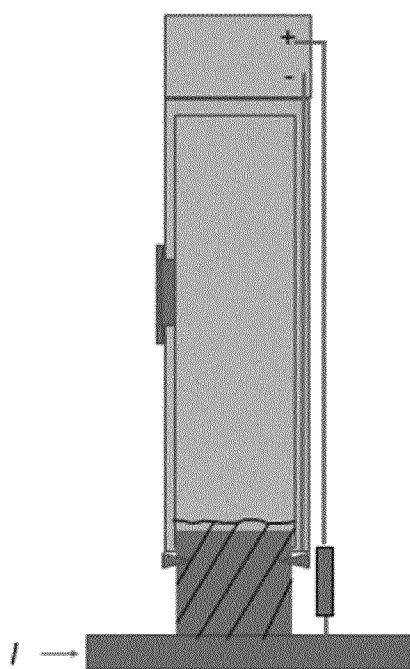


Figure 4b

**Figure 4c****Figure 4d**

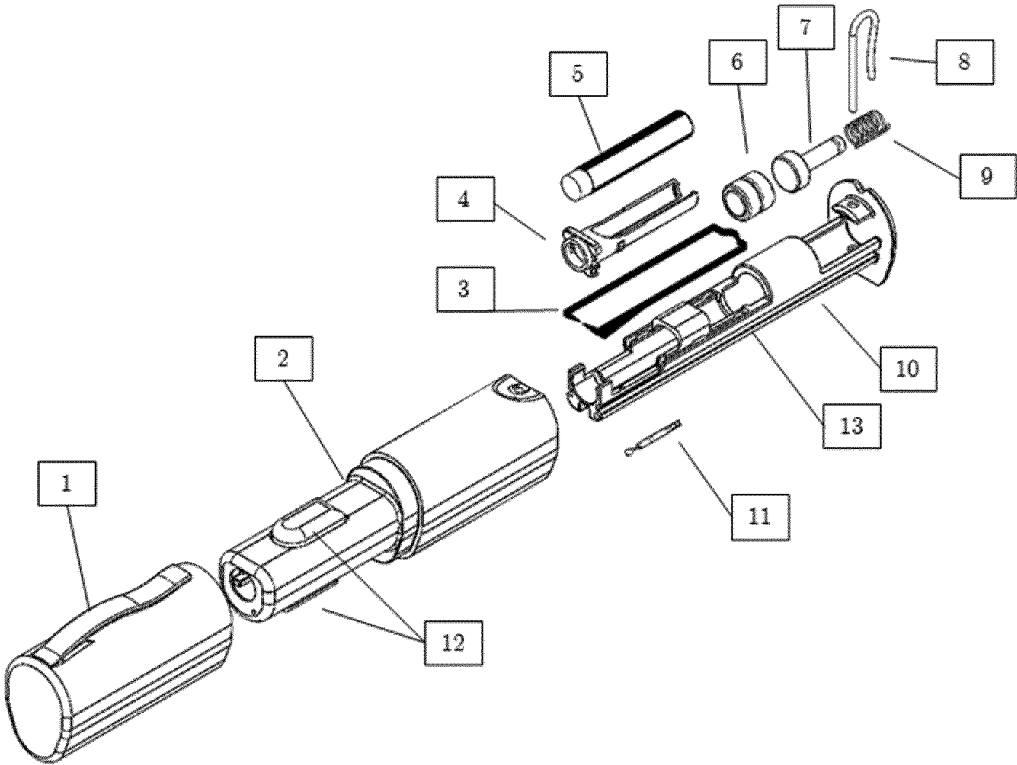


Figure 5.1

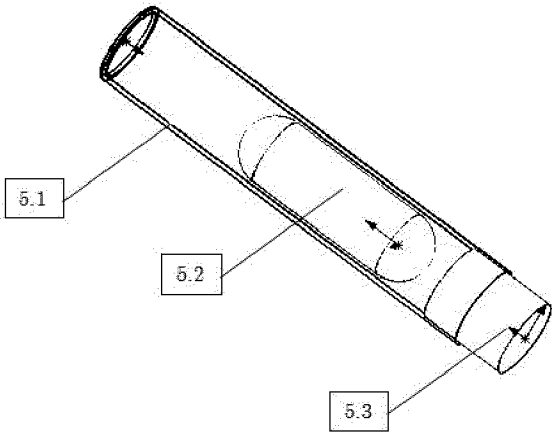


Figure 5.2

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2016/064686

A. CLASSIFICATION OF SUBJECT MATTER  
INV. G01N31/22 G01N27/42  
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)  
G01N

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 practicable, search terms used)

EPO-Internal, WPI Data, BIOSIS, EMBASE, FSTA, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP S56 125660 A (DAIDO STEEL CO LTD) 2 October 1981 (1981-10-02) the whole document -----	1-15
X	JP S56 125659 A (DAIDO STEEL CO LTD) 2 October 1981 (1981-10-02) the whole document -----	1-15
X	JP S56 125658 A (DAIDO STEEL CO LTD) 2 October 1981 (1981-10-02) the whole document -----	1-15
X	JP S56 125655 A (DAIDO STEEL CO LTD) 2 October 1981 (1981-10-02) the whole document ----- -/--	1-15

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

☒ See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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

15 September 2016

Date of mailing of the international search report

22/09/2016

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

Michalitsch, Richard

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2016/064686

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP S56 124043 A (DAIDO STEEL CO LTD) 29 September 1981 (1981-09-29) the whole document -----	1-15
X	JP S56 120944 A (DAIDO STEEL CO LTD) 22 September 1981 (1981-09-22) the whole document -----	1-15
Y	KR 2009 0100510 A (YIEH UNITED STEEL CORP [TW]) 24 September 2009 (2009-09-24) paragraphs [0005] - [0018] -----	1-6
X	US 4 829 007 A (KOSLOW RALF [US]) 9 May 1989 (1989-05-09)	7-15
Y	column 1, lines 1-44 column 4, line 57 - column 5, line 27 -----	1-6

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/064686

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP S56125660	A	02-10-1981	NONE	
JP S56125659	A	02-10-1981	NONE	
JP S56125658	A	02-10-1981	NONE	
JP S56125655	A	02-10-1981	NONE	
JP S56124043	A	29-09-1981	NONE	
JP S56120944	A	22-09-1981	NONE	
KR 20090100510	A	24-09-2009	NONE	
US 4829007	A	09-05-1989	NONE	