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Cosmetics — Analytical methods — Measurement of traces of heavy metals in cosmetic finished products using ICP/MS technique

Cosmétiques — Méthodes analytiques — Détermination de traces de métaux lourds dans les produits finis cosmétiques par ICP/MS

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Foreword

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This document was prepared by Technical Committee ISO/TC 217 *Cosmetics*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This standard specifies an analytical procedure for determination of trace elements (Chromium, Cobalt, Nickel, Arsenic, Cadmium, Antimony and Lead) in finished cosmetics products by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after pressure digestion of the sample. This type of analytical procedure is widely described in other areas such as environment,[1][2][3] food[1][2][3] and pharmaceutical industry [7][8][9][10].

Cosmetics — Analytical methods — Measurement of traces of heavy metals in cosmetic finished products using ICP/MS technique

1 Scope

The aim of this standard is to provide a method of quantification of heavy metal trace elements in cosmetic products that consumers might be exposed to in their usage. In the sample preparation procedure, nitric acid/hydrochloric acid mixture is used and most of the cosmetic ingredients are digested allowing heavy metal trace elements to be solubilized for measurement. Some cosmetic inorganic ingredients such as silica or titanium dioxide might not be completely digested under the conditions of this standard and heavy metal trace elements confined in such ingredients might not be fully extracted. However, the heavy metal trace elements trapped in these inorganic materials are considered less relevant for the evaluation of the exposure level of consumers to unwanted trace elements. The use of ICP-MS ensures reliable measurement of trace elements due to its proven high sensitivity and selectivity.

This analytical methodology can be applied to many other elements but this standard refers only to the above listed trace elements and it is to the responsibility of the analyst to prove that it fits for that purpose. In order to obtain comparable results, it is absolutely mandatory to comply with all the conditions linked to the digestion of the samples.

2 Normative references

There is no normative reference in this document.

3 Principle

Trace elements in cosmetic products are quantified by ICP-MS measurement of the solutions resulting from digestion of the cosmetic products. Digestion takes place with mineral acids in sealed vessels heated to 200ºC by microwaves, producing high pressures.

4 Reagents

The reagents and the water used shall be free of the elements to be determined to such an extent that the results are not impaired. Unless specified otherwise, solutions are understood to be aqueous solutions.

4.1 Ultrapure water, conductivity below 0,1µS/cm-1 at 25°C according to Type 1 water specifications defined in ISO 3696 standard[11]

4.2 Nitric acid, minimum w = 60%, density = 1,38 g/ml

4.3 Hydrochloric acid, minimum w = 30 %, density = 1,15 g/ml

4.4 Internal standard stock solutions

For storage and stability conditions of the internal standard stock solutions, follow the specifications of the suppliers.

4.4.1 **Rhodium stock solution**, 1 000 mg/l

4.4.2 **Lutetium stock solution**, 1 000 mg/l

4.5 **Analytes stock solutions (Chromium, Cobalt, Nickel, Arsenic, Cadmium, Antimony and Lead)**, 1 000 mg/l for each element

Commercially available single element or mixed stock solutions can be used. For this 2 cases, the used stock solutions shall not contain other elements that could interfere with the analytes to be quantified.

4.6 **Commercially available ICP-MS Tune solution**, containing e.g. Ce, Co, Li, Mg, Tl and Y (1 µg/l) according to instrument manufacturer's recommendations.

5 Apparatus and equipment

All apparatus and equipment that come into direct contact with sample or solutions shall be pre-cleaned with dilute nitric acid (6.1) and rinsed with ultrapure water (4.1) to ensure the lowest analyte background. To prevent contamination and adsorption, do not use lab materials made with borosilicate glass.

5.1 Digestion vessels

Use commercially available, safety-tested pressure vessels and inserts made of acid-resistant, low-contamination materials. The assembled vessels shall be able to safely withstand temperatures up to at least 200°C and pressures up to at least 40 bar.

For determination of antimony, use only digestion containers with minimal surface roughness to prevent its adhesion to the container surface (6)[12]. Quartz containers are recommended because they are usually more resistant to attrition. However, Teflon vessels without any scratch or damage on their inner surface or any deposits are appropriate. Scratched or etched containers should not be used. If there is any question regarding possible adsorption of antimony on vessels' walls, test for surface adsorption as described in section 7.3.3.

NOTE Dedicated digestion vessels are recommended for the digestion of cosmetic samples, which may have high levels of elements to be determined. To avoid memory effects, perform a blank digestion to clean vessels after digesting highly loaded samples, before digesting subsequent samples.

5.2 Microwave-assisted digestion instruments

Microwave-heated systems shall be equipped with a temperature measurement unit, which simultaneously regulates the power control of the microwave. Reliable temperature measurement is obtained e.g. through measurement sensors inserted into the pressure vessel. Only use microwave-assisted digestion instruments equipped with temperature sensors and calibrate the temperature sensor before use.

5.3 Membrane filter, 0,45 µm pore size

The membrane filter used shall be inert with regard to the acid concentration of the measurement solution and shall not bring any contamination into the measurement solution or adsorption of the analytes. Several types of membrane material are commercially available (PTFE, PP…) and their fit for purpose must be verified by means of appropriate measurements (blanks, QC samples…).

5.4 ICP-MS

Mass spectrometer with inductively coupled argon plasma is composed of a sample introduction and an atomisation system, as well as an instrument control and evaluation unit. To prevent interferences with the masses of the elements of chromium, nickel, arsenic and cadmium, use of a mass spectrometer that is capable of compensating or minimising such interferences (e.g. collision and/or reaction cell, resolution above 3000, alternatively corrective equations for higher concentrations).

6 Preparation of standards solutions

For all the solutions, the terminology "part" in the standard refers to either volume or weight. That means that standards and samples can be diluted by volume or weight. However, it should be consistent for both standards and samples.

6.1 Diluted nitric acid, produced by mixing nitric acid (**4.2**) with pure water (**4.1**) at a ratio of approximately 1+9 parts respectively.

6.2 Diluting solution

The composition of the diluting solution must have the same acid composition (total content and acid ratio) as the Analytical Solution (the diluted digest solution). This solution should contain:

— 2,5 part of nitric acid (4.2),

— 0,5 part of hydrochloric acid (4.3),

— 97 parts of water (4.1)

6.3 Internal Standard solutions.

The internal standards (IS) selected should cover all the mass range of the considered analytes and have similar ionisation energy to the trace element for which it is used for correction purposes. It shall also be checked that the native concentration of the internal standards in the sample to be analysed is negligible and that they are not interfered by sample constituents.

"Rhodium and Lutetium have proved to be well suited as internal standards (IS). Samples should be checked for negligible native concentrations of the IS and that the IS are not interfered with by sample constituents.

Rhodium is suitable for determination of Chromium, Cobalt, Nickel, Arsenic, Cadmium and Antimony, whereas Lutetium is suitable for determination of Lead. Alternatively, other elements may be used (for example Indium or Iridium). Scandium, however, is not suitable as an IS due to Calcium interferences. An IS with a mass (m/z) below 100 is not recommended because it may suffer from interferences from matrix components.

NOTES : - Internal standard solutions may be added in each sample and calibration solution at the same concentration or may be added through an on line Y-fitting to a pump tube.

- the concentration of the internal standard solutions must be included in the range 1 to 2 mg/l. In the following sections, a concentration of 1 mg/l has been used for all the calculations.

6.3.1 Rhodium(*) standard solution, 1 mg/l

Dilute the Rhodium stock solution (4.4.1) 1 + 999 with diluting solution (6.2). This internal standard solution is stable at room temperature for 6 months.

6.3.2 Lutetium(*) standard solution, 1 mg/l

Dilute the Lutetium stock solution (4.4.2) 1 + 999 with diluting solution (6.2). This internal standard solution is stable at room temperature for 6 months.

(*) NOTE : Indium or Iridium may also be used as internal standards

6.4 Standard solutions

The concentrations of these standard solutions are examples and shall be adjusted to the specific conditions in the laboratories.

6.4.1 High concentration mixed standard solution, 10 mg/l

Dilute 100 times the analyte stock solution(s) (3.5) by adding:

- in the case of single analyte stock solutions, 1 part of each of these 7 solutions to 93 parts of the diluting solution (6.2)
- in the case of mixed stock solution, add 1 part of this solution to 99 parts of the diluting solution (6.2).

This high standard solution is stable at room temperature for 6 months.

6.4.2 Low concentration mixed standard solution, 0.1 mg/l

Dilute 100 times the high concentration standard solution (5.4.1) by adding 1 part of this solution to 99 parts of the diluting solution (6.2). This low standard solution is stable at room temperature for 3 months.

6.5 Calibration blank solution

The calibration blank solution corresponds to the matrix solution without any analyte of interest. Generally, it corresponds to the diluting solution with the suitable concentration of the appropriate internal standards if not added via a Y-fitting during the measurement.

6.6 Calibration solutions

Mixed calibration solutions are prepared by diluting the low concentration mixed standard solution (6.4.2) with the diluting solution (6.2) to levels in the linear range of the instrument and within the targeted concentration range. Include a suitable concentration of the appropriate internal standards, or add on line the internal standards by means of pumping into the sample flow through a Y-fitting. At least 3 calibration solutions with various concentrations should be prepared. These calibration solutions must be prepared daily.

Examples of preparation procedure of calibration solutions are detailed in Table 1a (with addition of the internal standards in all the calibration solutions) and Table 1b (with on line addition of the internal standards via an Y-fitting).

Table 1a — Example of calibration solutions of the ICP-MS – addition of the internal standards in every calibration solution

Calibration solution	**Part of low conc. mixed standard solution** (6.4.2)	**Part of Rhodium standard solution** (6.3.1)	**Part of Lutetium standard solution** (6.3.2)	**Part of the diluting solution** (6.2)	*Analyte conc. in the calibration solution* *(µg/l)*
5.5.0 Calibration blank	0	2	2	496	*0*
5.5.1 Calibration solution 1	2,5	2	2	493,5	*0,5*
5.5.2 Calibration solution 2	5	2	2	491	*1*
5.5.3 Calibration solution 3	10	2	2	486	*2*
5.5.4 Calibration solution 4	25	2	2	471	*5*
5.5.5 Calibration solution 5	50	2	2	446	*10*

Table 1b — Example of calibration solutions of the ICP-MS – online addition of the internal standards via an Y-fitting

Calibration solution	Part of low conc. mixed standard solution (6.4.2)	Part of the diluting solution (6.2)	*Analyte conc. in the calibration solution (µg/l)*
5.5.0 Calibration blank	0	500	***0***
5.5.1 Calibration solution 1	2,5	497,5	***0,5***
5.5.2 Calibration solution 2	5	495	***1***
5.5.3 Calibration solution 3	10	490	***2***
5.5.4 Calibration solution 4	25	475	***5***
5.5.5 Calibration solution 5	**50**	**450**	***10***

7 Procedure

7.1 General

WARNING — The use of this standard can involve hazardous materials, operations and equipment. This standard does not address all the safety problems associated with its use. It is the responsibility of the user of this standard to take appropriate measures for ensuring the safety and health of the personnel prior to application of the standard and to fulfil statutory requirements for this purpose.

7.2 Preparation of samples

Homogenize the samples by means of suitable devices. After homogenization thoroughly clean the devices in order to rule out contamination of the subsequent sample. The sample preparation step shall ensure a homogeneous starting material for a weighed sample quantity.

7.3 Pressure assisted digestion

WARNING 1 Depending on the degree or reactivity of the sample, it may be required to weigh in lower quantities than specified in Section 7.3.1 in order to prevent extreme reactions or explosions. It shall be taken into account that digestion of samples with high carbon contents (e.g. carbohydrates, fats, oils, waxes) may cause explosions. Alcohols or solvents in combination with concentrated nitric acid may cause delayed severe reactions already at room temperature.Therefore it is highly recommended to gently evaporate all volatile components before adding the acid (Section 7.3.2).

WARNING 2 Samples that are not covered by acid can cause local overheating of the digestion vessel and thus lead to local melting and subsequent bursting of the digestion container. Prior to digestion, ensure that the entire sample is fully covered by the acid mixture.

Temperature and pressure into the vessels must be carefully controlled to ensure a proper digestion (section 5.2.). To avoid differences in temperature and pressure among vessels, one should only digest samples with similar composition in the same microwave-assisted digestion batch.

7.3.1 Preparation of Sample by Digestion – General case

Precisely weigh ca. 200 mg of sample into a digestion container.

Add 1 ml of water (4.1) and thoroughly mix with a shaking device until the sample is completely suspended in the water.

Add 5 ml nitric acid (4.2) to the mixture and mix again. The sample should be completely covered with the solution. Allow the mixture to rest in a closed digestion vessel to ensure that the preliminary