TECHNICAL REPORT

ISO/TR 17276

First edition
2014-05-01

Cosmetics — Analytical approach for screening and quantification methods for heavy metals in cosmetics

Cosmétiques — Approche analytique des méthodes pour l'évaluation et la quantification des métaux lourds dans les cosmétiques

Reference number
ISO/TR 17276:2014(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

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 on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 217, *Cosmetics*.

Introduction

Heavy metals occur naturally in the environment. Some heavy metals are utilized in many industries, and some in very small amount are essential minerals to life. On the other hand, heavy metals are often a concern due to their toxicity. Even for essential minerals, they can be a concern when excess amounts are ingested, or more generally, when the human exposure is too high, independently of the route of exposure.

Heavy metals are ubiquitous as they are found in nature (rocks, soil, water, amongst other sources). As such, these heavy metals can be found as impurities in raw materials, and, while not added intentionally to cosmetics, might be present as traces in finished products.[1][2]

The term "heavy metals" is widely used without a single definition. Commonly recognized heavy metals include, but are not limited to: lead, mercury, cadmium, arsenic, and antimony.

While it is acknowledged that heavy metal traces in cosmetic products are unavoidable due to the ubiquitous nature of these elements, companies have implemented numerous measures to monitor and control the amount that might be present.

This Technical Report presents the most common and typical analytical methods and tools for the detection of heavy metals in cosmetic raw materials and finished products.

Cosmetics — Analytical approach for screening and quantification methods for heavy metals in cosmetics

1 Scope

This Technical Report introduces most common and typical analytical approaches for screening and quantification of heavy metals of general interest at both raw material and finished product level. This Technical Report covers techniques from traditional colourimetric reaction, which can be executed without expensive instrument to the high-end one, like that of inductively coupled plasma-mass spectrometry (ICP-MS), which allows detection of elements at μg/kg level. Thus, this Technical Report covers the advantages and disadvantages of each analytical technique so that a suitable approach can be chosen.

The intent of this Technical Report is not to set or suggest acceptable concentration limits of heavy metals in both raw materials and finished products which have to be determined by each regulatory authority.

NOTE 1 The term “heavy metals” is widely used without single definition.

NOTE 2 Elements can be specified as heavy metals by one legislation, while not by others.

2 Principles

2.1 Planning

First, the approach is divided into screening and quantification of total heavy metals content. Heavy metals analysis requires not only technical knowledge and experience, but often requires expensive facilities and vigorous condition of sample preparation, especially when quantification of heavy metals content is investigated. The screening approach can contribute to identifying whether heavy metals levels should be determined using more quantitative methods.

An approach to analyse heavy metals in cosmetics products and raw materials consists of sample preparation method and detection method. Analytical testing conditions should be determined with appropriate combination of preparation method and detection method with acceptable validation data.

Sample preparation methods:

- leaching;
- digestion.

Detection tests and methods:

- colourimetric reaction;[3-8]
- x-ray fluorescence (XRF);
- atomic absorption spectrometry (AAS);
- inductively coupled plasma optical emission spectroscopy (ICP-OES), which is also known as inductively coupled plasma atomic emission spectroscopy (ICP-AES);
- inductively coupled plasma mass spectrometry (ICP-MS).

These approaches basically do not detect a difference between organic and inorganic compounds of an element. For example, they do not detect difference between metallic mercury and a phenylmercury compound. Also, they do not detect difference by valence state, such as, between chromium (III) and chromium (VI). If there is a specific interest in them, appropriate approaches should be taken, e.g. ICP-MS equipped with chromatography.

Typical approach for the screening and quantification on both raw materials and finished products are introduced in the Annex A, Annex B, and Annex C. Approaches other than introduced in the annexes can be effective.

2.2 Selection of a test substance

Screening and quantification of heavy metals can be performed on both raw materials and finished products.

As heavy metals are found in nature, certain raw materials, such as, inorganic materials can naturally contain heavy metals. Knowing the source and signature of raw materials is an effective approach to control the levels of heavy metals in finished products. Monitoring at raw material level can avoid the use of heavy-metal contaminated raw materials and is an effective way to control heavy metal concentration in finished products.

2.3 Preparation of samples

2.3.1 General

In many elemental analysis techniques, samples are converted into liquid. The preparation of the samples is related to the nature of the cosmetic matrix. The sample preparation techniques are basically classified into two: leaching method and digestion method.

2.3.2 Leaching method

Leaching method is a preparation method in order to determine an amount of heavy metals extracted from a sample under acidic conditions. The principle of the leaching method is modelling the conditions of a gastrointestinal fluid or sweat to liberate heavy metals that might be present in products. This allows estimating an amount of heavy metals to which users can be exposed.

2.3.3 Digestion method

Digestion method is a preparation method in order to determine the total amount of heavy metals present in a sample. When full digestion method is used, it reliably reveals the worst case scenario of exposure. Also, full digestion of the matrix reduces interferences in the detection, especially in ICP-MS.

Samples are sometimes simply heated to ashes (dry ashing) in order to remove organic matter. Dry ashing can be carried out with magnesium nitrate as ashing aids.[9][10] Other ashing aids might be applicable such as magnesium sulfate with sulphuric acid.[8] Since cosmetic matrix is complex, insoluble matter often remains after ashing and further digestion is often conducted.

Samples are digested by heating, usually with a single acid, sometimes with multiple acids (wet digestion), rarely with alkali (fusion), in open or closed vessels and are fully or almost entirely dissolved. It often requires vigorous conditions and cautions concerning possible volatilisation for some metals (such as cadmium, arsenic, or mercury) to obtain acceptable recovery.[8][11]

Recent trends are for closed vessel digestion with microwave assistance which can reduce losses of volatile elements and also improve efficiency in routine analysis. Choice of acids is the important factor to fully digest samples. For cosmetic products, the usage of hydrofluoric acid (HF) can be considered highly effective in digestion of silica compounds. The treatment with hydrofluoric acid needs a post-treatment with boric acid in order to mask remaining HF. Nitric acid, hydrochloric acid, sulphuric acid, and other acids are also selected to digest samples. Each acid, including HF, has their own advantage and therefore often used by combination to effect full digestion. There are many publications for heavy metals analysis, including assessments of sample digestion methods. There is a digestion method recently published with inter-laboratory results for lead, cadmium, and mercury on different finished products containing inorganic materials. This method describes a digestion process using nitric acid with hydrochloric acid in a closed vessel under high pressure heat to around 200 °C. The method specifies the detailed conditions in order to get reproducible results.[12] The study by the authority reports that analytical results obtained by nitric acid and those by nitric acid with HF, in comparison. Nitric acid digestion gave lower results than nitric acid with HF on some cosmetic products.[13] Nevertheless, if possible, it is recommended to avoid the use of hydrofluoric acid for safety and hygiene reasons, within the digestion.

2.4 Detection tests and methods

2.4.1 Colourimetric reaction

This technique has been described as detection test, mostly for raw materials, for heavy metals which form yellow to dark brown-coloured insoluble sulphide under pH 3,0 to 3,5 condition. Elements which can be detected by this technique are for instance, lead, bismuth, copper, cadmium, antimony, tin, and mercury.[8] The insoluble sulphide produced in the reaction shows dark colour in diluted solutions due to its colloidal dispersion. As the source of sulphide ion, either sodium sulphide or thioacetamide is normally used. The density of colour is increased in proportion to the concentration of heavy metals. The quantity of heavy metals is expressed in terms of concentration of lead, in comparison with a lead reference solution. The advantage of the technique is that it can be performed without expensive instruments. The colourimetric test is only applicable for sample solutions which are uncoloured and free from insoluble matter. Recovery should be determined in an accurate and suitable way, especially if dry-ashing is used to obtain such solutions. This technique cannot detect selenium and chromium. Also, zinc produces white precipitate which can cause interference. For this reason, it is important to confirm the reliability of the test by appropriate validation.

When difference in the hue of the developed colour is observed between samples solution and standard solution, other techniques should be explored.

NOTE Applications of colourimetric tests are found in several compendia for cosmetics and pharmaceuticals[3-7] such as Japanese Standards of Quasi-drug Ingredients (JSQI)[3] and European Pharmacopoeia.[4] Also, the Japanese Standards of Cosmetics Ingredients[5] and Japanese Cosmetics Ingredients Codex[6] can still be referred for actual applications, especially for English description, although they are not active compendia anymore as they have basically been consolidated to JSQI.

2.4.2 X-ray fluorescence

2.4.2.1 General

When a sample is irradiated with X-rays which have energy above a certain level, core electrons in atoms are excited, ejected, and then core holes are created. Subsequently, peripheral electrons fall into the created core holes and the excess energy which corresponds to the energy level difference are released as electromagnetic waves in the X-ray region called “X-ray fluorescence”[14]. Since the energy level difference is unique to each element, the emitted X-ray fluorescence is also termed a characteristic X-ray. Identification of the element is possible using these X-ray spectra and the elemental concentration in the sample can be estimated from the X-ray intensity. The advantage of this technique is that it is non-destructive analysis. Various sample forms such as solid, liquid, or powder are applicable for the measurement. The measurements are performed easily and quickly without complicated sample preparation. Complexity would be realized in quantitative or semi-quantitative analysis because this technique is matrix-dependent, and therefore, correction or appropriate validation would be required. For certain elements, sufficient sensitivity can not be obtained, particularly with portable equipment.

2.4.2.2 Types of equipment

Equipment can roughly be classified into two according to detection principles, one is the energy-dispersive type and the other one is wavelength-dispersive type. Each type has particular features, therefore, their advantages and disadvantages should be considered to select suitable one.

2.4.2.2.1 Energy-dispersive type

Its feature is a semiconductor detector. Since the detector itself has energy resolution, the configuration of the equipment can be simplified in comparison to the wavelength type. For this reason, size of the equipment is smaller than the wavelength-dispersive type. Disadvantages are lower sensitivity, and generally resolution is low as well compared to wavelength-dispersive type. The elements to be detected are generally from sodium to uranium, and sensitivity tends to be lower in lighter elements.

2.4.2.2.2 Wavelength-dispersive type

The advantages are high detection sensitivity and high energy resolution. The disadvantage is large equipment size. The elements to be detected are generally from beryllium to uranium. The X-ray fluorescence generated from the sample goes through a solar slit to be a parallel luminous flux. Then it strikes an analysing crystal to be diffracted so that specific wavelength is picked up by the detector.

Several types of analysing crystals are available. A crystal with appropriate intervals between crystalline surfaces has to be selected according to the wavelength range to be analysed. As for an X-ray detector, a proportional counter tube type is generally used for light elements (beryllium to scandium), and a scintillation counter is generally used in the detection of X-ray fluorescence having a short wavelength of around 0,2 nm to 0,3 nm or less (titanium to uranium).

2.4.3 Atomic absorption spectrometry (AAS)[15]

2.4.3.1 General

Electrons of atoms in the atomizer can be promoted to an excited state in nanoseconds by absorbing a defined quantity of energy radiation of a given wavelength. This amount of energy is specific to a particular electron transition for each element. In general, each wavelength corresponds to only one element. The signal without a sample and with a sample in the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyte concentration using Beer-Lambert law.

The technique requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on Beer-Lambert law.

The AAS is composed of radiation source, atomization chamber, monochromator, detector, and readout device. In order to analyse a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames and graphite tube atomizers.

AAS is a very common technique with a good sensitivity and a good specificity. Interference can occur for some elements in the presence of nitric acid with high amounts of iron, aluminium, and silicium. The main disadvantages are its mono-elemental capability requirement for complete dissolution of the samples (except the special application of graphite-furnace AAS with solid sample introduction) and the relatively high cost.

2.4.3.2 Flame AAS

In flame AAS, the sample solution is introduced into a flame of acetylene and an oxidation gas, such as air or nitric oxide, and the elements can be atomized. Flame AAS shows high sensitivity on the detection of alkaline metals and alkaline earth metals.

2.4.3.3 Hydride generation AAS (HG-AAS)

This technique is effective for the elements which are reduced to volatile hydrides by sodium tetrahydroborate ($NaBH_4$). Therefore, the applicable elements are limited, such as arsenic, bismuth, antimony, and selenium. Volatile hydrides are separated from matrices by introduction into an atomisation chamber. As a result, HG-AAS shows high sensitivity for these elements.

2.4.3.4 Graphite furnace AAS (GF-AAS)

In GF-AAS, an either liquid or solid sample is introduced into the graphite tube where it dries through electrical heating, and the residues are ashed. In order to achieve repeatability, accuracy, and higher sensitivity, use of platform for graphite tube is recommended. Matrix modifier is used when target elements are highly volatile in order to minimize the loss of the elements during heating. In a subsequent heating step at very high temperatures, elements present in the residue are atomized. During this phase, the attenuation of the lamp radiation by the atomization in the narrow volume of the graphite tube can be measured. GF-AAS generally shows higher sensitivity than flame-AAS on many elements, while background correction is required due to the use of high temperature. A background correction often applied is Zeeman background correction or deuterium background correction.

2.4.3.5 Cold vapour AAS (CV-AAS)

The analysis of mercury sometimes requires specially designed sample preparation techniques due to its physico-chemical behaviour and requires either a dedicated preparation of the sample or a dedicated technique. Since mercury does not require high temperature to be atomized, the technique called cold vapour is often used for the analysis by taking advantage of its property. Mercury is atomized either by reduction using reducing agents such as stannous chloride or by heating. Heating method is sometimes followed by amalgamation with gold to selectively introduce mercury to a cell to obtain higher sensitivity. Instruments specialized for mercury analysis are commercially available by taking advantage of its property.[10][16][17]

2.4.4 Inductively coupled plasma (ICP)

2.4.4.1 General

ICP has excellent ability to excite or ionize elements because of its very high temperature plasma.[18-20] When the torch of the ICP is turned on, an intense electromagnetic field is created. Argon gas flowing through the torch is ignited, and then, the plasma is created. The flow of argon to maintain the plasma is high (~20 l/min), and the temperature of the plasma is approximately 7 000 K or higher. In most cases, sample solution is introduced into a nebulizer by a peristaltic pump to create a mist. The mist is introduced directly into the argon plasma, immediately collides with the electrons and charged ions of the plasma, and elements of sample become ions. Molecules are destroyed into their respective atoms which lose electrons, and provoke light emission at the characteristic wavelengths of the elements involved. Detectors are either MS or OES, MS detectors detect ionized atoms on the basis of m/z, OES detectors utilizes the light emitted by excited atoms.[21]

2.4.4.2 ICP-OES

If the ICP is equipped with an optical spectrometer (ICP-OES), the intensity of this emission corresponds to the concentration of the element within the sample. The ICP-OES has good sensitivity, but some spectral interference should be considered (many emission lines as in the case of iron). Some interference equation can decrease this phenomenon.

2.4.4.3 ICP-MS

If the ICP is equipped with a mass detector (ICP-MS), the abundance of ions (isotopes) corresponds to the concentration of the sample. For ICP-MS, the plasma has higher temperature to increase ion production. Some mass interferences, such as polyatomic or isotopic can occur. Interference equation can be used, or some modern equipment install collision cell or high resolution analysers to decrease or eliminate this problem.

The great advantages of the ICP-OES and ICP-MS are the multi-element capability and the linear dynamic range. Cost and the fact that samples typically should be in solution are the main disadvantages.