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Rubber, raw, vulcanised — Determination of metal content by ICP-OES

Caoutchouc brut, vulcanisé — Dosage de la teneur en métaux par ICP-OES

Reference number
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Foreword

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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).

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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 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

Introduction

The ICP-OES (inductively coupled plasma – optical emission spectrophotometer) instrument is used to determine the concentrations of certain elements in materials of interest. The main advantage of ICP-OES over the AAS (atomic absorption spectroscopy) techniques in general is its multi-element capability, its longer linear dynamic ranges and fewer condensed phase interferences. In addition, besides the refractory compound-forming elements, elements such as iodine, phosphorus and sulfur are detected with more sensitivity by the ICP-OES technique. ICP-OES is also known as ICP-AES (inductively coupled plasma – atomic emission spectrophotometer).

ICP-OES was first introduced as a technique for trace elemental analysis. The technique experiences the least interference of any of the commonly used analytical atomic spectrometry techniques. Chemical interferences are largely eliminated by the high temperature of the plasma. Physical interferences can be compensated for by taking advantage of the ICP's multi-element capability.

In ICP-OES, the light emitted by the excited atoms and ions in the plasma is measured to obtain information about the sample. Because the excited species in the plasma emit light at several different wavelengths, the emission from the plasma is *polychromatic*. This polychromatic radiation has to be separated into individual wavelengths so the emission from each excited species can be identified and its intensity can be measured without interference from emission at other wavelengths.

An important feature of the ICP that is not common to most other emission sources is that since the sample aerosol is introduced through the centre of the ICP, it can be surrounded by the high temperature plasma for a comparatively long time, approximately 2 ms. It is this long residence time of the analyte particles in the centre of the plasma that is largely responsible for the lack of matrix interferences in the ICP.

The determination described in this International Standard is important with respect to product safety and the environment. ICP-OES is a state-of-the art instrument for accurate detection of the trace metals in raw and vulcanized samples of rubber including latex.

Rubber, raw, vulcanised — Determination of metal content by ICP-OES

WARNING 1 — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

WARNING 2 — Certain procedures specified in this International Standard may involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This International Standard describes the method of determination of both major and trace levels of metal contents in rubber — raw, vulcanized — by ICP-OES.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 123, *Rubber latex — Sampling*

ISO 124, *Latex, rubber — Determination of total solids content*

ISO 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

ISO 18899:2013, *Rubber — Guide to the calibration of test equipment*

3 Principle

An aqueous sample is converted to an aerosol via a nebulizer. The aerosol is transported to the inductively coupled plasma which has a high temperature zone (8 000 °C to 10 000 °C). The analytes are heated (excited) to different (atomic and/or ionic) states and produce characteristic optical emissions. These emissions are separated based on their respective wavelengths and their intensities are measured (spectrometry). The intensities are proportional to the concentrations of analytes in the aqueous sample. The quantification is carried out via an external multipoint linear standardization obtained by comparing the emission intensity of an unknown sample with that of a standard sample. A process flow of atomization of sample in ICP-OES is shown in Annex B.

4 Reagents

Use only reagents of recognized analytical grade, unless otherwise specified, and distilled or deionized water or water of equivalent purity.

4.1 Ultra-pure grade of concentrated nitric acid, density 1,42 g/ml.

4.2 Ultra-pure grade of concentrated hydrochloric acid, density 1,19 g/ml.

4.3 Ultra-pure grade of concentrated sulfuric acid, density 1,83 g/ml.

4.4 Multi-element primary standard solution, traceable to NIST (National Institute of Standards and Technology) or any national metrological institute (NMI).

4.5 Single-element primary standard solutions, traceable to NIST or any NMI.

4.6 Ammonium oxalate saturated solution.

4.7 Yttrium solution, 1 000 µg/g.

4.8 Diluted nitric acid.

4.9 Diluted HCl.

5 Apparatus

Usual laboratory apparatus and glassware and, in particular, the following.

5.1 ICP-OES system. A portion of the photons emitted by the ICP is collected with a lens or a concave mirror. This focusing optic forms an image of the ICP on the entrance aperture of a wavelength selection device such as a monochromator. The particular wavelength exiting the monochromator is converted to an electrical signal by a photodetector. The signal is amplified and processed by the detector electronics, then displayed and stored by a personal computer. Different components of the instruments are shown in Figure 1. A description of the different components is given in 5.1.1 to 5.1.4.

5.1.1 Test solution introduction, to produce a steady aerosol of very fine droplets. There are three basic parts to the sample introduction system as listed in 5.1.1.1 to 5.1.1.3.

5.1.1.1 Peristaltic pump, to draw up the test solution and deliver it to the nebulizer.

5.1.1.2 Nebulizer, to convert the solution to an aerosol that is sent to the spray chamber.

5.1.1.3 Spray chamber, to filter out the large, uneven droplets from the aerosol.

5.1.2 Energy source, to get atoms sufficiently energized such that they emit light. There are three basic parts to the energy source as listed in 5.1.2.1 to 5.1.2.3.

5.1.2.1 Radio frequency generator, to generate an oscillating electro-magnetic field at a frequency of 27,12 MHz. This radiation is directed to the load coil. Equipment are also available with electro-magnetic field at a frequency of 40,68 MHz.

5.1.2.2 Load coil, to deliver the radiation to the torch.

5.1.2.3 Torch, having argon flowing through it which will form a plasma in the RF field.

5.1.3 Spectrometer, to diffract the white light from the plasma into wavelengths. There are several types of spectrometers used for ICP. Regardless of type, all of them use a diffraction grating.

5.1.4 Detector, to measure the intensity of the wavelengths. The detector is a silicon chip that is composed of many individual photo-active sections called “picture elements”. These picture elements, or pixels, will build up charge as photons impinge on them. Individual pixels are of a size such that they can be used to measure individual wavelengths.

5.2 Analytical balance, capable of weighing to the nearest ± 0,1 mg.

5.3 Micro syringe, calibrated.

5.4 Hot plate.

5.5 Pipettes, of different capacities i.e. 10 ml, 20 ml.

5.6 Micro-Kjeldahl digestion flask.

5.7 Muffle furnace.

5.8 TFM (tetrafluoroethylene modified) vessel.

5.9 Microwave digestion system.

5.10 Sample rack of autosampler.

5.11 Filter paper, Whatman No. 44.

5.12 Silica or platinum dish.

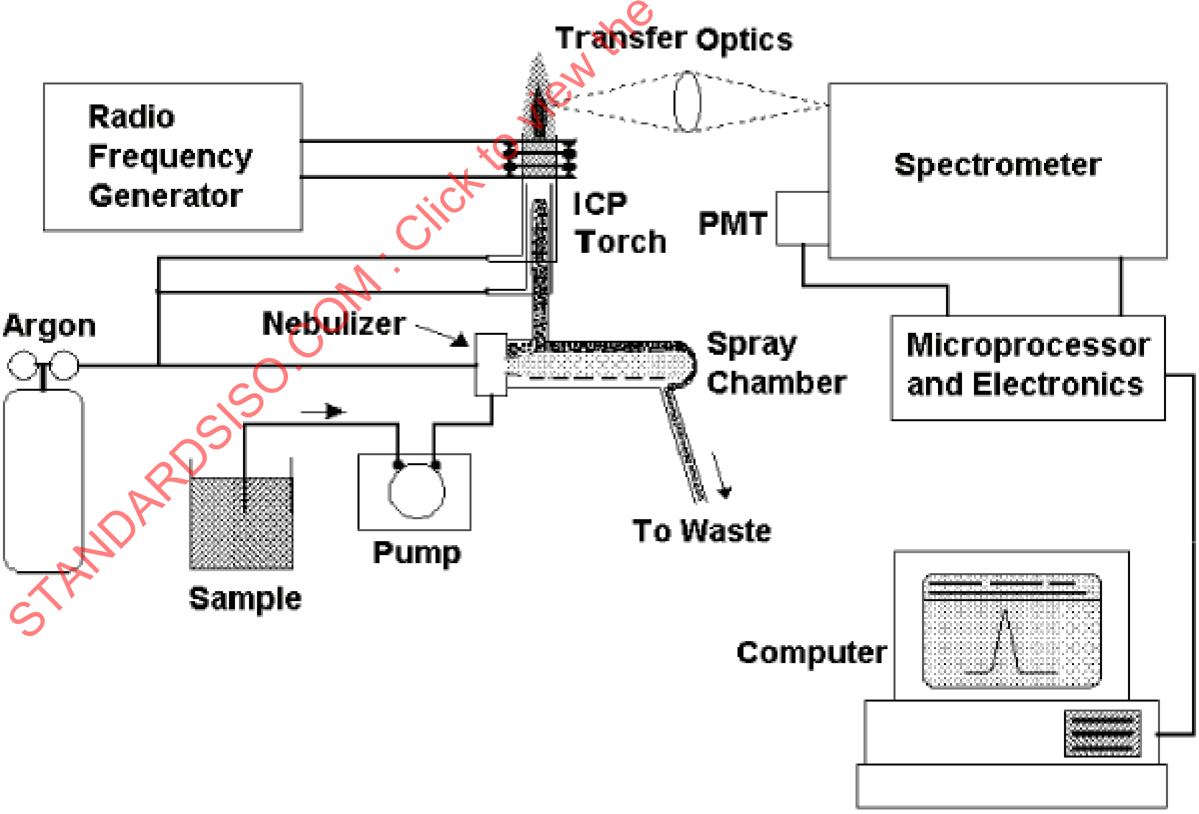

Figure 1 — Different components of a typical ICP-OES instrument

6 Calibration

The instrument shall be calibrated in accordance with the schedule given in Annex A.

7 Sample preparation

7.1 General

There are four major steps involved in the analysis of metal contents.

a) obtaining a representative laboratory sample from the bulk received for testing;

b) decomposition of organic matter;

c) separation and concentration of the element of interest;

d) determination.

7.2 Sampling

For solid rubber, take the laboratory sample and prepare the test piece in accordance with the method specified in ISO 1795.

For latex, take the laboratory sample in accordance with ISO 123 and prepare the dry latex test piece as specified in ISO 124.

7.3 Decomposition of organic matter

The commonly used methods of destruction of organic matter are:

a) wet oxidation (see 7.3.1);

b) dry ashing (see 7.3.2);

c) microwave digestion (see 7.3.3).

7.3.1 Wet oxidation

7.3.1.1 Transfer 0,5 g to 1,0 g of the test piece into a micro-Kjeldahl digestion flask.

7.3.1.2 Add 20 ml concentrated nitric acid and up to 20 ml water. Boil the contents of the flask to reduce the volume to 20 ml. Cool the solution, add 10 ml of concentrated sulfuric acid and boil again. Add further small quantities of nitric acid whenever the contents begin to blacken. When the addition of nitric acid is no longer necessary (i.e. when the liquid no longer blackens) continue heating till white fumes are evolved.

7.3.1.3 At this stage, cool the solution and add 10 ml of saturated ammonium oxalate solution and again boil until white fumes are again produced. The oxalate treatment assists in removing yellow coloration due to nitro compounds, so that the final solution is colourless. Make the final volume of 50ml in a polypropylene bottle using deionized water.

7.3.1.4 Blanks shall be prepared with the same quantities of the reagents as are used in the test but omitting the test portion.

Precaution should be taken during the wet oxidation procedure in case of titanium and tin.

7.3.2 Dry ashing

7.3.2.1 Weigh accurately 0,5 g to 1,0 g of the test piece in a tared silica or platinum dish.

7.3.2.2 Heat the dish firstly by means of a soft flame or hot plate to volatilise as much organic matter as possible, then transfer it to a temperature controlled muffle furnace held at about 300 °C.

7.3.2.3 Once the material has dried and charred, increase the temperature to 550 °C and ash at this temperature till no carbon remains. If it is suspected that all carbon has not been removed, cool the ash, add about 1 ml to 2 ml of concentrated nitric acid, evaporate to dryness and heat again in the muffle furnace.

7.3.2.4 After ashing is complete, remove the dish from the muffle furnace, cool, cover the dish with a watch glass, and gently add 40 ml to 50 ml of hydrochloric acid (1+1). Rinse down the watch glass with water and heat on a steam bath for 30 min, remove the cover and rinse. Continue heating for another 30 min.

7.3.2.5 Add 10 ml of hydrochloric acid (1+1) and water to dissolve the salts.

7.3.2.6 Filter into a 100 ml volumetric flask using Whatman No. 44 filter paper. Wash the residue twice using dilute HCl. Make up to volume with deionized water using a microsyringe.

It is necessary to use reagents and distilled water of suitably low metal content taking into consideration that the concentrated mineral acids are generally used in amounts several times more than the sample. Even when suitable reagents are used, reagent blank determination is still necessary.

NOTE In expressions like (1+2), (1+3) etc. used with the name of a reagent, the first numeral indicates (volume/mass) of (liquid/solid) reagent and the second numeral indicates volume of water. For example HCl (1+2) means reagent prepared by mixing one volume of HCl with two volumes of water.

7.3.2.7 Blanks shall be prepared with the same quantities of the reagents as are used in the test but omitting the test portion.

7.3.2.8 Alternatively dissolution of the inorganic residue using nitric acid can be carried out as described in ISO 6101.

7.3.3 Microwave digestion

7.3.3.1 Place a TFM vessel on the balance plate, tare and weigh the test piece of 0,5 g to 1,0 g.

7.3.3.2 Add 5 ml of concentrated HNO_3 to each vessel.

7.3.3.3 Assemble the vessel according to the manufacturer's instructions.

7.3.3.4 Place assembled vessels into the microwave oven according to the manufacturer's instructions.

7.3.3.5 Program the oven with parameters that are known to digest the material safely and effectively (producing a clear digest when diluted). Recommended parameters are listed in Table 1. It may be necessary to adjust these parameters to accommodate variations between individual instruments.

Table 1 — Typical parameters for microwave digestion

Power	1 200 W[a]
Ramp time	10 min
Final temperature	180 °C
Temperature hold time	10 min
Cool down time	10 min

[a] If there are less than eight vessels in the microwave the wattage can be lowered.

7.3.3.6 Initiate oven program and digest samples.

7.3.3.7 Allow vessels to cool, then transfer to a fume hood and allow vessels to equilibrate to room temperature.

7.3.3.8 Slowly open the vent fittings and vent to atmospheric pressure, then disassemble vessels.

7.3.3.9 Place vessel liners into the evaporation carousel and assemble according to the manufacturer's instructions.

7.3.3.10 Place the evaporation assembly into the microwave.

7.3.3.11 Program the oven to reduce solution volumes to approximately 1 ml. Typical program parameters are listed in Table 2.

Table 2 — Typical parameters for microwave evaporation

Power	600 W
Ramp time	5 min
Final temperature	120 °C
Temperature hold time	3,5 min [a]
Cool down time	10 min

[a] Typical value required when 8 vessels are used. Hold times required to achieve a final volume of 1 mL for any given number of vessels shall be determined experimentally.

7.3.3.12 Initiate the oven program and evaporate solutions.

7.3.3.13 Once the vessels have cooled to room temperature, remove the evaporation assembly from the oven and dismantle. Flush the evaporation manifold with deionized water. Transfer the material into 50 ml polypropylene bottle. Make up the volume with deionized water.

7.4 Preparation of standard solution and test solution

WARNING — Metals might be leached from glass by nitric acid. Store all standard solutions in polypropylene or other inert containers. If glassware is used, it should be cleaned with nitric acid and dedicated for trace metals analyses. Standards prepared in glassware should be used immediately or transferred to suitable containers for storage.

7.4.1 Prepare the multi-element standard solution as per manufacturer's instruction.

7.4.2 A solution of 3 % to 5 % (v/v) nitric acid prepared from the concentrated nitric acid, shall be used as a calibration blank.

7.4.3 Working standards, as required, are made by diluting 5 ml of multi-element primary standard to 500 ml with 3 % to 5 % nitric acid.

7.4.4 Prepare test solutions depending on the sample matrix or analyte concentrations.

NOTE Low-volume or "over concentrated" test solutions are diluted before analysis. Turbid solutions are left to stand overnight so that particles settle down to the bottom, or the samples are centrifuged. Yttrium (Y) may be used as an internal reference standard.

8 Procedure

8.1 Five working standard solutions or as applicable for analysis, are prepared from independent primary standard solutions.

8.2 Turn on the power to the instrument as per the manufacturer’s instructions.

8.3 The solution introduction system is checked and the wavelengths are tuned. Typical instrument conditions are given in Table 3. Instrumental conditions can be adjusted as per the manufacturer’s instructions.

Table 3 — Typical example of ICP-OES instrument conditions

ICP-OES parameters	Condition
Plasma forward power	1150 W
Coolant gas flow rate	Instrument default
Auxiliary gas flow rate	Low
Nebulizer pressure	16 psi
Pump rate	100 rpm
Sample uptake rate	1 ml/min to 2 ml/min
Sample uptake time	30 s
Acquisition	30 s low wavelength range, 10 s high wavelength range. Twice
Wash solution	Deionized water or very dilute acid (<15 v/v)
Wash time	15 s

8.4 Equipment check

8.4.1 Check the liquid nitrogen and the liquid argon.

8.4.2 Check the CID temperature (−90 °C).

8.4.3 Confirm that the exhaust fan is on.

8.4.4 Lock peristaltic pump platens down.

8.4.5 Drain the spray chamber if needed.

8.4.6 Ignite the plasma. Confirm that the waste is being pumped out.

If the plasma does not light, the most likely cause is either that there is a leak of air into the solution introduction system, or the purge was insufficient. Find the leak or increase the purge time.

8.4.7 Warm up for at least 30 min.

8.5 Preparation of Calibration Curve

Calibrate the ICP-OES. Then read the emission for the blank solution and for a series of respective metal solutions of working range in the ICP-OES. For optimum accuracy use the best emission line (given by the equipment supplier). Plot the absorbance against concentration of metal solutions [0 mg/l (sample blank), 0,1 mg/l, 0,2 mg/l, 0,5 mg/l, 1 mg/l and 2 mg/l].

8.6 Test Run

8.6.1 Aspire a 1 000 µg/g yttrium solution to the system, check and confirm that the yttrium bullet is half way between the coil top and the torch top. The bullet position is adjusted by setting the nebulizer pressure.

NOTE Use of yttrium as an internal standard is for drift correction, accuracy improvement and repeatability improvement. An internal standard is used to correct between sample variations – such as the differences in sample matrix.

8.6.2 Using an in-house tune solution (containing 1 µg/g to 50 µg/g of multi-elements), carry out "Auto peak adjustment."

8.6.3 Aspire 10 % to 30 % nitric acid for 1 min to 2 min to clean the system. Set up the ICP-OES working standards, measure, and carry out the standardization. Check and confirm the standardization result by checking the slopes, intercepts, and correlation coefficients.

8.6.4 Measure a 3 % to 5 % nitric acid solution for two times as the measurement blanks.

8.6.5 Set the sample rack(s) into place when using an autosampler. Start the whole acquisition sequence.

8.6.6 The concentration is determined from the measured absorbance using the prepared calibration curve. If the absorbance is going out of the calibration range, then dilute the solution further to bring it back into the calibration range.

8.6.7 After the analysis has been completed, thoroughly rinse the solution introduction system by aspiring deionized water for 5 min to 10 min.

8.6.8 Shut down the instrument (extinguish the plasma and shut down the RF generator).

8.6.9 Release the peristaltic pump.

8.6.10 Download all of the concentration data.

8.6.11 If applicable, the results are corrected based on yttrium, an internal reference standard.

8.6.12 The results of the measurement blanks are averaged. This averaged blank is subtracted from all of the other samples.

8.6.13 Check the analyte results against their respective detection limits.

8.6.14 Apply dilution factors if appropriate.

8.6.15 Generate out-going reports.

8.6.16 In order to check the efficiency of the procedure, prepare a spiked laboratory sample by adding a known concentration of metals to the laboratory sample and follow the solution preparation technique as applicable. Analyse the resulting solution. Subtract the result from the laboratory sample from this result and calculate the recovery factor from the known added amount.

NOTE 1 Percent recovery ($\%R$) of spiked samples = 100 × $(x_s - x_u)/K$, where x_s is the measured concentration of the spiked sample, x_u is the measured concentration of the unspiked sample, and K is the known concentration of spike.

NOTE 2 Percent recovery ($\%R$) for standard reference materials = 100 × x/K_1, where x is the measured concentration of the NIST standard, and K_1 is the known concentration of NIST standard.

8.6.17 Calculate the analyte concentration in digested samples, using Formula (1):

$$Cs = \frac{Ce \times Ve \times D}{m} \qquad (1)$$

where

Cs is the analyte concentration in digested samples (µg/g);

Ce is the analyte concentration (µg/l);

Ve is the final sample extract volume (ml);

D is the dilution factor (l/ml*mg/g), if secondary dilution was made;

m is the sample mass (mg).

9 Test Report

The test report shall include the following information:

a) sample details:
   1) full description of the sample and its origin,
   2) method of preparation of test piece from the sample,
   3) type of digestion method used;

b) test method:
   1) a full reference to the test method used, i.e. the number of this International Standard (ISO 19050),
   2) the test procedure used,
   3) the type of test piece used;

c) test details of any procedures not specified in this International Standard;

d) test results:
   1) the number of test pieces used,
   2) the individual test results,
   3) the mean results,
   4) the recovery factor;

e) date(s) of test.

Annex A
(normative)

Calibration schedule

A.1 Inspection

Before any calibration is undertaken, the condition of the items to be calibrated shall be ascertained by inspection and recorded on any calibration report or certificate. It shall be reported whether calibration is made in the 'as-received' condition or after rectification of any abnormality or fault.

It shall be ascertained that the apparatus is generally fit for the intended purpose, including any parameters specified as approximate and for which the apparatus does not therefore need to be formally calibrated. If such parameters are liable to change, then the need for periodic checks shall be written into the detailed calibration procedures.

A.2 Schedule

Verification/calibration of the test apparatus is a normative part of this International Standard. The frequency of calibration and the procedures used are, unless otherwise stated, at the discretion of the individual laboratory using ISO 18899 for guidance.

The calibration schedule given in Table A.1 has been compiled by listing all of the parameters specified in the test method, together with the specified requirement. A parameter and requirement can relate to the main test apparatus, part of that apparatus or to an ancillary apparatus necessary for the test.

For each parameter, a calibration procedure is indicated by reference to ISO 18899, to another publication or to a procedure particular to the test method which is detailed (whenever a more specific or detailed calibration procedure than in ISO 18899 is available, it shall be used in preference).

The verification frequency for each parameter is given by a code-letter.

The code letters used in the calibration schedule are:

R Use of certified reference material

U In use

Table A.1 — Calibration frequency schedule

Parameter	**Requirement**	**Subclause in** ISO 18899:2013	**Verification frequency guide**	**Notes**
Mass	Accurate to ± 0,01 mg	22.2	R	Calibrated weight
Reference materials	Different analytical standards	—	U	Every time during analysis

In addition to the items listed in Table A.1, use of the following is implied, which needs calibrating in accordance with ISO 18899:

— a thermometer for monitoring the conditioning and test temperatures.