



BSI Standards Publication

Determination of certain substances in electrotechnical products

Part 7-1: Determination of the presence of hexavalent chromium (Cr(VI)) in colorless and colored corrosion-protected coatings on metals by the colorimetric method

National foreword

This British Standard is the UK implementation of EN 62321-7-1:2015. Together with BS EN 62321-1:2013, BS EN 62321-2:2014, BS EN 62321-3-1:2014, BS EN 62321-3-2:2014, BS EN 62321-4:2014, BS EN 62321-5:2014, BS EN 62321-6:2015, BS EN 62321-7-2 and BS EN 62321-8 it supersedes BS EN 62321:2009, which will be withdrawn upon publication of all parts of the BS EN 62321 series.

The UK participation in its preparation was entrusted to Technical Committee GEL/111, Electrotechnical environment committee.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Determination of certain substances in electrotechnical products
- Part 7-1: Determination of the presence of hexavalent
chromium (Cr(VI)) in colorless and colored corrosion-protected
coatings on metals by the colorimetric method
(IEC 62321-7-1:2015)

Détermination de certaines substances dans les produits
électrotechniques - Partie 7-1: Chrome hexavalent -
Présence de chrome hexavalent (Cr(VI)) dans les
revêtements incolores et colorés de protection anticorrosion
appliqués sur les métaux à l'aide de la méthode
colorimétrique
(IEC 62321-7-1:2015)

Verfahren zur Bestimmung von bestimmten Substanzen in
Produkten der Elektrotechnik - Teil 7-1: Bestimmung des
Vorliegens von sechswertigem Chrom (Cr(VI)) in farblosen
und farbigen Korrosionsschutzüberzügen auf Metallen
durch das kolorimetrische Verfahren
(IEC 62321-7-1:2015)

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European Committee for Electrotechnical Standardization
Comité Européen de Normalisation Electrotechnique
Europäisches Komitee für Elektrotechnische Normung

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

European foreword

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The following dates are fixed:

- latest date by which the document has to be implemented at national level by publication of an identical national standard or by endorsement (dop) 2016-07-21
- latest date by which the national standards conflicting with the document have to be withdrawn (dow) 2018-10-21

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In the official version, for Bibliography, the following notes have to be added for the standards indicated:

ISO 3613	NOTE	Harmonized as EN ISO 3613.
ISO 648	NOTE	Harmonized as EN ISO 648.
DIN EN 15205:2007	NOTE	Harmonized as EN 15205:2006..

Annex ZA (normative)

Normative references to international publications with their corresponding European publications

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.

NOTE 1 When an International Publication has been modified by common modifications, indicated by (mod), the relevant EN/HD applies.

NOTE 2 Up-to-date information on the latest versions of the European Standards listed in this annex is available here: www.cenelec.eu.

<u>Publication</u>	<u>Year</u>	<u>Title</u>	<u>EN/HD</u>	<u>Year</u>
IEC 62321-1	-	Determination of certain substances in electrotechnical products -- Part 1: Introduction and overview	EN 62321-1	-
IEC 62321-2	-	Determination of certain substances in electrotechnical products -- Part 2: Disassembly, disjunction and mechanical sample preparation	EN 62321-2	-
ISO 78-2	-	Chemistry_ - Layouts for standards_ - Part_2: Methods of chemical analysis	-	-
ISO 3696	-	Water for analytical laboratory use - Specification and test methods	EN ISO 3696	-

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

**DETERMINATION OF CERTAIN SUBSTANCES
IN ELECTROTECHNICAL PRODUCTS –****Part 7-1: Hexavalent chromium – Presence of hexavalent chromium (Cr(VI))
in colourless and coloured corrosion-protected coatings
on metals by the colorimetric method**

FOREWORD

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International Standard IEC 62321-7-1 has been prepared by IEC technical committee 111: Environmental standardization for electrical and electronic products and systems.

The first edition of IEC 62321:2008 was a 'stand-alone' standard that included an introduction, an overview of test methods, a mechanical sample preparation as well as various test method clauses.

This first edition of IEC 62321-7-1 is a partial replacement of IEC 62321:2008, forming a structural revision and generally replacing informative Annex B.

Future parts in the IEC 62321 series will gradually replace the corresponding clauses in IEC 62321:2008. Until such time as all parts are published, however, IEC 62321:2008 remains valid for those clauses not yet re-published as a separate part.

The text of this standard is based on the following documents:

FDIS	Report on voting
111/380/FDIS	111/393/RVD

Full information on the voting for the approval of this standard can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC 62321 series can be found on the IEC website under the general title: *Determination of certain substances in electrotechnical products*.

The committee has decided that the contents of this publication will remain unchanged until the stability date indicated on the IEC website under "<http://webstore.iec.ch>" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

IMPORTANT – The 'colour inside' logo on the cover page of this publication indicates that it contains colours which are considered to be useful for the correct understanding of its contents. Users should therefore print this document using a colour printer.

INTRODUCTION

The widespread use of electrotechnical products has drawn increased attention to their impact on the environment. In many countries this has resulted in the adaptation of regulations affecting wastes, substances and energy use of electrotechnical products.

The use of certain substances (e.g. lead (Pb), cadmium (Cd) and polybrominated diphenylethers (PBDE's)) in electrotechnical products is a source of concern in current and proposed regional legislation.

The purpose of the IEC 62321 series is therefore to provide test methods that will allow the electrotechnical industry to determine the levels of certain substances of concern in electrotechnical products on a consistent global basis.

WARNING – Persons using this International Standard should be familiar with normal laboratory practice. This 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.

DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS –

Part 7-1: Hexavalent chromium – Presence of hexavalent chromium (Cr(VI)) in colourless and coloured corrosion-protected coatings on metals by the colorimetric method

1 Scope

This part of IEC 62321 describes a boiling water extraction procedure intended to provide a qualitative determination of the presence of hexavalent chromium (Cr(VI)) in colourless and coloured corrosion-protection coatings on metallic samples.

Due to its highly reactive nature, the concentration of Cr(VI) in a corrosion-protection coating can change drastically with time and storage conditions. Since storage conditions prior to sample submission are not often known or provided with the samples, this procedure determines the presence of Cr(VI) based on the levels detected in the coatings at the time of testing. For testing of freshly coated samples, a minimum waiting period of 5 days (after the coating process) is necessary to ensure the coatings have stabilized. This waiting period allows potential post-process oxidation of Cr(III) to Cr(VI) to occur prior to testing.

The presence of Cr(VI) is determined by the mass of Cr(VI) per surface area of the coating, in $\mu\text{g}/\text{cm}^2$. This approach is preferred since corrosion-protection coating weights are often difficult to measure accurately after production. From a coating technology perspective, the industry as a whole has transitioned to either using the non-Cr(VI) based chemistries – where little to no Cr(VI) should be present – or using the traditional Cr(VI) based chemistries – where significant levels of Cr(VI) are present and can be detected reliably. Given this industry shift, the presence or absence of Cr(VI) is often sufficient for compliance testing purposes.

In this procedure, when Cr(VI) in a sample is detected below the $0,10 \mu\text{g}/\text{cm}^2$ LOQ (limit of quantification), the sample is considered to be negative for Cr(VI). Since Cr(VI) may not be uniformly distributed in the coating even within the same sample batch, a “grey zone” between $0,10 \mu\text{g}/\text{cm}^2$ and $0,13 \mu\text{g}/\text{cm}^2$ has been established as “inconclusive” to reduce inconsistent results due to unavoidable coating variations. In this case, additional testing may be necessary to confirm the presence of Cr(VI). When Cr(VI) is detected above $0,13 \mu\text{g}/\text{cm}^2$, the sample is considered to be positive for the presence of Cr(VI) in the coating layer.

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.

IEC 62321-1, *Determination of certain substances in electrotechnical products – Part 1: Introduction and overview*

IEC 62321-2, *Determination of certain substances in electrotechnical products – Part 2: Disassembly, disjointment and mechanical sample preparation*

ISO 78-2, *Chemistry – Layouts for standards – Part 2: Methods of chemical analysis*

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

3 Terms, definitions and abbreviations

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in IEC 62321-1 apply.

3.2 Abbreviations

For the purposes of this document, the abbreviations given in IEC 62321-1 apply.

4 Reagents

4.1 General

Use only reagents of recognized analytical grade, unless otherwise specified.

4.2 Reagents

The following reagents shall be used:

- a) 1,5-diphenylcarbazide, analytical reagent grade.
- b) Potassium dichromate ($K_2Cr_2O_7$) stock solution: in a glass container, weigh (5.2 a)) and dissolve 0,113 g of $K_2Cr_2O_7$ (analytical reagent grade, dried at 100 °C for 1 h before use) in water (4.2 f)) and dilute with water (4.2 f)) to the mark of a 1,000 ml volumetric flask (5.2 e)). Cap or stopper the container tightly. The shelf life of this solution is one year.
- c) Potassium dichromate ($K_2Cr_2O_7$) equivalent comparison standard solutions, 0,10 $\mu\text{g}/\text{cm}^2$ and 0,13 $\mu\text{g}/\text{cm}^2$: in this method, the 0,10 $\mu\text{g}/\text{ml}$ and 0,13 $\mu\text{g}/\text{ml}$ standards are equivalent to 0,10 $\mu\text{g}/\text{cm}^2$ and 0,13 $\mu\text{g}/\text{cm}^2$, respectively. Prepare the 0,10 $\mu\text{g}/\text{cm}^2$ equivalent comparison standard by pipetting (5.2 f)) 2,5 ml of the $K_2Cr_2O_7$ stock solution (4.2 b)) into a 1,000 ml volumetric flask and dilute to mark. Prepare the 0,13 $\mu\text{g}/\text{cm}^2$ comparison standard by pipetting (5.2 f)) 3,3 ml of the $K_2Cr_2O_7$ stock solution (4.2 b)) into a 1,000 ml volumetric flask (5.2 e)) and dilute to mark.
- d) Acetone, analytical reagent grade.
- e) Orthophosphoric acid (H_3PO_4) solution (mass fraction of 75 %), analytical reagent grade.
- f) Water: Grade 1 specified in ISO 3696, which shall be free of interferences.

5 Apparatus

5.1 General

All re-usable labware (glass, quartz, polyethylene, polytetrafluoroethylene (PTFE), etc.) including the sample containers shall be soaked overnight in laboratory-grade detergent and water, rinsed with water, and soaked for 4 h or more in HNO_3 (volume fraction of 20%) or in a mixture of dilute acids ($HNO_3:HCl:H_2O = 1:2:9$ by volume) followed by rinsing with water (4.2 f)). Alternative cleaning procedures are permitted, provided adequate cleanliness can be demonstrated through the analysis of method blanks.

5.2 Apparatus

The following items shall be used for the analysis:

- a) Analytical balance with an accuracy of 0,10 mg.
- b) Thermometer or other temperature measurement device capable of measuring up to 100 °C.

- c) Colorimetric instrument: either a spectrophotometer for use at 540 nm providing a light path of 1 cm or longer; or a filter photometer providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.
- d) Boiling chips.
- e) Volumetric glassware: Class A or equivalent of acceptable precision and accuracy. Alternative volumetric equipment (e.g. automatic dilutors) with equivalent precision and accuracy can be used.
- f) Assorted calibrated pipettes: Class A glassware or other with equivalent precision and accuracy.
- g) Borosilicate glass or quartz beaker with a volume graduation of 250 ml, or equivalent.
- h) Heating device: capable of maintaining boiling of the extraction solution.
- i) Filter membranes (0,45 µm), cellulose-based or polycarbonate types preferred.
- j) Silicon carbide (SiC) grinding paper with 800 grit size, or equivalent.
- k) Watch glass.

6 Sampling

Samples shall not be stored in environments where oxidation of Cr(III) to Cr(VI) can occur. Samples shall be stored at ambient conditions upon arrival until the start of testing. Ambient conditions are defined as 45 % RH to 75 % RH (relative humidity) and temperature between 15 °C and 35 °C.

In some cases, disassembly or mechanical disjointment may be necessary to obtain samples for testing; refer to IEC 62321-2 for sample preparation.

Prior to the test, the sample surface shall be free of all contaminants, fingerprints and stains. If the surface is coated with thin oil, the oil shall be removed prior to the test by using a clean, soft laboratory wipe wetted with a suitable solvent, or by rinsing the surface with a suitable solvent at ambient temperature. The samples shall not be subject to forced drying at temperature in excess of 35 °C. Treatment in alkaline solutions shall not be performed as corrosion-protection coatings are broken down by alkalis.

If there is a polymer coating on a sample surface, gentle abrasion with a fine grinding paper (5.2 j)) may be performed to expose the corrosion protection layer for extraction; however, care shall be taken not to remove the entire corrosion protection coating beneath the polymer coating. Other top coat removal methods may be applied if they are shown to be of equal or greater effectiveness.

Since Cr(VI) is toxic to human beings, all potential Cr(VI)-containing samples and reagents used in the method shall be handled with appropriate precautions. Solutions or waste material containing Cr(VI) shall be disposed of properly. For example, ascorbic acid or other reducing agents can be used to reduce Cr(VI) to Cr(III) prior to disposal.

7 Boiling water extraction procedure

The boiling water extraction procedure is as follows:

- a) Prepare the test solution as follows: dissolve 0,5 g of diphenylcarbazide (4.2 a)) in 50 ml of acetone (4.2 d)). Dilute slowly, while stirring, with 50 ml of water (4.2 f)) (rapid mixing may result in precipitation of diphenylcarbazide). For maximum stability, store this test solution under refrigeration at $7\text{ °C} \pm 2\text{ °C}$ in an amber glass bottle. Discard when the solution becomes discoloured.
- b) The sample to be tested should have a surface area of $50\text{ cm}^2 \pm 5\text{ cm}^2$. For fasteners or samples with smaller surface area, use a suitable number of samples to obtain the total required surface area. In cases where obtaining a total surface area of $50\text{ cm}^2 \pm 5\text{ cm}^2$ is

not possible, a reduced total sample surface area may be used by reducing the water extraction volume, while maintaining the same surface area to extraction volume ratio (1 cm²:1 ml). A minimum surface area of 25 cm² is recommended. Similarly, a higher sample surface area can be used by keeping the same ratio. The type of adjustment shall be recorded in the final report.

The surface area of complex geometry samples can be estimated according to its manufacturing specifications (e.g. mechanical drawings) if available, or by using its dimensions and shape. For example: a flat-headed countersunk screw may be considered as one metal cylinder (the screw body) adjacent to one metal cone (the screw head), as shown in Figure 1.

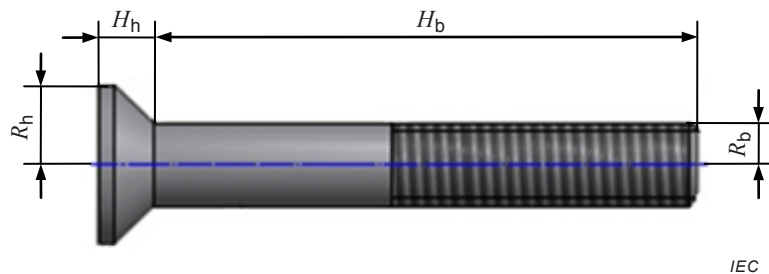


Figure 1 – Screw body and screw head measurements

Estimated surface area of the screw body:

$$S_b = 2\pi R_b H_b + \pi(R_b)^2 \quad (1)$$

where

S_b is the estimated surface area of the screw body;

R_b is the radius of the screw body;

H_b is the height of the screw body.

Estimated surface area of the screw head:

$$S_h = \pi R_h \sqrt{(H_h)^2 + R_h^2} + \pi R_h^2 \quad (2)$$

where

S_h is the estimated surface area of the screw head;

R_h is the top radius of the screw head;

H_h is the height of the screw head.

Total estimated surface area of the screw:

$$S_t = S_h + S_b \quad (3)$$

where

S_t is the total estimated surface area of the screw.

NOTE The German Fastener Association, Deutscher Schraubenverband E.V. (DSV), offers a surface area program for fastener surface area calculation via the International Material Data System (IMDS). Limitations of this tool are documented within the program and users shall ensure this tool is applicable to the sample of interest.

- c) Add boiling chips (5.2 d)) and 50 ml of water (4.2 f)) to a beaker with volume graduation (5.2 g)). Bring the water (4.2 f)) to boiling temperature (5.2 b) and 5.2 h)) for at least 10 min to deoxygenate the water; maintain the water volume by covering the beaker (5.2 g)) with a watch glass (5.2 k)). After boiling for at least 10 min, totally immerse the sample into the boiling water. Cover the beaker (5.2 g)) with a watch glass (5.2 k)). Extract the sample for 10 min \pm 0,5 min once boiling is resumed. If necessary, add water (4.2 f)) to ensure sample is totally submerged during the extraction. Remove the sample and allow the resulting solution to cool to ambient temperature. The solution should be colourless

and free of precipitate. Adjust the volume to 50 ml. If the solution is milky or has a precipitate, filter the solution through a membrane filter (5.2 i)) into a dry beaker (5.2 g)) and adjust the volume back to 50 ml.

- d) Add 1 ml of orthophosphoric acid solution (4.2 e)) and mix well. Pour 25 ml of the solution using a graduated cylinder (5.2 e)) into another dry beaker (5.2 g)). Add 1 ml test solution (7 a)), mix, and observe the colour. After a 10 min reaction time, a red to violet colour indicates the presence of Cr(VI). The remaining portion of the extract will serve as the blank.
- e) If there is a colour interference (e.g. from a coating dye), a correction against the blank shall be performed. Transfer a portion of the sample solution to an absorption cell (5.2 c)). Measure the absorbance at 540 nm against the blank (7 d)) with the colorimetric instrument (5.2 c)). Make three measurements and take the average as the final absorbance of the sample. In some cases, depending on the type of spectrometer used, the correction for the blank may have to be made manually in the collected data.
- f) Place 50 ml of the 0,10 $\mu\text{g}/\text{cm}^2$ equivalent comparison standard solution (4.2 c)) in a beaker (5.2 g)). Add 1 ml of orthophosphoric acid solution (4.2 e)) and mix well. Add 2 ml test solution (7 a)), mix, and wait 10 min for colour development. Measure the absorbance three times as above. Take the average of three measurements as the final absorbance of the standard solution.
- g) Place 50 ml of the 0,13 $\mu\text{g}/\text{cm}^2$ equivalent comparison standard solution (4.2 c)) in a suitable beaker (5.2 g)). Add 1 ml of orthophosphoric acid solution (4.2 e)) and mix well. Add 2 ml test solution (7 a)), mix, and wait 10 min for colour development. Measure the absorbance three times as above. Take the average of three measurements as the final absorbance of the standard solution.
- h) If the absorbance value obtained in 7 d) or 7 e) is less than absorbance of the 0,10 $\mu\text{g}/\text{cm}^2$ equivalent comparison standard solution (4.2 c)) obtained in 7 f), the sample is considered to be negative for Cr(VI) (see Table 1).
- i) If the absorbance value obtained in 7 d) or 7 e) is in between the values of the 0,10 $\mu\text{g}/\text{cm}^2$ and 0,13 $\mu\text{g}/\text{cm}^2$ equivalent comparison standard solutions (4.2 c)) obtained in 7 f) and 7 g), the sample is in the "grey zone" where the presence or absence of Cr(VI) in the sample is inconclusive (see Table 1).
- j) If the absorbance value obtained in 7 d) or 7 e) is greater than the absorbance value of the 0,13 $\mu\text{g}/\text{cm}^2$ equivalent comparison standard solution (4.2 c)) obtained in 7 g), the sample is considered to be positive for Cr(VI) (see Table 1).

In the case where the sample colour after the colorimetric reaction is significantly more intense than the 0,13 $\mu\text{g}/\text{cm}^2$ equivalent comparison standard such that the result can clearly be determined as positive for Cr(VI), measurement via a colorimetric instrument is not necessary. However, the report shall clearly state that the result is significantly above 0,13 $\mu\text{g}/\text{cm}^2$ based on visual observation and no colorimetric measurement was performed. Colorimetric measurement shall be performed if the Cr(VI) is not clearly above 0,13 $\mu\text{g}/\text{cm}^2$.

Table 1 – Comparison to standard solution and interpretation of results

Colorimetric result (Cr(VI) concentration)	Qualitative result
The sample solution is < the 0,10 µg/cm ² equivalent comparison standard solution	The sample is negative for Cr(VI) – The Cr(VI) concentration is below the limit of quantification. The coating is considered a non-Cr(VI) based coating
The sample solution is ≥ the 0,10 µg/cm ² and ≤ the 0,13 µg/cm ² equivalent comparison standard solutions	The result is considered to be inconclusive – Unavoidable coating variations may influence the determination. Recommendation: if additional samples are available, perform a total of 3 trials to increase sampling surface area. Use the averaged result of the 3 trials for the final determination.
The sample solution is > the 0,13 µg/cm ² equivalent comparison standard solution	The sample is positive for Cr(VI) – The Cr(VI) concentration is above the limit of quantification and the statistical margin of error. The sample coating is considered to contain Cr(VI)

8 Calibration

8.1 Permanent calibration instruments

Colorimetric instruments designed specifically for hexavalent chromium detection at 540 nm may have a permanent calibration provided by the manufacture and no further calibration is needed. Refer to the manufacturer's instructions to ensure that the instrument is functioning properly and its working range is appropriate for this analysis.

8.2 Traditional calibration instruments

8.2.1 Traditional colorimetric instrument calibration shall be conducted using a blank and three standard solutions at a minimum. The standard solution concentrations shall bracket the two equivalent comparison standard solution concentrations (0,10 µg/ml and 0,13 µg/ml).

8.2.2 Zero the colorimetric instrument with the 0,0 µg/ml blank standard and save this solution to re-zero the instrument before reading samples and standards.

8.2.3 Read the standard solutions. Construct a calibration curve and determine a line equation by plotting absorbance values (ordinate or y-axis) against µg/ml of Cr(VI) (abscissa or x-axis) for each standard including the 0,0 µg/ml standard.

8.2.4 The calibration curve (linear fit with zero intercept) shall have a correlation coefficient ≥ 0,995 or a new curve shall be built.

8.2.5 Calibration curves can be used for up to one month from initial generation.

9 Calculation

The concentration of Cr(VI) shall be calculated according to Equation (4):

$$C(\text{VI}) = \frac{(C - B) \times V}{A} \times DF \quad (4)$$

where

$C(\text{VI})$ is the sample coating concentration of chromium (VI) (µg/cm²);

- C* is the sample solution concentration of chromium (VI) reading ($\mu\text{g/ml}$);
- B* is the concentration of reagent blank for sample preparation ($\mu\text{g/ml}$);
- V* is the volume of extract (ml);
- A* is the sample surface area (cm^2);
- DF* is the dilution factor (if no dilution is made, $DF = 1$).

10 Precision

Since the qualitative nature of this method does not lend itself to quantitative repeatability and reproducibility statements (see ISO 78-2:1999, Annex B), the precision statements below have been gleaned from 111/320/INF [1]¹.

- Seven laboratories submitted triplicate results and one laboratory submitted duplicate results collected from a metal plate coated with hexavalent chromium (IIS4B-A1). All 23 results were positive for the presence of hexavalent chromium ($> 0,13 \mu\text{g/cm}^2$).
- Eight laboratories submitted triplicate results collected from a metal screw coated with hexavalent chromium (IIS4B-D4). All 24 results were positive for the presence of hexavalent chromium ($> 0,13 \mu\text{g/cm}^2$).
- Eight laboratories submitted triplicate results collected from a metal plate coated with trivalent chromium (IIS4B-B2). Twenty (20) results were negative for the presence of hexavalent chromium ($< 0,10 \mu\text{g/cm}^2$), 3 results were inconclusive for the presence of hexavalent chromium ($\geq 0,10 \mu\text{g/cm}^2$ and $\leq 0,13 \mu\text{g/cm}^2$) and one result was positive for the presence of hexavalent chromium ($> 0,13 \mu\text{g/cm}^2$).
- Eight laboratories submitted triplicate results collected from a metal screw coated with trivalent chromium (IIS4B-E5). All 24 results were negative for the presence of hexavalent chromium ($< 0,10 \mu\text{g/cm}^2$).
- Eight laboratories submitted triplicate results collected from a metal plate coated without any chromium (IIS4B-C3). All 24 results were negative for the presence of hexavalent chromium ($< 0,10 \mu\text{g/cm}^2$). See Annex A for supporting data.

11 Quality assurance and control

11.1 Colorimetric instrument performance verification

11.1.1 Regardless of the instrument type, a performance verification using the two equivalent comparison standard solutions shall be carried out prior to sample measurements and at the end of each sample sequence to ensure the instrument is functioning properly.

11.1.2 In the event that either of the equivalent comparison standard solutions measured prior to sample measurements result in concentrations that differ from the expected values ($0,10 \mu\text{g/ml}$ and $0,13 \mu\text{g/ml}$) by more than 15 %, the calibration shall be re-measured.

11.1.3 In the event that either of the equivalent comparison standard solutions measured at the end of instrumental sequence result in concentrations that differ from the expected values by more than 15 %, the calibration and all of the samples in the sequence shall be re-measured.

11.2 Limits of detection (LOD) and limits of quantification (LOQ)

In its simplest form, a limit of detection (LOD) or method detection limit (MDL) is typically described as the lowest amount or concentration of analyte in a test sample that can be reliably differentiated from zero for a given measurement system.

¹ Numbers in square brackets refer to the Bibliography

Instrument detection limits represent an instrument's ability to differentiate low concentrations of analytes from "zero" in a blank or standard solution, and are commonly used by manufacturers to demonstrate the measurement capability of a system (e.g. atomic absorption spectrometer). While instrument detection limits are useful, they are often considerably lower than a limit of detection representing a complete analytical method measurement process.

Complete analytical method detection limits are most appropriately determined experimentally by performing replicate, independent measurements on low-level or fortified sample matrices carried out through the entire test procedure, including sample digestion or extraction. A minimum of six replicates and analyte concentrations of 3 to 5 times the estimated method detection limit have been suggested as suitable for this analysis. The complete method detection limit for an entire test procedure is determined by multiplying the standard deviation of the replicates by an appropriate factor. The International Union of Pure and Applied Chemistry (IUPAC) recommends a factor of 3 for a minimum of six replicates, while the United States Environmental Protection Agency (US EPA) utilizes a one-sided confidence interval with the multiplier equal to Student's *t* value chosen for the number of replicates and the level of confidence (e.g. *t* = 3,36 for six replicates for 99 % confidence).

All analyses used to calculate an MDL should be consecutive. The LOD or MDL was determined using the appropriate Student's *t* values and *t*-statistic shown in Table 2.

Table 2 – Student's *t* values used for calculation of method detection limit (LOD or MDL = *t*-statistic × standard deviation (sn-1))

Number of samples	Student's <i>t</i> -statistic (99 % confidence)
6	3,36
7	3,14
8	3,00
9	2,90
10	2,82

The limit of quantification (LOQ) or estimated quantification limit for a given measurement system is typically described as the lowest concentration that can be reliably determined within specified or acceptable limits of precision during routine laboratory operating conditions. The acceptable precision limit is often defined as 10 % relative standard deviation or simply expressed as a fixed multiple (2 to 10) of the method detection limit.

12 Test report

Clause 12 specifies which information is to be included in the test report and shall require information on at least the following aspects of the test:

- the sample;
- the International Standard used (including its year of publication);
- the method used (if the standard includes several);
- the limit of detection (LOD) or limit of quantification (LOQ);
- any deviations from the procedure (e.g. surface area, extract volume, etc.);
- any unusual features observed;
- the date of the test;
- the numeric result(s) in 2 significant figures, following the format laid out in Table 3 and the text within Table 3 that correspond to the numeric result(s).

Visual comparison is only allowed in the case of a positive Cr(VI) determination. Otherwise, the numeric result (in $\mu\text{g}/\text{cm}^2$) shall be stated in the report.

Table 3 – Reporting table

Sample identification	Colorimetric results (in mass per surface area, $\mu\text{g}/\text{cm}^2$)	Sample Cr(VI) concentration is:	Results
Sample name	Numeric result obtained from colorimetric measurement and Equation (4)	$< 0,10 \mu\text{g}/\text{cm}^2$	The sample is negative for Cr(VI) – The Cr(VI) concentration is below the limit of quantification. The coating is considered a non-Cr(VI) based coating.
		Or	
		$\geq 0,10 \mu\text{g}/\text{cm}^2$ and $\leq 0,13 \mu\text{g}/\text{cm}^2$	The result is considered to be inconclusive – unavoidable coating variations may influence the determination. Recommendation: if addition samples are available, perform a total of 3 trials to increase sampling surface area, use the averaged result of the 3 trials for the final determination.
		Or	
		$> 0,13 \mu\text{g}/\text{cm}^2$	The sample is positive for Cr(VI) – The Cr(VI) concentration is above the limit of quantification and the statistical margin of error. The sample coating is considered to contain Cr(VI).
Or			
Sample name	Sample solution is significantly more intense than the $0,13 \mu\text{g}/\text{cm}^2$ equivalent comparison standard	$> 0,13 \mu\text{g}/\text{cm}^2$	The sample is positive for Cr(VI) based on visual comparison only. No colorimetric measurement was performed. (Visual comparison is allowed only in the case of a positive Cr(VI) determination, and the actual value in $\mu\text{g}/\text{cm}^2$ is not required).

Table 4 shows examples of reporting with test results:

Sample N° 1: $0,060 \mu\text{g}/\text{cm}^2$

Sample N° 2: $0,19 \mu\text{g}/\text{cm}^2$

Sample N° 3: $0,11 \mu\text{g}/\text{cm}^2$

Sample N° 4: Sample solution is significantly more intense than the $0,13 \mu\text{g}/\text{cm}^2$ equivalent comparison standard and submitter does not require actual numeric results

Table 4 – Example of a completed reporting table

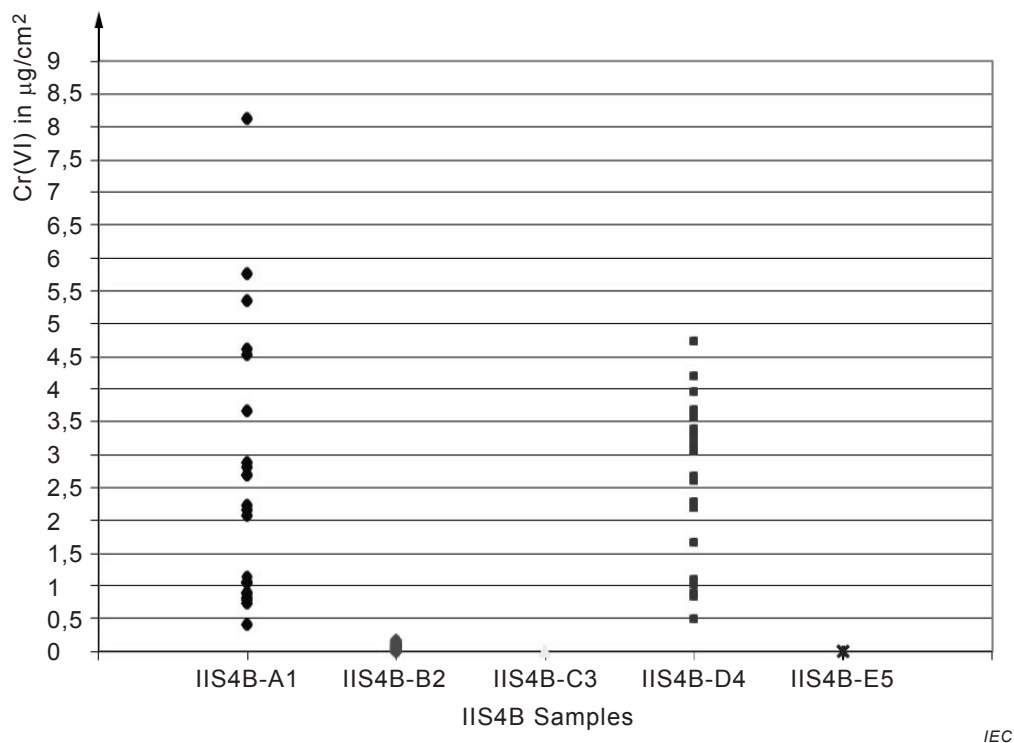
Sample identification	Colorimetric results (in mass per surface area, $\mu\text{g}/\text{cm}^2$)	Sample Cr(VI) concentration is:	Results
Sample N° 1	0,060 $\mu\text{g}/\text{cm}^2$	Less than 0,10 $\mu\text{g}/\text{cm}^2$	The sample is negative for Cr(VI) – The Cr(VI) concentration is below the limit of quantification. The coating is considered a non-Cr(VI) based coating.
Sample N° 2	0,19 $\mu\text{g}/\text{cm}^2$	Greater than 0,13 $\mu\text{g}/\text{cm}^2$	The sample is positive for Cr(VI) – The Cr(VI) concentration is above the limit of quantification and the statistical margin of error. The sample coating is considered to contain Cr(VI).
Sample N° 3	0,11 $\mu\text{g}/\text{cm}^2$	Between 0,10 $\mu\text{g}/\text{cm}^2$ and 0,13 $\mu\text{g}/\text{cm}^2$	The result is considered to be inconclusive – unavoidable coating variations may influence the determination. Recommendation: if addition samples are available, perform a total of 3 trials to increase sampling surface area, use the averaged result of the 3 trials for the final determination.
Sample N° 4	Sample solution is significantly more intense than the 0,13 $\mu\text{g}/\text{cm}^2$ equivalent comparison standard	Greater than 0,13 $\mu\text{g}/\text{cm}^2$	The sample is positive for Cr(VI) based on visual comparison only. No colourimetric measurement was performed. (Visual comparison reporting is only allowed in the case of a positive Cr(VI) determination, and the actual value in $\mu\text{g}/\text{cm}^2$ is not required).

Annex A (informative)

International inter-laboratory study on corrosion-protected coatings – Data overview

For samples containing hexavalent chromium (Cr(VI)), the Cr(VI) concentration reported via a colorimetric instrument varied widely across the laboratories within each sample type (see Figure A.1). The concentration values range from 0,40 $\mu\text{g}/\text{cm}^2$ to 8,12 $\mu\text{g}/\text{cm}^2$ (IIS4B-A1) and 0,48 $\mu\text{g}/\text{cm}^2$ to 4,70 $\mu\text{g}/\text{cm}^2$ (IIS4B-D4). However, all reported values were clearly above 0,10 $\mu\text{g}/\text{cm}^2$. Given that all samples within each sample type were produced in the same sample batch, one explanation to this wide distribution within each sample type is incomplete extraction. The instrumental concentration measurement was effective for distinguishing Cr(VI) containing coatings within the time frame specified in the procedure; however, the results may not represent the total Cr(VI) content in the samples.

IIS4B: Part 7-1 results

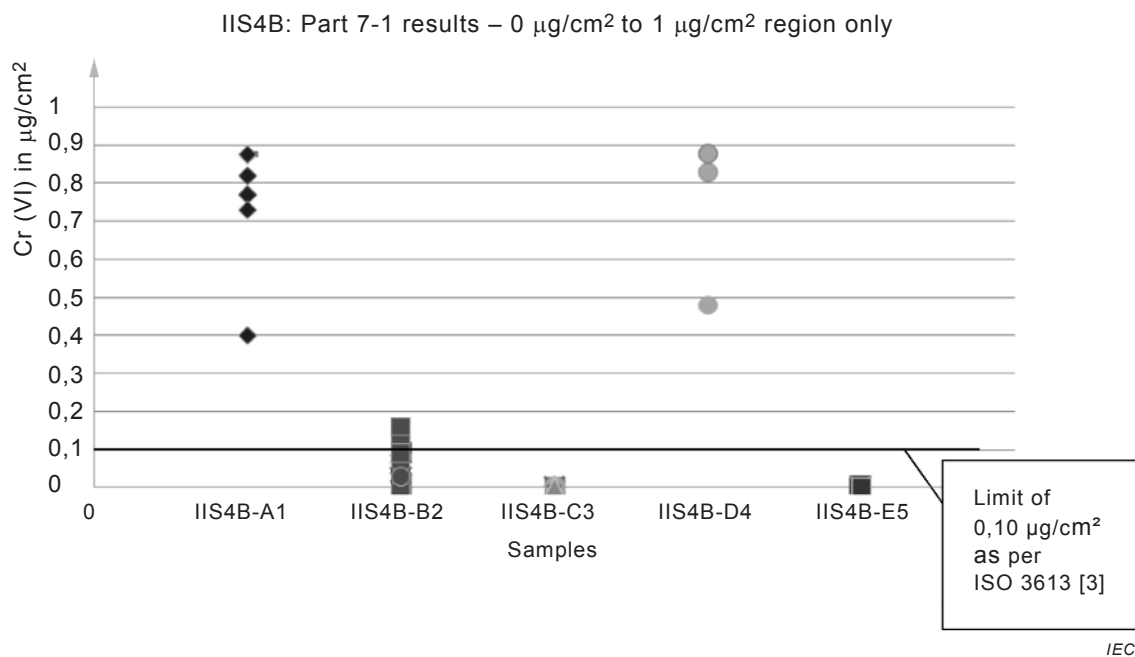


**Figure A.1 – Concentration of chromium VI
based on surface area for all samples**

For samples not expected to contain Cr(VI), most of the detected Cr(VI) concentrations were reported with a value less than 0,10 $\mu\text{g}/\text{cm}^2$ (sample IIS4B-B2, C3, and E5), and in only one case (laboratory B05, sample IIS4B-B2) a mean value (X) of 0,109 $\mu\text{g}/\text{cm}^2$ was reported. The highest reported value was 0,16 $\mu\text{g}/\text{cm}^2$ (see Figure A.2); however, the mean value (X) reported by this laboratory was below 0,10 $\mu\text{g}/\text{cm}^2$ (laboratory B02, sample IIS4B-B2). This study confirmed the DIN-EN 15205 [2] standard's 0,10 $\mu\text{g}/\text{cm}^2$ limit of quantification value provides a more reliable judgement on the presence or absence of Cr (VI).

In addition, the average of all 24 ($n = 24$) data values in sample IIS4B-B2 was 0,058 $\mu\text{g}/\text{cm}^2$ with a standard deviation of $\pm 0,043 \mu\text{g}/\text{cm}^2$. This variation is most likely due to the distribution of Cr(VI), which, if present, are not uniformly distributed across the sample even within the same batch. At 95 % confidential level, the value is $0,058 \pm 0,018 \mu\text{g}/\text{cm}^2$; a relative deviation of $\pm 31 \%$. Given this relative deviation, it is justified that a Cr(VI) concentration value up to

0,13 $\mu\text{g}/\text{cm}^2$ is still within the error uncertainty, where it is statistically the same as a value below the 0,10 $\mu\text{g}/\text{cm}^2$ threshold limit, with 95 % confidence.



**Figure A.2 – Concentration of chromium VI based on surface area –
Expanded view between 0 $\mu\text{g}/\text{cm}^2$ to 1 $\mu\text{g}/\text{cm}^2$**

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