INTERNATIONAL STANDARD

ISO 23821

First edition
2022-08

Cosmetics — Analytical methods — Determination of traces of mercury in cosmetics by atomic absorbtion spectrometry (AAS) cold vapour technology after pressure digestion

Cosmétiques — Méthodes d'analyse — Dosage des traces de mercure dans les cosmétiques par la technique de spectrométrie d'absorption atomique (SAA) de vapeur froide après digestion sous pression

Reference number
ISO 23821:2022(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 217, *Cosmetics,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 392, *Cosmetics,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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 document has been developed in parallel with ISO 23674. Knowing this, an interlaboratory test using either one or the other method was performed on same tailor-made cosmetic products in order to establish that both methods fulfilled the same requirements (see Annex B). This method was validated by means of an interlaboratory test according to ISO 5725-2[7] using lipstick, body lotion, toothpaste and eyeshadow, with a mercury concentration in the range of 0,110 mg/kg to 5,84 mg/kg. Statistical characteristics regarding this interlaboratory test are provided in Annex A, Table A.1.

Cosmetics — Analytical methods — Determination of traces of mercury in cosmetics by atomic absorbtion spectrometry (AAS) cold vapour technology after pressure digestion

1 Scope

This document specifies a method for determination of mercury in cosmetics by means of cold vapour atomic absorption spectrometry (AAS) with a prior pressure digestion.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

As a first step, the finished cosmetic product is digested in a closed vessel at high temperatures and pressure using mineral acids. Pressure digestion is carried out at a temperature of 200 °C obtained by means of microwave-assisted heating.

After digestion of the cosmetics, the concentration of mercury is determined by quantification using the AAS cold vapour technology.

During mineralisation of the sample, it is not possible to dissolve all cosmetics without residues, depending on their type and composition. In order to obtain comparable results, it is absolutely mandatory to conform with the conditions specified for this method.

The measurement solution is transferred to the reaction vessel of the mercury analysis unit. From there, mercury is rinsed out into the cuvette of the AAS instrument with the help of a carrier gas flow after reduction with divalent tin or sodium borohydride. Absorption at the mercury line of 253,7 nm is used as a measure for mercury concentration in the cuvette. By using a gold/platinum mesh (amalgam technology) for concentration of the rinsed-off mercury prior to measurement in the cuvette, it is possible to achieve lower limits of quantification (LOQs).

5 Reagents

The reagents and the water used shall be free of mercury to such an extent that the analysis is not impaired. Unless specified otherwise, pure-analysis chemicals shall be used, and solutions are

understood to be aqueous solutions. Use water conforming to Grade 1 of ISO 3696 (conductivity below 0,1 µS/cm at 25 °C).

5.1 Hydrochloric acid, minimum mass fraction w = 30 %, density = 1,15 g/ml, suitable for elemental analysis.

5.2 Nitric acid, minimum w = 65 %, density = 1,4 g/ml, suitable for elemental analysis.

5.3 Diluted nitric acid, produced by mixing nitric acid (5.2) at a ratio of approximately 1 + 9 with water respectively.

5.4 Reducing agents, for example tin(II) chloride or sodium borohydride.

Alternating operation with both reducing agents (5.4.1 and 5.4.2) is not recommended. For this purpose, the appropriate information from the manufacturer of the instrument shall be followed.

The mass concentrations of the reducing agent solutions can vary, depending on the system. The corresponding data of the manufacturer of the instrument shall be conformed with.

5.4.1 Tin(ll) chloride solution, for example mass concentration ρ = 100 g/l.

Weigh 50 g tin(ll) chloride, $SnCl_2 \cdot 2H_2O$ in a 500 ml volumetric flask, dissolve in approximately 100 ml hydrochloric acid (5.1), and fill up to 500 ml with water. The solution shall be freshly prepared prior to use.

5.4.2 Sodium borohydride solution, for example ρ = 30 g/l.

Dissolve 3 g of sodium borohydride and 1 g of sodium hydroxide pellets in water and fill up with 100 ml water. The solution shall be freshly prepared every day and filtered prior to use.

WARNING — Compliance with the safety instructions is mandatory when working with sodium borohydride. Sodium borohydride forms hydrogen when combined with water and especially on reaction with acids, which can result in an explosive air/hydrogen mixture. A fixed exhaust system shall be installed/present in the area where measurements are carried out.

5.5 Stabilization

The standard, calibration and sample digestion solutions are stabilized with hydrochloric acid (5.1). It is recommended to set a hydrochloric acid concentration of around ω = 1 % in the solutions. Alternative stabilizing reagents can also be used (see Clause 10).

5.6 Mercury stock solution, mercury ρ = 1 000 mg/l.

The stock solution is commercially available. It is recommended to use certified stock solutions.

5.7 Mercury standard solutions

Dilute the stock solution to the concentrations required for calibration and add the necessary amount of stabilisation reagent (5.5). In doing so, select concentrations that the linear range of the reference function is not exceeded. It is recommended to use at least three (3) standard solutions with different concentrations.

The acid concentration in the standard solutions shall correspond to the acid concentration of the measurement solution. Mercury standard solutions have a rather short shelf life, even at higher concentrations; therefore, they shall be freshly prepared every day.

5.8 Calibration blank solution

The calibration blank solution shall contain water, the same amount of stabilisation reactant as the mercury standard solutions (5.7) per litre and the quantities of nitric acid (5.2) and hydrochloric acid (5.1) that correspond to the acid concentrations in the measurement solution.

6 Apparatus and equipment

For the determination of mercury all apparatus and equipment that come into direct contact with the sample and the solutions used shall be thoroughly pre-treated to ensure minimisation of contamination. The following steps are recommended for cleaning: Rinse with drinking water, treat with a scouring agent solution, repeat rinsing with drinking water and soak in diluted nitric acid (5.3) over night or a prolonged period. Prior to use, rinse the apparatus with ultrapure water and dry. Steaming of chemically inert vessels (e.g. made of quartz glass) using nitric acid (5.2) is an effective cleaning method and is regularly used in element trace analysis. To prevent contamination and adsorption, only use lab materials made with borosilicate or quartz glass.

6.1 Digestion vessels.

Use commercially available, safety-tested pressure vessels and inserts made of acid resistant and, 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. The specific size of the vessels is not mandatory and depends on the used type of microwave.

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 sequent samples.

6.2 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, for example, 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.

6.3 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 (e.g. PTFE, PP) and their fit for purpose shall be verified by means of appropriate measurements (e.g. blanks, QC samples).

6.4 Atomic absorption spectrometer, optionally available with background correction and including accessories for cold vapour technology or amalgam technology.

Flow injection systems can be used as an alternative of manual processes.

6.5 Element-specific light for mercury

Measurement at 253,7 nm.

7 Procedure

7.1 General

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

During all process steps it shall be ensured that there are no losses of analyte and that contamination is kept as low as possible.

7.2 Preparation of samples

Before the digestion of the sample, a suitable preparation shall be carried out (e.g. homogenizing, mixing, crushing[13]). 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 test portion quantity.

7.3 Pressure assisted digestion

7.3.1 General

WARNING 1 Depending on the type of reactivity of the sample, it can be required to weigh in lower quantities than specified in 7.3.2 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) can cause explosions. Alcohols or solvents in combination with concentrated nitric acid can cause delayed severe reactions already at room temperature. Therefore, it is highly recommended to gently evaporate all volatile components before adding the acid (7.3.3).

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 vessel. Prior to digestion, ensure that the entire sample is fully covered by the acid mixture.

Temperature and pressure inside the vessels shall be controlled to ensure a proper digestion. To avoid differences in temperature and pressure among vessels, one should only digest samples with similar composition in the same microwave-assisted digestion batch.

7.3.2 Preparation of sample by digestion — General case

Precisely weigh about 200 mg of sample into a digestion vessel.

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

Add 5 ml nitric acid (5.2) 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 reaction takes place. Depending on the reactive behaviour of the sample the duration of the preliminary reaction can require resting periods of 30 min up to overnight.

Then add 1 ml of hydrochloric acid (5.1) and briefly mix. After addition of the hydrochloric acid, the pressure vessel shall be closed and sealed immediately to make sure that the formed chlorine gas is available for the reaction and does not evaporate.

7.3.3 Preparation of sample by digestion — Specific cases

— For highly water-based cosmetic products, such as lotion, milky lotion, cleanser or micellar water, a test portion could reach 400 mg. In this case no addition of water is required before addition of acids (7.3.2).

— For all the other specific cases, test portion can be adapted but the ratio between test portion and acid volumes (7.3.2) shall not be changed.

In case of products with a significant content of volatile components, for safety reasons, it is highly recommended to remove volatile components by carefully heating up the sample (e.g. in a water bath at 60 °C) after weighing the sample in the digestion vessel, but prior to the addition of the acid. The loss of volatile components should be determined at the end of the process. In this context, special care shall be taken to prevent losses of the specific elements.

Due to sample heterogeneity concern, a test portion below 100 mg is not recommended.

7.3.4 Microwave digestion procedure

WARNING 1 During all steps of the digestion process, the manufacturer's safety information shall be accurately followed.

7.3.4.1 Process the samples using, for example, a three-step heating program:

a) ramp the heat up from room temperature to 200 °C in, for example, 30 min;

b) hold the temperature at 200 °C for 30 min;

c) cool down to 50 °C, before removing the vessels from the microwave.

It is mandatory to maintain a temperature of 200 °C for 30 min to obtain comparable results, since complete digestion is not possible for all types of samples.

WARNING 2 Depending on reactivity of the sample, it can be necessary to select a lower heat-up rate than specified in order to prevent extreme reactions or explosions.

7.4.3.2 For reactive samples, a 7-step heating program with a slower heating ramp has been efficiently used:

a) ramp the heat up from room temperature to 160 °C in 25 min;

b) hold the temperature at 160 °C for 15 min;

c) ramp the heat up from 160 °C to 180 °C in 10 min;

d) hold the temperature at 180 °C for 10 min;

e) ramp the heat up from 180 °C to 200 °C in 35 min;

f) hold the temperature at 200 °C for 30 min;

g) cool down to 50 °C, before removing the vessels from the microwave.

NOTE This information is given as an example of program that can be used in case of reactive samples. This alternative digestion program was not included in the validation studies. It is up to the user to show equivalency when used.

7.3.5 Preparation of measurement solutions

The digestion solution obtained after pressure digestion is filled up with water after cooling to obtain a defined volume, for example 20 ml, and is used for measurement. If required, further dilution steps can be performed using calibration blank solution (5.8).

Ensure that the measurement solution obtained in this way contains the same acid concentrations as the calibration solutions prepared according to 5.7.

Remove any residue by decanting or filtering the final solution by a membrane filter (6.3).