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Metallic coatings — Test methods for electrodeposited gold and gold alloy coatings —

Part 2:
Mixed flowing gas (MFG) environmental tests

Revêtements métalliques — Méthodes d'essai des dépôts électrolytiques d'or et d'alliage d'or —

Partie 2: Essais climatiques aux gaz mixtes à écoulement (MFG)

Reference number
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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this part of ISO 4524 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 4524-2 was prepared by Technical Committee ISO/TC 107, *Metallic and other inorganic coatings*, Subcommittee SC 7, *Corrosion tests*.

This second edition cancels and replaces the first edition (ISO 4524-2:1985), which has been technically revised.

ISO 4524 consists of the following parts, under the general title *Metallic coatings — Test methods for electrodeposited gold and gold alloy coatings*:

— *Part 1: Determination of coating thickness*

— *Part 2: Mixed flowing gas (MFG) environmental tests*

— *Part 3: Electrographic tests for porosity*

— *Part 4: Determination of gold content*

— *Part 5: Adhesion tests*

— *Part 6: Determination of the presence of residual salts*

Annexes A, C and E form a normative part of this part of ISO 4524. Annexes B and D are for information only.

Introduction

Mixed flowing gas (MFG) tests are used to simulate or amplify exposure to environmental conditions that electrical contacts or connectors can be expected to experience in various application environments (see references [2] and [3]).

Test samples that have been exposed to MFG tests have ranged from bare metal surfaces, to electrical connectors and to complete assemblies.

The specific test conditions are usually chosen so as to simulate, in the test laboratory, the effects of certain representative field environments or environmental severity levels on standard metallic surfaces, such as copper and silver coupons or porous gold coatings (see references [2] and [3]).

Because MFG tests are simulations, both the test conditions and the degradation reactions (chemical reaction rate, composition of reaction products, etc.) may not always resemble those found in the service environment of the product being tested.

The MFG exposures are generally used in conjunction with procedures that evaluate contact or connector electrical performance such as measurement of electrical contact resistance before and after MFG exposure.

The MFG tests are useful for connector systems, the contact surfaces of which are electroplated or clad with gold or other precious metal finishes. For such surfaces, environmentally produced failures are often due to high resistances or intermittences caused by the formation of insulating contamination in the contact region. This contamination, in the form of films and hard particles, is generally the result of pore corrosion product migration or tarnish creepage from pores in the precious metal coating and from unplated metal boundaries, if present.

Metallic coatings — Test methods for electrodeposited gold and gold alloy coatings —

Part 2:
Mixed flowing gas (MFG) environmental tests

WARNING — This part of ISO 4524 does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this part of ISO 4524 to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1   Scope

This part of ISO 4524 provides procedures for conducting mixed flowing gas (MFG) environmental tests involving exposures to controlled quantities of corrosive gas mixtures.

It describes the required equipment and the methods for gas, temperature and humidity control that enable tests to be conducted in a reproducible manner. Reproducibility is measured through the use of control coupons the corrosion films of which are evaluated by mass gain, coulometry or by various electron and X-ray beam analysis techniques. Reproducibility can also be measured by *in situ* corrosion rate monitors using electrical resistance or mass frequency change methods.

MFG tests can be used to:

— evaluate novel electrical contact metallization for susceptibility to degradation due to environmental exposure to the test corrosive gases;

— evaluate the shielding capability of connector housings that may act as a barrier to the ingress of corrosive gases;

— evaluate the susceptibility of other connector materials such as plastic housings to degradation from the test corrosive gases.

MFG tests are not normally:

— used as porosity tests (for guidance on porosity testing, see ISO 10308, *Metallic coatings — review of porosity tests*);

— applicable where the failure mechanism is other than pollutant gas corrosion such as in tin-coated separable contacts.

2   Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 4524. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 4524 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 4221:1980, *Air quality — Determination of mass concentration of sulphur dioxide in ambient air — Thorin spectrophotometric method.*

ISO 4677-1:1985, *Atmospheres for conditioning and testing — Determination of relative humidity — Part 1: Aspirated psychrometer method.*

ISO 4677-2:1985, *Atmospheres for conditioning and testing — Determination of relative humidity — Part 2: Whirling psychrometer method.*

ISO 6349:1979, *Gas analysis — Preparation of calibration gas mixtures — Permeation method.*

ISO 6767:1990, *Ambient air — Determination of the mass concentration of sulfur dioxide — Tetrachloromercurate (TCM)/pararosaniline method.*

ISO 7934:1989, *Stationary source emissions — Determination of the mass of concentration of sulfur dioxide — Hydrogen peroxide/barium perchlorate/Thorin method.*

ISO 7996:1985, *Ambient air — Determination of the mass concentration of nitrogen oxides — Chemiluminescence method.*

ISO 9096:1992, *Stationary source emissions — Determination of concentration and mass flow rate of particulate material in gas-carrying ducts — Manual gravimetric method.*

ISO 10313:1993, *Ambient air — Determination of the mass concentration of ozone — Chemiluminescence method.*

ISO 12687:1996, *Metallic coatings — Porosity tests — Humid sulfur (flowers of sulfur) test.*

IEC 60050, *International Electrotechnical Vocabulary.*

3   Terms and definitions

For the purposes of this part of ISO 4524, the terms and definitions relating to electrical contacts given in IEC 60050 apply.

4   Reagents and materials

4.1   Water for humidity generation, equivalent to grade 1 or better of ISO 3696.

4.2   Carrier gas, such as nitrogen. It shall not introduce reactive constituents into the test atmosphere to an amount of more than 5 % of any specified corrosive test atmosphere constituent.

4.3   Clean filtered air, as required for make-up to support the necessary exchange rate, in accordance with 6.6.7.1 b), as specified in 5.3.2.

4.4   Corrosive gases, chemically pure grade or equivalent.

4.5   Corrosivity monitor materials (CMMs), comprised of the coupons that are exposed to the test atmosphere for mass gain (annex A), coulometric reduction in accordance with annex C, or resistance monitoring in accordance with annex E.

5 Apparatus

5.1 General

Apparatus required to conduct MFG tests is divided into four major categories: corrosion test chamber, gas supply system, chamber monitoring system and chamber operating system.

5.2 Corrosion test chamber

5.2.1 The chamber shall consist of an enclosure made of non-reactive, low-absorbing, non-metallic materials contained within a cabinet or oven capable of maintaining the temperature to a maximum tolerance of ± 1° C with a preferred tolerance held to ± 0,1° C within the usable chamber working space in accordance with 6.3 with a means of introducing an exhaust gas from the chamber. The chamber isolates the reactive gases from the external environment. Chamber materials that are not low-absorbing can affect test conditions by absorbing or emitting reactive gases, leading to control and reproducibility problems. The chamber construction shall be such that the leak rate is less than 3 % of the volume exchange rate.

5.2.2 The chamber shall have provision for maintaining uniformity of the average gas flow velocity within ± 20 % of the specified value or of the chamber average when the chamber is empty. For chambers with a dimension of more than 0,1 m, measurement points shall be in accordance with A.3.2. For chambers with all dimensions of less than 0,5 m, a minimum of five points shall be measured at locations in the plane of sample exposure (perpendicular to the expected flow direction) that are equidistant from each other and the walls of the chamber. After all five or more data values are recorded, all the measurements shall be repeated a second time. When the two sets of measurements have been recorded a third complete set shall be recorded. The arithmetic average of the 15 or more measurements shall be the chamber average, see 6.5 and 6.6.8. If a hot wire anemometer is used for velocity measurements these shall be made in accordance with ISO 9096, with the exception that sample sites shall be in accordance with annex A.

5.2.3 A sample access port is desirable. This should be designed such that control coupons can be removed or replaced without interrupting the flow of gases. Corrosion test chamber corrosion rates have been shown to be a function of the presence or absence of light (see [4] and [5]). Provision shall be made for controlling the test illumination in accordance with a test specification.

5.2.4 Examples of test chamber systems are shown in Figures 1, 2 and 3.

They shall not be considered as exclusive examples.

Key

1 Working volume
2 Exhaust
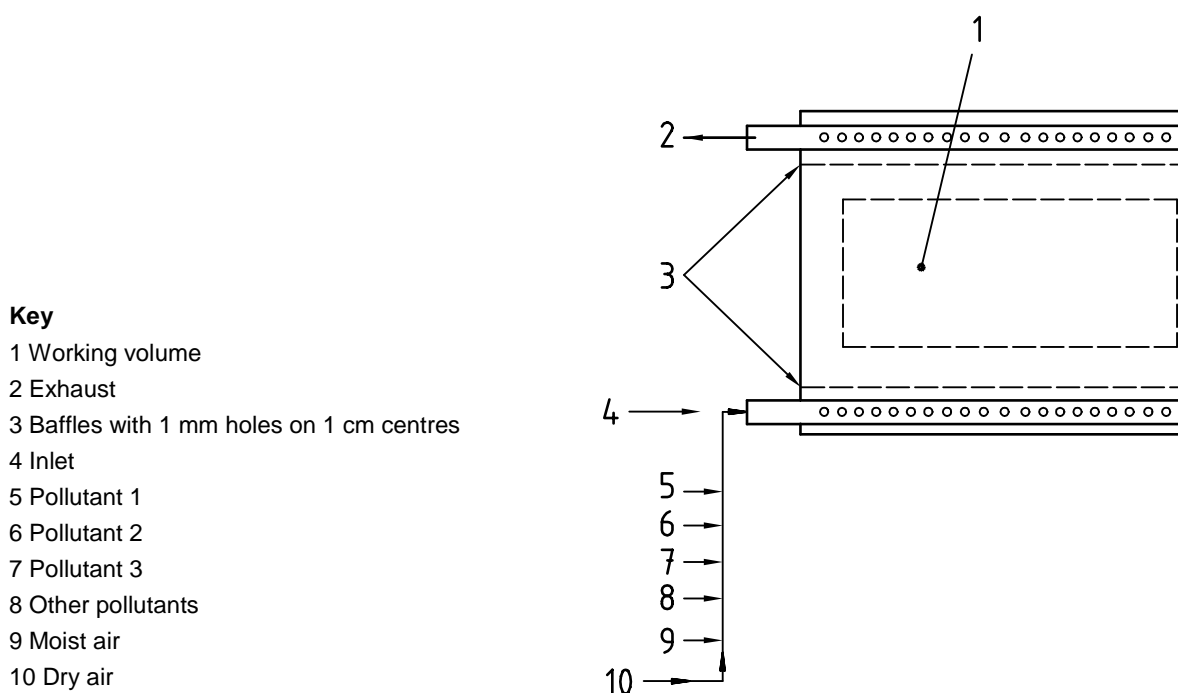3 Baffles with 1 mm holes on 1 cm centres
4 Inlet
5 Pollutant 1
6 Pollutant 2
7 Pollutant 3
8 Other pollutants
9 Moist air
10 Dry air

Figure 1 — Schematic flow through mixed flowing gas (MFG) test system

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Key

1 Working volume
2 Test chamber insert
3 Exhaust
4 Temperature controlled chamber
5 Gas monitoring meters
6 Fans
7 Mixed gas / humidified air blending area
8 Main flow
9 Humidity source
10 Air
11 Flow meters
12 Nitrogen
13 Permeation tubes
14 Limiting orifices
15 Mixing chamber
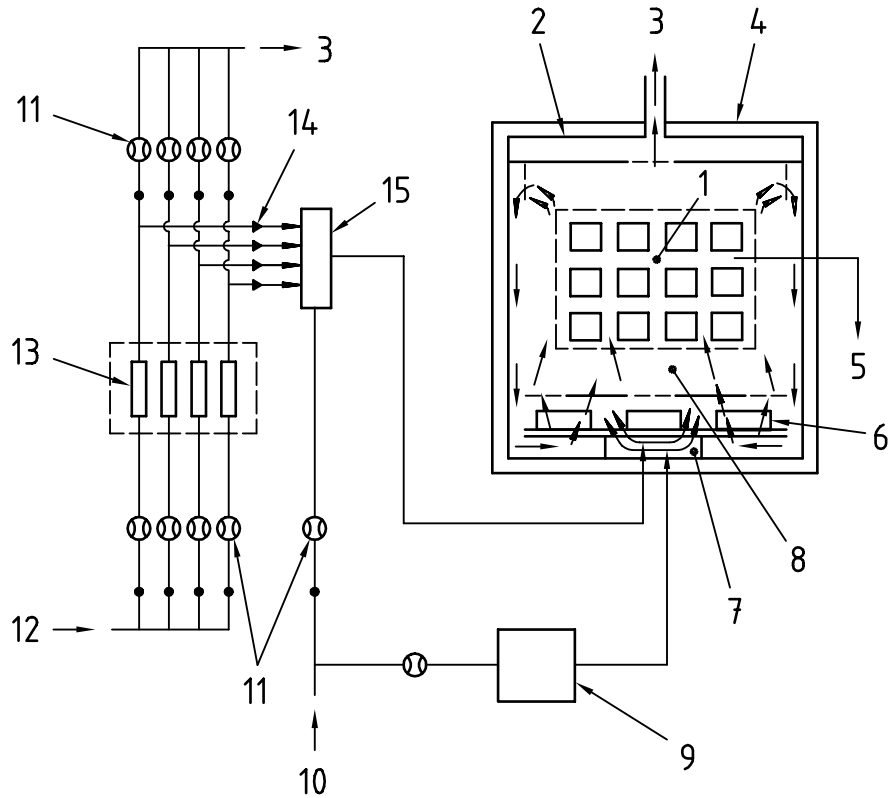
Figure 2 — Schematic vertical recirculating mixed flowing gas (MFG) test system

Key

1 Gas concentration measurement points
2 Temperature and humidity measurement
3 Gas velocity measurement
4 Test sample region
5 Baffles
6 Gas concentration analysis
7 Test sample data collection
8 Chamber exhaust
9 Mixed gas supply
10 Fans
11 Air flow direction
12 Humidity source
13 Multiple gas sources
14 Make-up air
15 Gas mixing manifold
16 Temperature control chamber
17 Corrosive gas chamber

Figure 3 — Schematic horizontal recirculating mixed flowing gas (MFG) test system

5.3 Gas supply system

5.3.1 Description and requirements

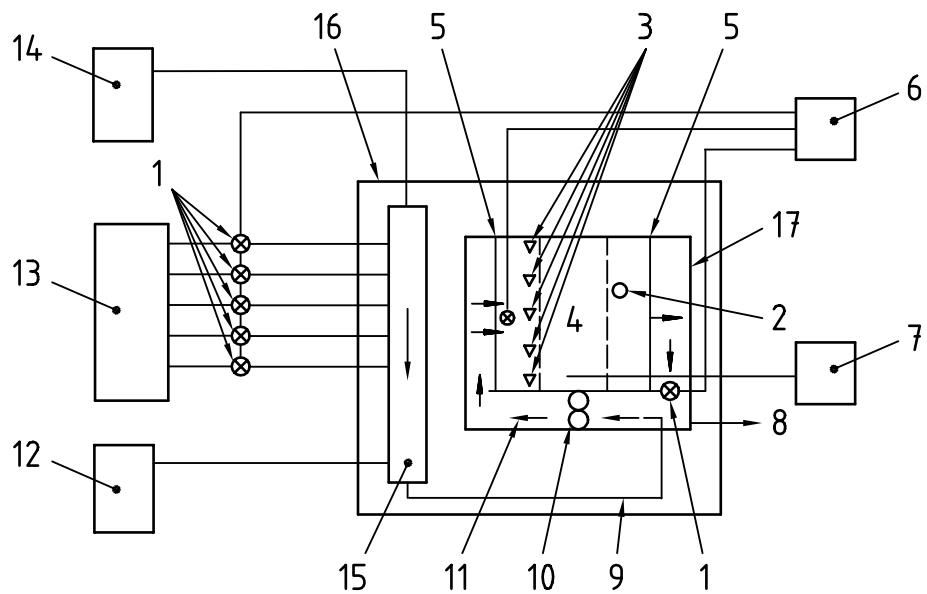The gas supply system consists of five main parts:

— a source of clean, dry, filtered air;

— a humidity source;

— corrosive gas source(s);

— gas delivery system;

— corrosive gas concentration monitoring system(s).

Total supply capacity shall be such as to meet requirements for control of gas concentrations. The minimum number of volume changes is determined by the requirement that the concentration of corrosive gases be maintained within ± 15 % between gas inlet and outlet. This is verified by measurement of the gas concentrations near the gas inlet upstream of the usable chamber working volume and comparing with gas concentrations measured downstream of the usable chamber working volume just prior to the chamber exhaust. These values shall be within ± 15 % (see 6.3). Alternative methods of demonstrating compliance with the maximum allowable concentration gradient are acceptable. Normally a conditioned chamber equilibrates within several hours of sample loading and start of corrosive gas supply. Times longer than 2 h shall be reported in the test report; see clause 7. A guide to estimating supply requirements is provided in annex B.

5.3.2 Clean, dry, filtered air source

Gases other than oxygen and nitrogen that are present in the dry air source shall be less than or equal to those defined by OHSA Class D limits. In addition, gases other than nitrogen, oxygen, carbon dioxide, noble gases, methane, nitrous oxide and hydrogen shall be less than 0,005 (cm^3/m^3) by volume total and shall be high efficiency particulate arrestant (HEPA) filtered.

5.3.3 Humidity source

The humidity source shall use distilled or deionized water, of ISO 3696 grade 1 or better, and shall introduce no extraneous material. The humidity source shall be maintained equivalent to ISO 3696 grade 2 or better, with the exception that electrical resistivity shall be maintained equivalent to ISO 3696 grade 3. The time-averaged value of humidity shall be within ± 1 % relative humidity of the specified value with absolute variations no greater than ± 3 % relative humidity from the specified value.

Table 1 — Instrumental methods for gaseous components

Gas	Suitable instrumental method	Suitable procedure
H_2S	Photometric or luminescence	Commercial equipment is available
SO_2	Photometric or luminescence	ISO 4221, ISO 6767, ISO 6349, ISO 7934. Commercial equipment is available
NO_2	Chemiluminescence	ISO 7996. Commercial equipment is available
Cl_2	Electrochemical	ISO 10313
NOTE The instrument manufacturer's instructions for delivering samples to the instrument should be followed.		

5.3.4 Corrosive gas sources

Corrosive (test) gases, such as nitrogen dioxide, hydrogen sulfide, chlorine, sulfur dioxide etc. shall be of chemically pure grade or better. Such gases are frequently supplied in a carrier gas such as nitrogen which shall be of pre-purified grade or better.

5.3.5 Gas delivery system

The gas delivery system is comprised of three main parts: gas supply lines, gas control valves and flow controllers, and a mixing chamber. The test delivery system shall be capable of delivering gases at the required concentrations and rates within the test chamber.

a) All materials used for the gas transport system shall not interact with the gases to the extent that chamber gas concentrations are affected.

b) Gases, make-up air and water vapour shall be thoroughly mixed before gas delivery to the samples under test in the chamber. Care shall be taken to ensure absence of aerosol formation in the mixing chamber whereby gases are consumed in the formation of particulates that can interfere with gas concentration control and can introduce corrosion processes that are not representative of gaseous corrosion mechanisms. Aerosol formation can be detected by the presence of a visible film or deposit on the interior surface of the gas system where the gases are mixed.

c) Any fogging of the tubing walls or mixing chamber walls can be taken to be an indication of a loss of corrosive gases from the atmosphere. Final mixing of the specified gases shall occur inside a separate area of, or as close as possible to, the test chamber so as to ensure thermal equilibration with the test chamber.

d) There shall be a means for measuring the flow at the inlet of the chamber and also at the exhaust of negative pressure chambers to ensure the absence of uncalibrated gas streams.

5.3.6 Corrosive gas concentration monitoring system

Standard measurement systems for very low level gas concentrations are listed in Table 1, which provides for gases in common use in present mixed flowing gas systems, for testing electrical contact performance.

a) Each instrument shall be characterized for interference with the gases specified, both individually and mixed.

b) Depending on the exact equipment set used, it may not be possible to measure accurately the concentration of some gases, such as chlorine, in combination with any of the other gases.

c) The analytical instruments shall be maintained and calibrated electronically in accordance with the manufacturers' recommendations. Standard gas sources shall be calibrated in accordance with the manufacturers' specifications. Analysers shall be calibrated to standard gas sources in accordance with the manufacturers' recommendations. They shall be calibrated before and after each test and whenever the indicated concentration changes exceed the permitted variation in the test specification.

NOTE   If the chlorine monitor is not being used during the test, it need not be calibrated during the test.

d) Control of the humidity within the test chamber itself is part of the chamber monitoring system which is described in 5.4.

5.4 Chamber monitoring system

5.4.1 General

Chamber monitoring systems shall be used to ensure test reproducibility from one test run to the next. Monitoring instruments shall be calibrated periodically because the corrosive effects of mixed gas environments can affect instrument sensitivity and accuracy. The chamber monitoring system shall address four test parameters: temperature, humidity, gas concentrations and corrosivity.

5.4.2 Temperature monitoring

The temperature should be monitored using a simple thermocouple or other temperature measurement device capable of the required resolution of 0,2 °C and accuracy of ± 0,5 °C within the temperature range required by the test specification. For test temperatures above 40 °C, see 6.6.5.

5.4.3 Humidity monitoring

Humidity shall be determined by an apparatus with a resolution of 0,5 % relative humidity and an accuracy of ± 1 % relative humidity. ISO 4677-1 and 4677-2 describe a dew point method that meets this requirement. For test temperatures above 40 °C, see 6.6.5.

5.4.4 Corrosive gas monitoring

The chamber corrosive gas concentration shall be monitored by provision of sampling lines from the test chamber to the gas concentration analysers. These sampling lines shall be maintained above the chamber dew point temperature. The interior of the gas concentration analysers shall also be maintained above the chamber dew point temperature. For test temperatures above 40 °C, see 6.6.5.

5.4.5 Chamber corrosivity monitoring

Chamber corrosivity can be monitored using a number of complementary techniques, none of which provides both a comprehensive analysis of the corrosion process and an instantaneous indication of the corrosion rate. Four acceptable techniques are as follows: metal coupon corrosion mass gain, corrosion film analysis by coulometric reduction, corrosion film analysis by electron or X-ray beam analysis, and electrical resistance measurement of corroding metal conductors. The first three provide information subsequent to the test whereas the last can be used *in situ* in the test chamber to provide information during the test itself. See annexes A, C, D and E for a discussion of these methods. The party requesting the test should specifiy the chamber corrosivity monitoring methods to be used.

5.5 Chamber operating system

The chamber operating system comprises equipment and software necessary for adequate control of all the variables of the test. This will include data logging and alert procedures for operation outside of desired bounds. Some form of computer control is generally used to assure satisfactory operation during unattended periods, or data tracking for failure analysis in case the test is disrupted.

6 Procedure

6.1 Methods

This procedure covers two methods, method A on low exchange rate chambers and method B on high exchange rate chambers. Method B tests on high exchange rate systems typically have gas exchange rates of 60 changes/h (l/min) or greater, while method A tests on low exchange rate systems generally operate between 5 exchanges/h and 15 exchanges/h. These methods are necessary because sample loading affects chamber gas concentration. The following procedures are comprised of requirements and other comments provided as a general guide to achieving reproducible results with MFG testing. These procedures are compatible with most test facilities; however, differences in apparatus, test conditions or local safety requirements may necessitate alternative procedures. Any deviations shall be reported in the test report [see 7 j)].

6.2 Stages

The procedure is comprised of the following major activities: test chamber calibration, sample preparation, test chamber set-up, test chamber start-up, test chamber operations during test chamber shut-down, and reporting requirements. In the remainder of this clause, method A and method B are identified only where the procedure elements are not common to both methods.

6.3 Test chamber calibration

The spatial uniformity of the corrosivity of test chambers larger than 0,5 m on a side shall be measured in accordance with annex A, which describes the required placement scheme for calibration samples that are used to determine corrosion rate uniformity over the entire chamber volume. For chambers smaller than 0,5 m on a side or chambers of unusual geometry, use sufficient samples for corrosivity characterization in order to delineate clearly the usable chamber working volume as defined by this paragraph. This profiling shall be done when the chamber is initially built and after any structural change to the chamber that may affect the flow of test gas over the samples. Annex A describes procedures using mass gain. Alternative means to characterize corrosion rates such as coulometric reduction (see annex C), or in accordance with 5.4.5, are also acceptable. A minimum of three corrosivity monitors of a given type shall be used, if possible, in each chamber location. The average corrosivity for that location shall be within 15 % of the average for the entire chamber. When a single monitor has to be used at a location, due to chamber size limitations or monitor geometry, the average corrosivity for that location shall be based upon three consecutive calibration runs. These requirements define the usable chamber working space.

NOTE   Profiling does not remove the necessity to provide and evaluate CMMs for each test run of the test chamber.

6.4 Sample preparation

6.4.1 Two types of sample are used for these tests, CMMs and the test samples being evaluated. Prepare CMMs in accordance with their respective standards.

6.4.2 Prepare the test samples in accordance with any agreement between vendor and user of the samples being tested. Such preparation shall be consistent with normal preparations expected when test samples would be exposed to normal application environments in their intended applications except when evaluation of preparation methods is the object of the test.

6.5 Test chamber set-up

6.5.1 Place test samples and CMMs in the chamber in a manner that is representative of the way the test samples would be used in the application environment, if known. Ensure that this is done in a consistent manner such that the test results will be reproducible over time.

6.5.2 In general, the samples shall be suspended or held with their long dimension parallel to the flow of air and a minimum of 5 cm away from any surface to avoid boundary layer effects. No test samples or CMMs shall be shielded from the source of the pollutant gases by any control coupon, test fixture, test samples, test rack or other obstruction placed upstream.

6.6 Test chamber start-up

6.6.1 Test conditions

Test conditions such as those given in 7 g) shall be specified by the party requesting the test.

6.6.2 Avoidance of condensation

Establish an apparatus specific start-up and shut-down procedure to avoid visible water condensation on the test samples and CMMs at time of insertion into the chamber. Such condensation on the parts invalidates the test.

6.6.3 Chamber preparation

6.6.3.1 When contaminants such as condensed gases (for example, free sulfur or organic material from test samples) or corrosion particulate deposits are present or suspected, clean the inside of the chamber to reduce the concentration of adsorbed gases by wiping the interior walls with a clean, lint-free cloth before installing samples at the start of any test. Residual contamination can affect the accuracy of subsequent chlorine measurements.

6.6.3.2 An indication of the need for a wipe down would be an abnormally long time [in excess of 20 chamber gas exchanges for low-sulfur (for example, < 0,020 cm^3/m^3 H$_2$S) tests or in excess of 200 chamber gas exchanges for high-sulfur tests] to reach 10 % or 0,001 ppm corrosive gas concentration levels after chamber shut-down.

6.6.3.3 For method B, after cleaning the chamber, establish the specified temperature and humidity conditions and allow these to stabilize within the specified tolerances. Next set the chlorine concentration at the level specified at the maximum chlorine supply rate available; allow to stabilize over one or more days as the chlorine equilibrates to specified tolerances, add the remaining gases required by the test specification and bring them to their specified level at the maximum exchange rate available. Allow them to equilibrate over a period of 1 d and reconfirm that non-chlorine gases are within specification.

6.6.4   Chamber loading

6.6.4.1   Method A

Place the test samples and control materials in the chamber when the samples, materials and chamber are at ambient temperature and relative humidity in order to avoid visible condensation.

Alternatively, samples at chamber temperature can be placed directly into a heated chamber at or below specified humidity. See 6.6.7.1 d) 2) for related information regarding chlorine.

6.6.4.2   Method B

Test samples and CMMs shall be at chamber temperature prior to loading as they are to be loaded into a chamber at test humidity and gas concentrations.

6.6.4.3   Methods A and B

For tests that require *in situ* measurements on the test samples, install necessary electrical access cabling at this time and make initial measurements, as required by the test specification.

6.6.5   Chamber heating

6.6.5.1   General

The practical upper limit to the test temperature for this procedure is determined by the initial temperature of the analysers, including any auxiliary heating, such that condensation of the sampled gas stream will not occur in the instrument. In order to avoid condensation in the analytical instruments and sampling lines, the relative humidity of the sampled gas mixture in the analytical instruments and sampling lines shall not exceed 80 % relative humidity. This is generally accomplished by heating the sampling lines and instruments as required. Manufacturers of the analysers should be consulted to determine maximum temperatures at which analysers can be maintained. Modifications of this procedure such as limiting chamber humidity to a wet-bulb temperature less than the instrument internal temperature during corrosive gas supply settings and subsequent elevation of humidity to specified values may be required for high temperature (for example 70 °C), high humidity corrosive gas tests.

6.6.5.2   Method A

Heat the chamber to the specified test temperature, if required. A holding time of at least 1 h is recommended to ensure temperature equilibration of the test samples. A longer time may be necessary for massive assemblies.

6.6.5.3   Method B

See 6.6.3.3.

6.6.6   Chamber humidification

6.6.6.1   Method A

Increase the chamber humidity to the specified test relative humidity, if required.

6.6.6.2 Method B

See 6.6.3.3.

6.6.7 Gas level setting

6.6.7.1 Method A

a) Confirm that temperature and humidity are at equilibrium at specified test conditions.

b) Introduce all corrosive gases to the level specified and measure gas concentrations [see 5.3.6 and 6.6.7.1 d) 2)] in the test chamber in accordance with 5.4.4; adjust the gas supply rates and volume exchange rate until the down-stream gas concentrations are within $\pm$ 15 % or 0,003 cm^3/m^3, whichever is larger, of the upstream concentrations and at the gas concentrations specified. Allow to stabilize and repeat measurement after 1 h to 2 h to confirm gas supply and volume exchange rate setting. Circulating fans shall be running during this gas supply setting in recirculating-type chambers.

c) Inability to achieve 15 % (0,003 ppm) gas concentration tolerance between upstream and down-stream values may indicate insufficient exchange rate or excessive loading of test samples.

d) Exceptions in the case of chlorine are as follows.

   1) When conducting multiple gas tests with chlorine as one of the corrosive gases, chlorine shall be the first gas whose supply setting is established. This is because of interferences from other gases which are due to present limitations of the chlorine gas monitoring equipment in common use.

   2) Depending on the absolute accuracy of the supply system, it may be desirable to set the initial chlorine level in an empty chamber that is at specified temperature and humidity conditions in order to ensure that test samples will not be inadvertently exposed to excessive chlorine levels. After sample placement, ensure conformity with 6.6.7.1 b).

   3) When chlorine is used, the initial chlorine level is set at the end of the day and the final setting is made in the morning to allow additional stabilization time for chlorine level setting unless it is shown to stabilize more rapidly.

e) Once gas levels are set initially, any change in the gas supply system requires confirmation of conformity with the requirements of 6.6.7.1 b) and may necessitate resetting of the gas controls; any such actions shall be reported in accordance with clause 7.

f) For assembly level testing, for example, a disk drive assembly or large wiring harness, gas levels should be set upstream of the test object at the maximum exchange capacity of the system, with the assembly in place. Record the down-stream gas concentrations and report them in the test report as a deviation; see clause 7. When testing at assembly level, the requirement that the gas concentration in the exhaust stream is within 15 % (or 0,003 cm^3/m^3, whichever is larger) of the inlet stream may not be applicable since it is possible that under operating conditions exhaust streams from the assembly may be depleted of pollutants due to absorption within the assembly itself. The party requesting the test and the test operator should discuss the expected deviation from the 15 % concentration variation for assembly testing.

6.6.7.2 Method B

Under method B, the gas levels have been previously set. However it remains necessary to confirm gas concentrations after chamber loading with test samples. This is only possible for gases other than chlorine; such gas levels shall be measured upstream and down-stream of the test samples in accordance with 5.3.1 for conformance to its requirements. Verify the chlorine level by means of an integrating sampler such as an environmental monitoring device (EMD) (see [4]) installed down-stream of the samples after chamber loading and removed for evaluation of the test chlorine levels at time of removal of test samples from the chamber. For interrupted tests, turn off the EMD sampler while test samples are outside the test chamber. Report the results of the EMD analysis as a deviation if they indicate that chlorine levels were not as specified in the test specification.

6.6.8   Air velocity confirmation

For tests specifying air velocity, after test samples are placed in the chamber, and gas and exchange rates are set, measure the velocity of the corrosive gas air stream impinging on the test samples between 5 cm and 8 cm upstream of the test samples for compliance with the air velocity specified and the allowable tolerance of $\pm$ 20 %.

6.6.9   Corrosivity setting

Where corrosivity is required to be monitored by means of one or more *in situ* continuous monitors such as a quartz crystal microbalance (QCM) or a resistance monitor (RM) [e.g. a corrosion indicating device (CID)], maintain the corrosivity within the bounds specified by the test specification. Deviations from the expected corrosivity require immediate attention to the controlling parameters such as temperature, humidity and gas concentration to rectify the deviation. Report the inability to attain the specified corrosivity at the specified test sample loading with all other parameters in the specified range as a test deviation in accordance with clause 7.

6.6.10 Test duration

The test duration can be specified in two different ways. The test may be specified to last a set period of time, or it may be specified to last until a required total corrosion, as measured by an *in situ* corrosivity monitor, is achieved.

6.7   Test chamber operation

6.7.1   General

Monitor the test chamber for temperature, humidity and pollutant gas concentrations to demonstrate chamber stability with respect to short-term fluctuations and long-term drifts. Place CMMs in the test chamber adjacent to the test samples. This will provide a measure of chamber corrosivity after the test is completed. For a plane array of test samples place a minimum of five CMMs, one at each corner and one at the centre of the array of test samples, Corrosivity monitors such as resistance monitors or quartz crystal microbalances are recommended to provide an integrated continuous assessment of chamber status.

6.7.2   Test tolerances

Maintain the following tolerances on test parameters unless otherwise specified by the party requesting the test.

a)   Maintain the temperature to within $\pm$ 1 °C with a preferred tolerance of $\pm$ 0,5 °C.

b)   Maintain the humidity at an average value within $\pm$ 1 °C relative humidity with an absolute variation less than 3 % relative humidity.

c)   Maintain the gas concentrations within $\pm$ 15 % or $\pm$ 0,003 cm^3/m^3, whichever is larger.

d)   If specified, maintain the corrosivity within 15 % of the specified value.

e)   Maintain the test duration within $\pm$ 2 % or $\pm$ 2 h, whichever is longer.

6.7.3   Psychrometric monitoring

6.7.3.1   The temperature and humidity shall be monitored by continuous or periodic means. The maximum period between measurements shall be 30 min.

6.7.3.2   Air velocity need not be monitored during the test unless significant changes in sample placement occur during the test. In recirculating-type chambers there shall be some means of verifying that the fans are operating properly in order to ensure that air velocity remains within the tolerance band specified or the range for which chamber calibration was obtained.

6.7.4 On-line control

In addition to monitoring, some type of on-line control is recommended. This allows dynamic adjustments to be made in the gas concentrations, to increase the probability of a valid test.

6.7.5 Test continuity

6.7.5.1 Test exposure

The test exposure should be run continuously with as few interruptions as possible, unless otherwise specified. Interruptions for removal or replacement of test samples or CMMs, during which time chamber conditions may vary outside the limits defined in 6.7.2, shall not be considered deviations provided the total duration of all interruptions is less than 5 % of the total test time.

6.7.5.2 Test integrity

The test shall not be disrupted by the addition of new samples for a different test during the operation of the test. New samples introduce fresh absorbing surfaces that can significantly alter the gas concentrations at which the original samples were being tested; such a disruption would lead to problems reproducing the test results and is unacceptable.

6.8 Test chamber shut-down

6.8.1 Electrical power down

6.8.1.1 Discontinue electrical power to any devices under test and to *in situ* corrosivity monitors.

6.8.1.2 For method B, keep chamber test conditions constant at all times, with or without test samples in the chamber. Accordingly, remove test samples, corrosivity monitor materials and the integrating chlorine monitor from the chamber at this time to an oven at chamber temperature to allow the items removed from the test to dry. For a test conducted at room temperature, where room temperature is above the dew point of the chamber humidity content, test materials can be removed to ambient conditions. For test samples, such as assemblies, that can entrain quantities of corrosive gas, remove the test samples to a fume hood to allow for degassing to a safe level. At this point, method B is complete except for the test report as required by clause 7.

6.8.2 Corrosive gas shut-down, method A

6.8.2.1 Discontinue the corrosive gas supply, except for chlorine, if used. Allow the chlorine level to equilibrate in the absence of the other gases. Measure the chlorine level and residual levels of other gases to ensure conformity to 6.6.7.1 b) and report if it is outside the test specification. Then, discontinue the chlorine supply.

6.8.2.2 If high levels of H_2S or SO_2, or both, are used, it may not be possible to measure accurately the Cl_2 concentration because the sulfur species emitted from the test samples can interfere in a negative manner to reduce the oxidant-caused signal in some chlorine monitors (e.g., MAST oxidant monitor). If such interference is suspected, the test samples shall be removed prior to verifying the chlorine concentration. Record the chlorine flow settings and shut off all corrosive gas supply. Empty the test chamber of test samples and CMMs. Reseal the test chamber and restart the chlorine flow at the prior setting. Measure the chlorine level and record for inclusion in the report as detailed in clause 7. Discontinue the chlorine flow.

6.8.3 Humidity control, method A

Discontinue humidity generation while maintaining the chamber temperature if it is necessary to reduce chamber temperature. When the relative humidity has stabilized at a low level, the chamber temperature can be reduced in convenient increments while ensuring freedom from condensation until the chamber can be safely opened and the test samples and CMMs removed from the chamber.

7 Test report

The test report shall contain the following information:

a)   reference to this part of ISO 4524, i.e. ISO 4524-2;

b)   the nature of the substrate and of any intermediate underlayer(s);

c)   the nature of the coating;

d)   the date of the test and the name of the test engineer;

e)   a description of the test samples: the number of test samples, the condition in which the samples were tested, the exposure intervals and data summary;

f)   a description of each type of CMM: the number of CMMs, a description of CMM placement, the exposure intervals, data from the CMMs, the procedures used for preparation and analysis, the equilibration time to stabilize gases at $\pm$ 15 % (or 0,003 cm^3/m^3) and details of inlet to exhaust if longer than 2 h;

g)   details of the test conditions: levels and relevant tolerances of gas concentrations, the temperature and air humidity, the air velocity and direction, the illumination conditions, the exchange rate, the test duration, and details of test methods A and B;

h)   the chamber dimensions;

i)   the usable chamber working space in accordance with 6.3;

j)   deviations from the conditions specified in this part of ISO 4524;

k)   a record of all interruptions (reasons and duration).

Annex A
(normative)

Mass gain coupons

A.1 Reagents and materials

A.1.1 Reagent purity. Reagent grade chemicals, or other grades of sufficiently high purity to permit use without lessening the accuracy of determination, shall be used in all tests.

A.1.2 Acetone, reagent grade.

A.2 Apparatus

A.2.1 Racks or fixtures, suitable for holding copper coupons in the test chamber. Make these fixtures from a material that is not attacked by the corrosion test. The fixtures shall be designed to:

a) hold the coupons in a vertical orientation;

b) hold the coupons so that they do not show any perceptible motion when observed with the unaided eye during the test;

c) cover less than 5 % of the entire coupon surface area;

d) touch the coupon only with electrically insulating parts;

e) allow free circulation of ambient air on both sides of the coupon.

In general, design all parts of the fixture in order to permit maximum circulation of the ambient air around the coupon surfaces. The size and positioning of the holding fixtures depend on the chamber size. Requirements on the number and spacing of coupons are listed in A.3; the holding fixtures shall be designed to conform to these requirements.

A.2.2 Balance, with a capacity of at least 2 g and a resolution of 5 μg. Maintain the ambient air in the vicinity of the balance at between 20 % and 50 % relative humidity.

A.2.3 Fume cupboard, to conduct the chemical cleaning procedure of the coupons.

A.3 Procedure

A.3.1 The number of copper coupon specimens to be prepared shall be determined in accordance with A.3.2 to A.3.4.

A.3.2 For chambers with cubic working volumes, use the length of an edge to determine the number and placement of coupons in accordance with the following rules. For chambers with an edge dimension of 0,9 m or less, construct a reference grid with three equally spaced lines in each direction with the outer lines 0,1 m from the chamber wall and the third line centred between the outer lines. Place a coupon at each intersection of grid lines (27 coupons required). For chambers with an edge dimension of 0,9 m to 1,5 m construct a reference grid with four equally spaced lines in each direction. The outer lines are placed 0,1 m from the chamber wall. Place a coupon at each intersection of grid lines (64 coupons required). For chambers with a maximum edge dimension greater than 1,5 m but less than 2 m, construct a reference grid with five equally spaced lines in each direction. The outer lines are placed 0,1 m from the chamber wall. Place a coupon at each intersection of grid lines (125 coupons required).

A.3.3 For rectangular chambers with non-cubic working volumes, the guidelines for each dimension of the chamber along the x, y and z axes of the chamber shall follow the appropriate guidelines applied to cubic chambers. Thus, if the x and z axes are 1,4 m and the y axis is 0,8 m, four grid lines would be used for the x and z axes and three grid lines would be used for the y axis when determining the grid for coupon location.

A.3.4 For chambers with working volumes of shapes other than those covered in the preceding sections, devise a logical placement pattern with a coupon density roughly equal to that specified for rectangular chambers.

A.3.5 Select an appropriate duration of exposure for the copper coupons. Base this selection primarily upon the time required for the test conditions to produce a statistically significant mass change. Additional exposure time may be added in order to comply with other applicable requirements, specifications, agreements, etc., or for convenience of the test operator, or both. Generally, the test time shall be one or more whole days with a tolerance of ± 1 h.

A.3.6 Prepare the test coupons from wrought, annealed, oxygen-free copper ($\geqslant 99,95$ % pure copper alloy UNS C10200) sheet. Select a thickness of sheet sufficiently stiff to resist bending during handling during the test but not so thick that the edges become a significant portion of the surface area. In general, thicknesses between 0,1 mm and 0,6 mm are recommended. Obtain material with a surface roughness less than 0,15 μm centre line average and use the material with the as-rolled surface finish. Make the coupons squares or rectangles preferably 12,5 mm $\pm$ 0,5 mm wide. One or two holes 2,5 mm or less in diameter may be added to aid in mounting. Inspect the edges of the coupons at × 10 magnification for the presence of burrs or slivers. If such features are found, they shall be removed as they may corrode at a much higher rate than the coupon surface.

A.3.7 Mark all coupons with a code giving each coupon a unique identity. Make the characters in the code marking about 2 mm high by engraving or stamping without ink.

A.3.8 During the cleaning procedure and at all times after cleaning, handle the coupons only with clean tweezers grasping the region around the identification marking. Place each copper coupon in a separate clean, dry glass vial of appropriate size such that only the edges and corners of the coupons touch the glass surfaces.

A.3.9 Clean all coupons in accordance with the procedure given in A.3.10 to A.3.22. Where a liquid bath is required, fill an appropriate vessel to a depth equal to or greater than 25 mm plus the largest dimension of the coupon sample to be cleaned. Unless otherwise directed, change the fluid in all baths after 50 coupons have been processed. Unless otherwise directed, use all baths at room temperature.

PRECAUTIONS — Conduct all operations involving acids and solvents in a fume cupboard. Dispose of all acids and solvents in a safe, legally acceptable manner.

NOTE   The goal of A.3.10 to A.3.17 is to produce a coupon surface reasonably free of oils, greases, particulate debris and similar contaminants. Alternative test methods that achieve the same result are acceptable. Such alternative test methods may be necessary or desirable depending upon local conditions or facilities.

A.3.10 Prepare two baths of boiling acetone.

A.3.11 Suspend the coupon vertically in boiling acetone in the first vessel for 30 s to 60 s.

A.3.12 Remove the coupon from the acetone and lay the coupon on a clean surface.

A.3.13 Dip a clean, adhesive-free cotton swab into the same vessel of acetone, scrub all areas of the coupon surface with a swab.

A.3.14 Turn the coupon over, rewet the swab, and repeat the scrub treatment on the other surface.

A.3.15 Suspend the coupon vertically in the second vessel of boiling acetone for 30 s to 60 s.

A.3.16 Slowly withdraw the coupon from the liquid, allowing the liquid to drip from one corner.

A.3.17 Suspend the coupon vertically for a minimum of 1 min (1 h maximum) in ambient air.

A.3.18 Transfer the coupon to a solution of 1 part concentrated hydrochloric acid and 3 parts deionized water; suspend the coupon vertically for 120 s $\pm$ 5 s in this solution.

A.3.19 Without allowing the surface to dry, immediately suspend the coupon vertically in deionized water for 15 s $\pm$ 5 s then immediately repeat in a second vessel of fresh deionized water.

A.3.20 Without allowing the surface to dry, transfer the coupon immediately to a bath of methanol; suspend the coupon vertically for 30 s to 60 s with agitation in the bath.

A.3.21 Remove the coupon from the methanol; immediately blow dry with pre-purified nitrogen or with clean dry air.

A.3.22 Place the coupon immediately in its glass vial, leave the vial uncapped for 10 min, then cap the vial unless proceeding immediately to the next step.

A.3.23 Allow all copper coupons to equilibrate in the vicinity of the balance for at least 30 min by placing the vials containing the coupons near the balance and removing the cap from each vial. Also, wait until at least 60 min has elapsed from the time that the cleaning procedure is completed until the weighing begins.

Weigh each coupon individually, replacing each in its vial after weighing. Reweigh two of the coupons to check the reproducibility. If the second mass reading does not differ from the first reading by more than 0,1 ng/mm^2 of exposed surface area, proceed to the next step. If readings differ by more than the preceding requirement, reweigh all coupons and repeat as required until stable masses are obtained.

A.3.24 Immediately install all coupons on holding fixtures in the corrosion test chamber. Record the time that the coupons are placed in the chamber in the corrosion test.

A.3.25 After the appropriate test time for the test method has elapsed, remove the coupons from the holding fixture, placing each in an uncapped vial. Place the vials containing the coupons in the vicinity of the balance and wait at least 30 min to allow the coupons to come to equilibrium with ambient temperature and humidity.

A.3.26 Weigh all coupons; reweigh each coupon as required until a stable reading is obtained from each coupon.

A.3.27 Calculate the difference in mass before and after exposure to the corrosion test.

A.4 Report

Report the results in the data report format shown in Figure A.1.

<table>
<tbody>
<tr><td colspan="5">

1. Date test started

2. Date test ended

3. Duration of exposure, i.e., hours or days in the test chamber

4. Test operator(s)

5. Designation of test chamber in which coupons were exposed

6. Dimensions of test coupons (normal dimensions may be reported provided that the actual dimensions do not differ by more that 2 % from normal)

7. Test conditions, e.g., gas concentrations, temperature, relative humidity, air flow rates in the chamber

8. Deviations from the procedure specified in this part of ISO 4524 (if none, this shall be stated)

9. Map or similar documentation that relates the identification number of each sample to the position of that sample in the test chamber

</td></tr>
</tbody>
</table>

Test results				
Identification number of sample	**Exposed area of sample** [a]	**Initial mass**	**Final mass**	**Mass change**

[a] Record total area of all exposed coupon surfaces.

Figure A.1 — Sample data report form

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Annex B
(informative)

Estimating required corrosive gas exchange rate

B.1   The required rate of corrosive gas exchange can be estimated from the total gas consumption required to obtain the expected corrosion rate for the test being performed. In a typical MFG test the initial corrosion rate can be as high as 8 nm/h of copper corrosion film growth over the first 8 h of the test. The most conservative assumption of one atom of corrosive gas per atom of copper implies that such a film thickness requires 2×10^{16} chlorine atoms/(h·cm^2) of exposed copper surface, if the entire film is comprised of CuCl. Thus the amount of chlorine supplied to the test chamber is 2×10^{17} atoms/(h·cm^2) if no more than 10 % loss of concentration can be accepted downstream of the exposed copper surface in accordance with the requirements of this practice. If the chlorine is being supplied at a concentration of 0,01 ppm in carrier gas, then 0,83 m^3 of such supply is required per hour per square centimetre of exposed copper surface. For 100 cm^2 of exposed copper, the gas supply rate is 83 m^3/h.

B.2   If half of the film is oxide and half is basic copper chloride [$Cu_2(OH)_3Cl$] as is more likely, then the chlorine consumption rate is reduced by a factor of 4,7 m^3/h to 17,7 m^3/h per 100 cm^2 of exposed copper.

Annex C
(normative)

Coulometric reduction

C.1 Reagents

The only reagents required for routine procedures are ACS reagent grade potassium chloride (for the electrolyte), pre-purified grade nitrogen or other inert gas, and a source of distilled or deionized water (grade 2 or better as specified in ISO 3696).

C.2 Apparatus

C.2.1 Electrolytic reduction cell and ancillary equipment

C.2.1.1 Reduction cell, preferably of glass, with a total internal volume of at least 600 ml. The cell shall be enclosed, but should have a suffecent number of entry ports or tubes to accommodate the required ancillary equipment (see Figures C.1 and C.2 for examples of a typical cell system).

C.2.1.2 Reference electrode, preferably silver/silver chloride since much of the data in the technical literature have been obtained with this type of electrode. It can be obtained commercially or made from silver strip or wire (see C.7).

These electrodes shall be checked periodically by testing them against a standard reference electrode (e.g. saturated calomel electrode) using a potentiometer or pH meter. The potential exhibited when measuring these silver/silver chloride electrodes in potassium chloride solution at 0,1 mol/l against a saturated calomel reference should be 0,05 V $\pm$ 0,01 V (see reference [6]).

C.2.1.3 Inert-gas purging tube, the end of which that is in the electrolyte being fitted with fritted glass or drawn to a fine tip (e.g. 0,5 mm inner diameter or less).

C.2.1.4 Counter electrodes, of pure platinum foil or wire. The number of counter electrodes may vary from two to four and they shall be positioned symmetrically around the sample. The area of the counter electrodes preferably should be equal to or greater than the sample area.

C.2.1.5 Wire hook or clip, for holding the sample. The upper part of the hook or clip shall be attached to a wire (inserted into a glass or plastic tube) for ultimate connection to the negative output of the power supply. If the wire hook is to be immersed in the solution, it shall be made of the same metal as the sample. If a clip is used, it shall be heavily gold plated (3 µm or more in thickness) and attached to a platinum wire hook for electrical contact.

C.2.2 Electronic equipment

NOTE   Three basic functional modules (see C.2.2.1 to C.2.2.3) are used to produce the constant cathodic current and to measure the resulting voltages as a function of time (for routine tarnish film analysis).

C.2.2.1 Constant current power supply, such as a potentiostat/galvanostat, capable of supplying a constant direct current, and adjustable from 0,02 mA to 2 mA with a precision of $\pm$ 1 %. However, for certain limited applications (for example, very large area samples), currents greater than 20 mA might conceivably be required.

C.2.2.2 Strip chart or digital recorder, or both. For a strip chart recorder, two pens are preferred, one pen for voltage and the other for a voltage-time derivative curve. The chart recorder shall have a variable speed capability from 10 mm/h to 100 mm/min and full scale voltage ranges from 0,5 V to 2 V. A resolution of the order of 0,5 % (i.e.

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Not for Resale

10 mV with 2 V full scale), though not essential, is helpful in data evaluation, and is easily obtained with any 250 mm chart recorder. A digital recording system, capable of data storage and graphic representation can be used instead of, or in conjuction with, the strip chart recorder system. Both systems shall have an input impedance of at least 10 Ω, preferably higher.

C.2.2.3 Differential circuit, or commercial differential voltage output apparatus. If a digital recording system is used in conjunction with, or to replace, an analog recording system, the following method can be used to create a differential curve. After the reduction is recorded completely, each data point, except for the first and last, shall be analysed. For a given point, X, determine the slope to the previous point X_p, and the subsequent point, X_s. Knowing the time interval, t, between each reading, the required slopes are as follows:

$$S_p = (X - X_p)/t S_s = (X_s - X)/t$$

An approximation of the slope at X is then found by taking the average of the slopes S_p and S_s as follows:

$$S = (S_p - S_s)/2$$

Each value of S is recorded with the concurrent value of X for later analysis. Slopes at the first and last data points can be assumed to be zero. A method for enhancing these digitally produced differential curves can be found in C.8.

C.3 Procedures

C.3.1 Cell preparation

C.3.1.1 Assemble the reduction cell in accordance with either Figure C.1 or C.2, making sure that all components are chemically clean. For each sample size or geometry, determine in advance the level of the liquid that is required to cover the specified sample surface. Mark this level on the outside of the cell. A minimum volume of 300 ml of solution is recommended for each analysis.

C.3.1.2 Attach the tubing system for the inert gas (assembled in advance) to the regulator of the gas tank.

C.3.1.3 De-aerate potassium chloride solution (KCl) at 0,1 mol/l prepared in advance, with the gas (to displace dissolved oxygen) using either procedure A in accordance with C.3.1.4 or procedure B in accordance with C.3.1.5.

NOTE   If any oxygen gas (O_2) is present in the working electrolyte, it will tend to interfere with the coulometric determinations, since O_2 is easily reduced in the same voltage range as many oxide layers and tarnishing components. Dissolved oxygen is eliminated by de-aerating the electrolyte solution prior to use and by running the reduction in a closed cell under an inert atmosphere.

C.3.1.4 For procedure A, boil the solution in the storage reservoir of Figure C.1 for 30 min while inert gas is bubbled through the system. Cool the electrolyte solution to room temperature while maintaining the inert gas purge. After cooling, keep the solution in a covered glass container and continually purge slowly with inert gas prior to use. Unused electrolyte solution can be stored in the glass container (with inert gas purging) for up to 7 d, after which it shall be discarded.

C.3.1.5 For procedure B, transfer the electrolyte solution to the reduction cell so that the solution level is slightly above the specified mark. Close the cell and bubble the inert gas through the purging tube (the end of which is at the bottom of the solution) for 50 min or more (see Figure C.2).

NOTE   Shorter purge times can be used, but their adequacy should be verified by measuring the oxygen reduction current on a non-filmed sample.

C.3.1.6 Calculate the current to be applied, and pre-set the controls on the electronic equipment accordingly. This current is the absolute current that shall be applied to produce the desired current density on the particular sample used.
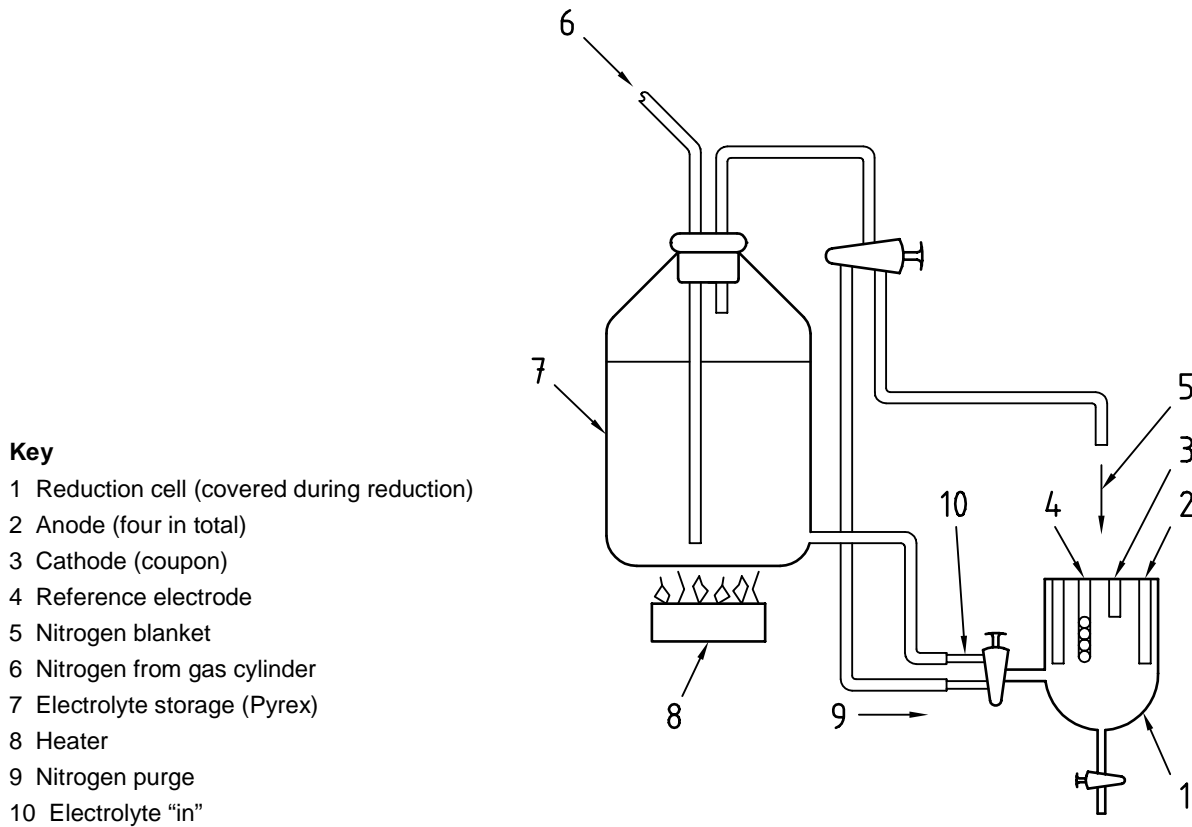
Key

1 Reduction cell (covered during reduction)

2 Anode (four in total)

3 Cathode (coupon)

4 Reference electrode

5 Nitrogen blanket

6 Nitrogen from gas cylinder

7 Electrolyte storage (Pyrex)

8 Heater

9 Nitrogen purge

10 Electrolyte "in"

Figure C.1 — Schematic of reduction cell with storage reservoir for procedure A (see C.3.1.4)
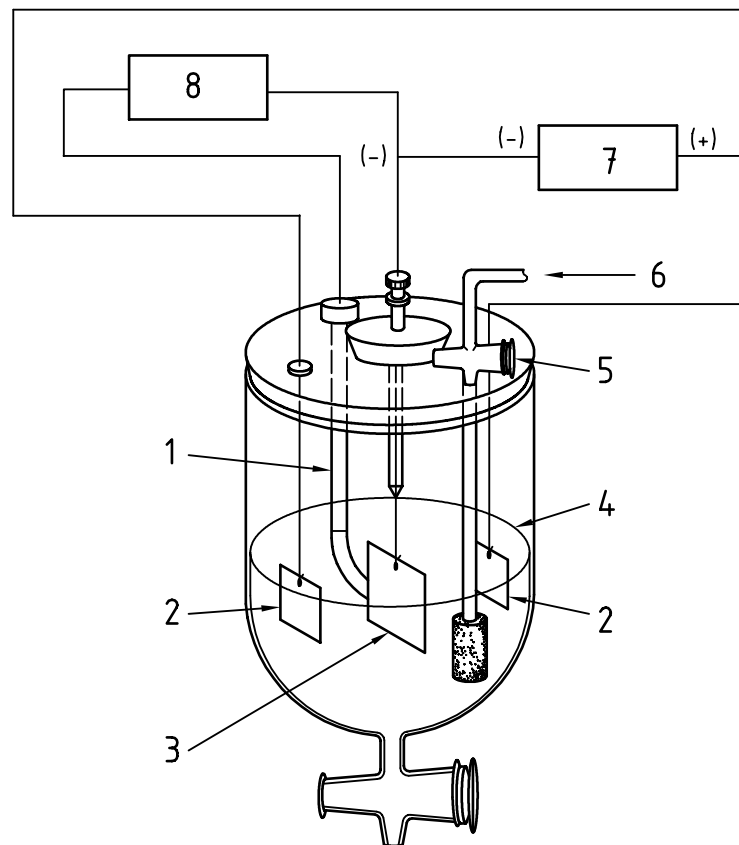
Key

1 Reference electrode

2 Counter electrodes

3 Coupon

4 Solution level

5 Three-way stopcock

6 Inert gas

7 Constant current source

8 Voltage read-out recorder

Figure C.2 — Schematic of reduction cell for Procedure B (see C.3.1.5)

C.3.1.7 For the most common types of mixed flowing gas control coupon (that is, 24 h to 96 h exposure in moderate to severe environments) a current density of 50 μA/cm^2 (0,05 mA/cm^2) of immersed metal is required. The same current density is also commonly used to analyse tarnish films from other types of environmental test. For very thick films, the current density might be increased (up to a maximum of 0,25 mA/cm^2) so that the reduction can proceed at a reasonable rate of not more than 4 h to 6 h for the total reduction time of any one sample. Since the observed reduction potentials will become more negative with increasing current density, exercise care when comparing samples reduced at different current densities. List all deviations from the preferred current density of 0,05 mA/cm^2 in the test report.

C.3.2 Coupon preparation (prior to exposure to the test atmosphere)

C.3.2.1 The metallic coupons shall normally be prepared from sheets or strips of at least 99,9 % purity, and preferably at least 10 mm wide and 0,1 mm thick. Preferred areas range from 300 mm^2 to 1 000 mm^2 maximum per flat side. Preferred thicknesses, in accordance with annex A, are 0,1 mm to 0,6 mm. However, coupon dimensions shall not exceed 32 mm in width and 77 mm in length.

C.3.2.2 Samples of the same shape and thickness shall be used for all tests for which sample-to-sample comparisons are made.

C.3.2.3 Prepare and clean the metallic coupons in accordance with standard procedures, such as those in reference [2] or annex A. If no standard procedure is available for the metal used, describe the cleaning and preparation procedure in detail in the test report (see clause 7).

C.3.2.4 Do not apply masking lacquers (or similar non-metallic coatings) to the coupons, unless it has first been determined that the masking finishes will have no contaminating effects on the tarnish films or electrolyte solution under the conditions of the reduction procedure.

C.3.3 Reduction procedures (following exposure to the test atmosphere)

C.3.3.1 If a hook is used to suspend the sample coupon, ream the hole in the latter with a round file (such as a jeweller's file) in order to remove the insulating tarnish film from the hole wall and ensure good electrical contact between the coupon and the wire hook.

C.3.3.2 For the set-up shown in Figure C.1, suspend the sample from the hook or clip, using clean tweezers to avoid contaminating the sample, and insert into the empty cell. Introduce inert gas through the lower part of the empty cell to purge the air for a minimum of 2 min after which divert the gas to the upper part of the cell. The recording system is then engaged and turned on. Introduce the de-aerated electrolyte solution into the reduction vessel to the pre-set mark.

C.3.3.3 For the cell design shown in Figure C.2, first divert the inert gas so that it passes over the de-aerated solution to the cell. Attach the sample to the hook or gold-plated clip then lower the solution level to the pre-set mark by opening the bottom stopcock. The recording system is then engaged and turned on.

C.3.3.4 Apply the pre-calculated current between the sample and the counter-electrodes, and mark the time on the recorder chart, if used. Allow the reduction to proceed until the hydrogen reduction step is established before turning off the current. Hydrogen reduction shall be determined by the presence of an endless flat or gently rising constant voltage step, which is often accompanied by the evolution of masses of small bubbles from the sample. Once this hydrogen step is reached no higher potential reduction process can occur.

C.3.3.5 At the completion of each coulometric run, remove the sample and drain and clean the cell in preparation for the next run.

C.4 Data evaluation

C.4.1 Constant current coulometry

The results of the constant current coulometry procedure can be expressed as the elapsed time in seconds, required to complete the reduction of a particular film component at its observed voltage step (see C.4.3 for method) as well as total time needed to complete the reduction of all reducible components of the film. The elapsed time values can also be multiplied by the total applied current to give the number of coulombs of electrical charge required to complete the reduction processes at the various respective voltages as follows:

$$Q = It$$

where

Q is the charge, in millicoulombs;

I is the current, in milliamperes;

t is the time, in seconds.

If the chemical identity of the reducible component is known (see reference [2]), calculations can be made of both the mass of that substance and its thickness (assuming that it is present as a homogenous layer in the film). Methods of calculation are given in C.9.

C.4.2 Voltage determination

Record a reduction potential or potential range, in volts, for each voltage step of arrest (see Figures C.3, C.4 and C.5). The portion of the curve corresponding to this potential or potential range shall encompass at least 75 % of the reduction time for the segment of the total curve.

C.4.3 Reduction time determinations

C.4.3.1 For simple films, the substance having the lowest (least negative) reduction potential will reduce first, the reduction going to completion before the substance having the next greater potential begins to reduce. The differential voltage indicator, which shows where the reduction potentials are changing most rapidly, indicates the beginning and the end of a reduction, and is thus used to determine reduction times (see Figures C.3, C.4 and C.5).

NOTE   See references [2] to [5] and [7] to [13] for proposed chemical identities for the films shown in Figures C.3, C.4 and C.5.


Key

1 Derivative of potential

2 Reduction potential
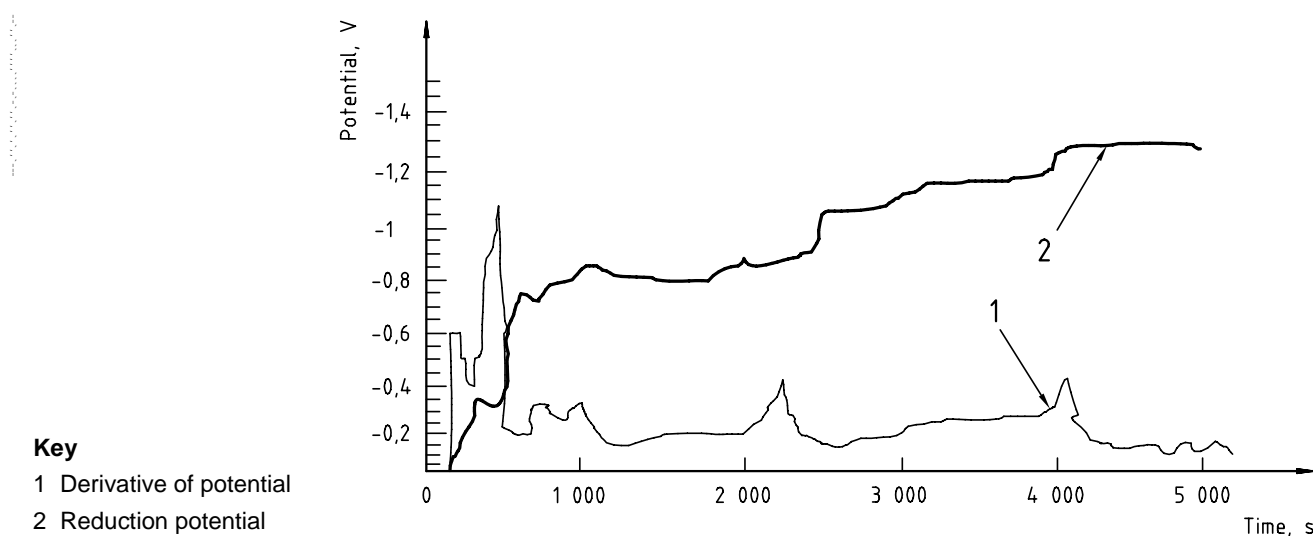
NOTE   No chlorine is present in the test environment.

Figure C.3 — Typical reduction behaviour of films on copper from 72 h exposure to humid sulfur vapour test (see ISO 12687)

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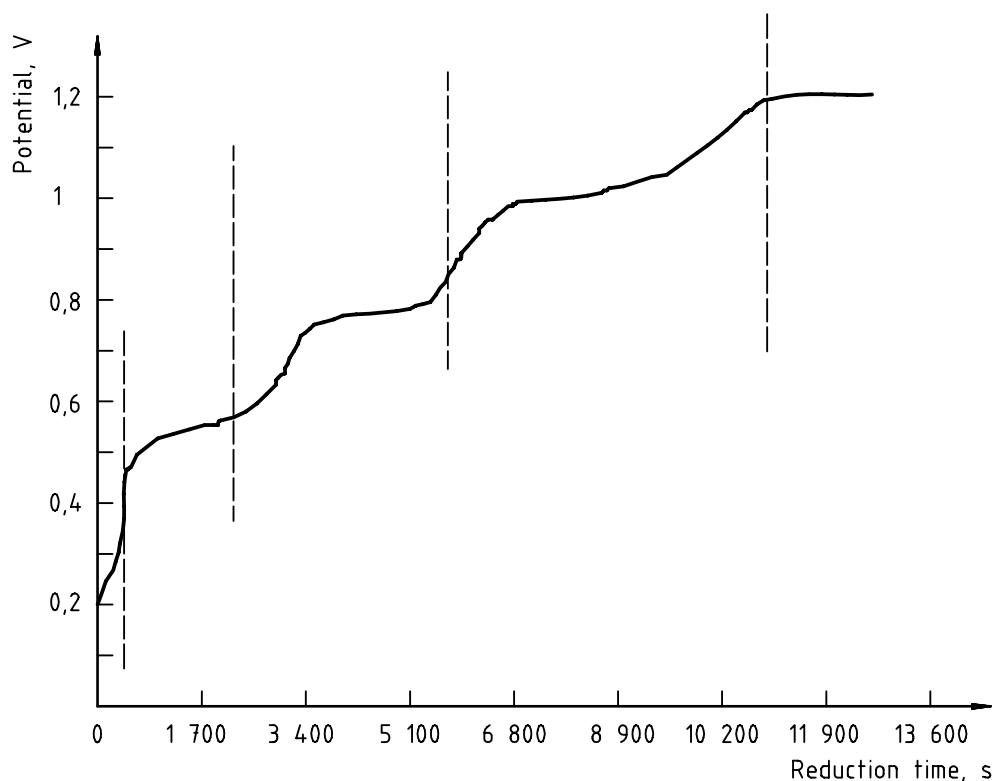
NOTE   The vertical lines correspond to major peaks in the differential curve (not shown) and delineate the main reproducible film types from this environment.

Figure C.4 — Typical reduction curve for copper from 48 h exposure to high sulfide (100 ppb H$_2$S) mixed flowing gas (with 20 ppb Cl$_2$ and 200 ppb NO$_2$)
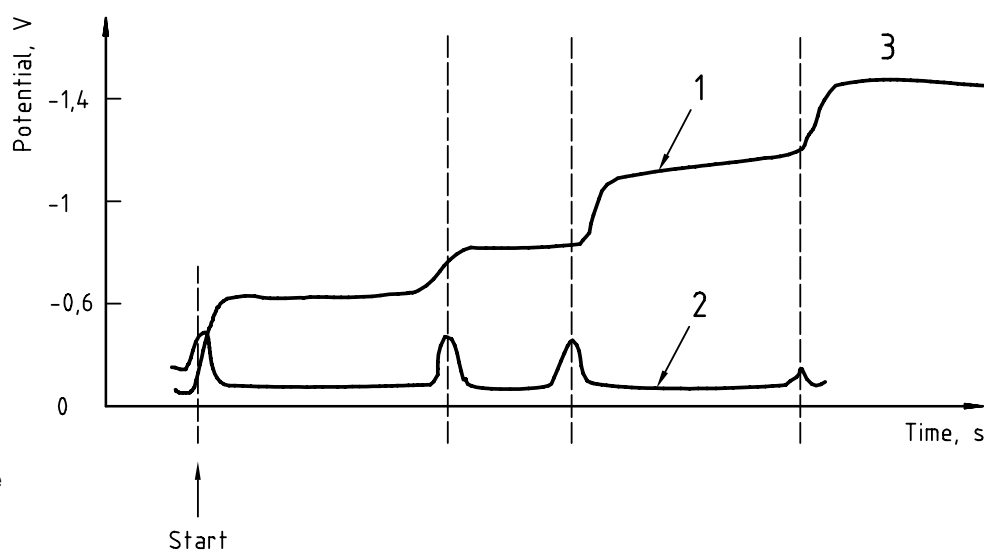
Key

1 Reduction potential trace

2 Differential voltage trace
   (arbitrary units)

3 Hydrogen

Figure C.5 — Ideal reduction behaviour of oxide and sulfide films on copper
(from reference [2])

C.4.3.2 With many environmentally produced films there may be some overlap between the reductions of the different film constituents, and the reduction steps may not be sharply defined. This will generally occur with thicker films, where the thickness of the various components might not be uniform over the sample area. This is often indicated by a rounding of the differential of voltage peaks such as those shown in Figures C.3, C.4 and C.5, as the reduction potential changes gradually between the two voltage arrests or steps. If this should occur, one or both of the following methods may be used to determine the transition points.

C.4.3.3 The appropriate midpoints of the differential maxima for the beginning and end of the particular reduction arrest can be estimated by inspection and measurement.

C.4.3.4 The voltage time traces may be inspected at a near grazing angle to the line of sight, using a straight-edge to lay out lines that best fit the steps. The transitions will then be seen and their midpoints estimated (and recorded as the beginning and end times for that particular step). When transitions are determined by this technique, they shall be reported as graphical transitions or transitions by graphical analysis to alert the test specifier to additional considerations when comparisons are to be made.

C.5 Test report

Complete a test report using a format similar to that shown in Figure C.6.

Job/project No.		Date samples received		Date completed		Sample dimensions	
Current density			Absolute current applied			Environmental exposure	
Sample No.	Date reduced	Mass gain before reduction [a]	Product No. 1		Product No. 2		Product No. 3		Etc.	Total reduction time	Hydrogen reduction voltage
			Potential	Time	Potential	Time	Potential	Time			
Size of cell			Volume of electrolyte			Sample dimensions					
[a] If available.											

Figure C.6 — Coulometric reduction of films on copper

C.6 Precision and bias

C.6.1 Precision

C.6.1.1 The precision of the coulometric reduction test method was determined for copper coupons exposed to the humid sulfur vapour test atmosphere in accordance with ISO 12687 for 72 h (see reference [2]).

C.6.1.2   The voltage level determinations for four different reduction steps (all greater than 0,5 V) showed a maximum standard deviation (really a coefficient of variation) of 5 % for three separate tests involving a total of 26 samples. The average of the 12 coefficients of variation (four levels from each of the three tests) was 1,8 %.

C.6.1.3   The reduction times for these four voltage levels showed a maximum coefficent variation of 46 % with an average coefficient of 27 % for the 12 reduction times. However, these reduction time numbers are not necessarily related to the precision of the coulometric reduction method itself, because the reduction times depend on the different tarnish thicknesses imparted to the individual samples during enviromental exposure. Independent measurements of total film thicknesses on each sample by the mass gain method in accordance with annex A showed a coefficient of variation (s/X) of 27 % for Test No. 2 and 23 % for Test No. 3 (see Table C.1) in good agreement with the values observed for coulometric reduction times. It can be inferred that the coefficients of variation for the coulometric reduction times can be expected to be less than 2 % on the basis of these results, in close agreement with the coefficients of variation in the voltage level determinations.

C.6.1.4   Results as precise as these may not be achieved for films formed in mixed flowing gas environments due to the increased complexity of the tarnish films. Under these circumstances, do not expect to obtain exactly the same voltage values for corresponding steps of different samples. The main reason for this is the variation in the real areas of the filmed specimens (and the corresponding changes in the true current density) as the metal surfaces are etched by the corrosive environments, and films of different surface roughnesses are produced. In addition, the various films may not have uniform thicknesses over the entire surface of the sample (see C.6.1.3).

C.6.1.5   The precision of coupons exposed to mixed flowing gas test environments is being determined as part of a planned inter-laboratory (round-robin) test programme.

C.6.2 Bias

Since there is no accepted standard reference material for adherent tarnish films, the bias in the reduction potentials and reduction times has not been determined.

Table C.1 — Total reduction time versus mass gain for copper coupons in the humid sulfur vapour test atmosphere (see ISO 12687 and [2])

Number of test	Total reduction time s		s/X	Mass gain µg		s/X
	mean X	standard deviation s		mean X	standard deviation s	
2 (12 samples)	2 855	768	26,9 %	1 183	310	26,7 %
3	3 823	884	23 %	166	38,6	23,3 %

C.7 Fabrication of *in situ* silver/silver chloride reference electrode

Immerse two pieces of pure silver, of approximately the same size and shape, in a saturated KCl solution, keeping them at least 3 cm apart. Apply 2 V to 4 V, using batteries or a d.c. power supply. After a few seconds reverse the electrical connections. Repeat this procedure, reversing the direction of current flow at least three times. The silver that was last connected to the positive terminal of the power source is covered with a mixture of silver chloride and metallic silver.

C.8 Recommended procedures for digitally enhancing produced differential curves

C.8.1 General

The differential curve values are typically a few hundredths of a volt per second, which is well below those of the reduction curve. Therefore, when plotted on the same scale (normally 0 V to 1,5 V), it is difficult to analyse the

differential curve. The following procedure has been developed to enhance the differential curve resolution when plotted with this scaling. While the difference between high and low values is exaggerated, the overall character of the curve is unaffected.

C.8.2 Procedure

C.8.2.1 Determine the maximum value of the differential curve.

C.8.2.2 Divide the value determined into 2,75.

C.8.2.3 Multiply all points in the differential curve by the value determined in C.8.2.2.

C.8.2.4 Take all points in the differential curve with positive values to the 0,4 power.

C.8.2.5 All other points (negative and zero values) are set equal to zero.

C.8.3 Result

The procedure results in the following. The new maximum differential curve value is approximately 1,5 (matching the full-scale maximum). C.8.2.4 allows small peaks to be enhanced without causing larger peaks to go off the scale.

C.9 Recommendations for calculating the mass and thickness of known film

C.9.1 For the mass of a known substance,

$$m = It\left(\frac{M}{nF}\right) \tag{C.1}$$

where

- m is the mass, in grams;
- I is the current, in amperes;
- t is the time, in seconds;
- M is the molar mass, in grams per mole;
- F is Faraday's constant ($9{,}65 \times 10^4$ C/mol);
- n is the number of electrons involved in the reaction, e.g. 1 for AgCl and 2 for Cu_2O.

C.9.2 For the equivalent film thickness of the known substance,

$$m = AT\rho \tag{C.2}$$

Substituting the value of m from equation C.2,

$$T = It\left(\frac{M}{nF}\right)\left(\frac{1}{A}\right)\left(\frac{1}{\rho}\right)$$

where

- T is the thickness, in centimetres;
- A is the area, in square centimetres;
- ρ is the density, in grams per cubic centimetre.

C.9.3 The total mass of all components and the apparent thickness of the entire film can be obtained by adding the respective values for these known or inferred constituents. If mass gains have previously been determined for the samples, these can be compared with the total mass values of the respective samples, and appropriate correlations made.

Annex D
(informative)

Surface analysis

Surface analysis of corrosion films has been performed by a number of analytical techniques including X-ray diffraction, X-ray emission spectroscopy, X-ray photoelectron spectroscopy, Auger electron analysis and secondary ion mass spectroscopy. All of these techniques yield different data that can be correlated to develop a more complete understanding of corrosion behaviour. These techniques are more important when metals other than copper or silver are being examined for susceptibility to mixed flowing gas testing because of the absence of extensive data bases on those other metals in the environments considered in this part of ISO 4524.

Annex E
(normative)

Resistance monitoring

E.1 Apparatus

E.1.1 Resistance monitor (RM) probe, consisting of two elements of identical material in thermal contact with each other. One element shall be capable of interaction with a corrosive gas environment and is the detector of test chamber corrosivity. The second element shall be capable of interaction with the corrosive gases from the chamber by means of an impervious overcoat such as epoxy or other polymer and serves as a reference. The electrical properties of the elements shall be chosen with regard to the expected amount of corrosion to be detected. Mildly corrosive environments should be monitored by means of thinner conductors than would be employed in strongly corrosive environments so as to be more sensitive to the decreased amount of corrosion expected.

Resistance monitor probes are measured with standard electrical resistance measurement equipment or with suitable commercial systems. A Kelvin bridge or a potentiometer shall be used when measuring resistance to less than 10 Ω. A Wheatstone bridge may be used with resistances greater than 10 Ω. The resistance shall be measured to an accuracy of 0,1 %. The measuring current shall be so small that the resistance being measured changes by less than 0,1 % due to temperature rise.

E.1.2 It is recommended that a means for continuous monitoring of the probe be available so that a record is maintained during times when the test facility is unattended.

E.2 Calibration

Calibrate electrical resistance measuring apparatus in accordance with the manufacturer's instructions once every 6 months or more frequently if drift indicates that the requirement of 0,1 % accuracy cannot be met with semi-annual calibration.

E.3 Procedure

E.3.1 Store probes in a glass desiccator after manufacture, free from exposure to plastic materials that emit volatile plasticizers or other organic vapours. Handle and store commercial probes in accordance with the manufacturer's instructions. Take care to ensure that the exposed metal conductor of the probe remains free of contaminants prior to use in the test chamber for corrosivity monitoring. Some commercial probes are supplied with a removable protective film covering the conductor that is to be exposed to the corrosive gases. Remove this film just prior to installation of the RM probe in the gaseous corrosion test chamber or other location where corrosivity is to be monitored.

E.3.2 Install probes in the corrosive gas stream within the test chamber at between 4 cm and 6 cm from the test samples being evaluated in the test chamber. The RM probes and the test samples shall all be in a single plane that is perpendicular to the gas flow direction. Probes shall not be behind any gas flow obstruction such as a test sample or test sample support rack, nor shall they obstruct the gas flow to any test sample. The plane of the metal conductor of the RM probe shall be parallel to the gas flow with the exposed metal conductor closest to the source of the gas flow and protected reference conductor downstream from the exposed metal conductor. The long axis of the probe shall be perpendicular to the gas flow direction. The RM probe may be mounted with the plane of the conductor vertical or horizontal in the case of horizontal gas flow; for vertical gas flow, the plane of the conductor shall be vertical. In some cases, it may be desirable to have the conductor facing downward to avoid settling of particulate material on the face of the conductor (see Figure E.1).

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E.3.3 Installation of the probes shall be consistent with installation of the test samples in accordance with 6.6.4. Alternatively, if use of resistance probes, as a complement to mass gain for corrosion chamber calibration, is a requirement, probe placement shall be consistent with annex A.

NOTE   Probes can only be used for one test. It is optional to use more than one probe sequentially during a test in order to capture the most sensitive period when the corrosion film is thinner before a thicker, more slowly responding, corrosion film has formed.

E.3.4 Check the probe circuit and the internal calibration of the instrument for proper functioning, as recommended in the manufacturer's instructions.

E.3.5 Connect the instrument to the probe, record the measured resistances of the probe elements, and check the element resistances against expected values. Alternatively, check commercial equipment that provides a scale reading for corrosivity instead of resistance values for expected behaviour of the scale reading in accordance with the manufacturer's instructions. In the event of discrepancies, check all parts of the apparatus and correct installation until desired values are obtained.

E.3.6 Monitor RM probe electrical resistances for values within the expected range. Calculate and record the ratio of the resistance of the exposed metal conductor to that of the covered metal conductor and compare with specified values of the ratio for the test time at which measurements were made. Take corrective action by adjusting test parameters when RM probe ratio values move outside the expected range in order to bring RM probe ratio values within the required range if corrosivity control by RM probe is required by the test specification.

E.3.7 At completion of test, record the RM ratio values versus time with other required data in the report (see clause 7).
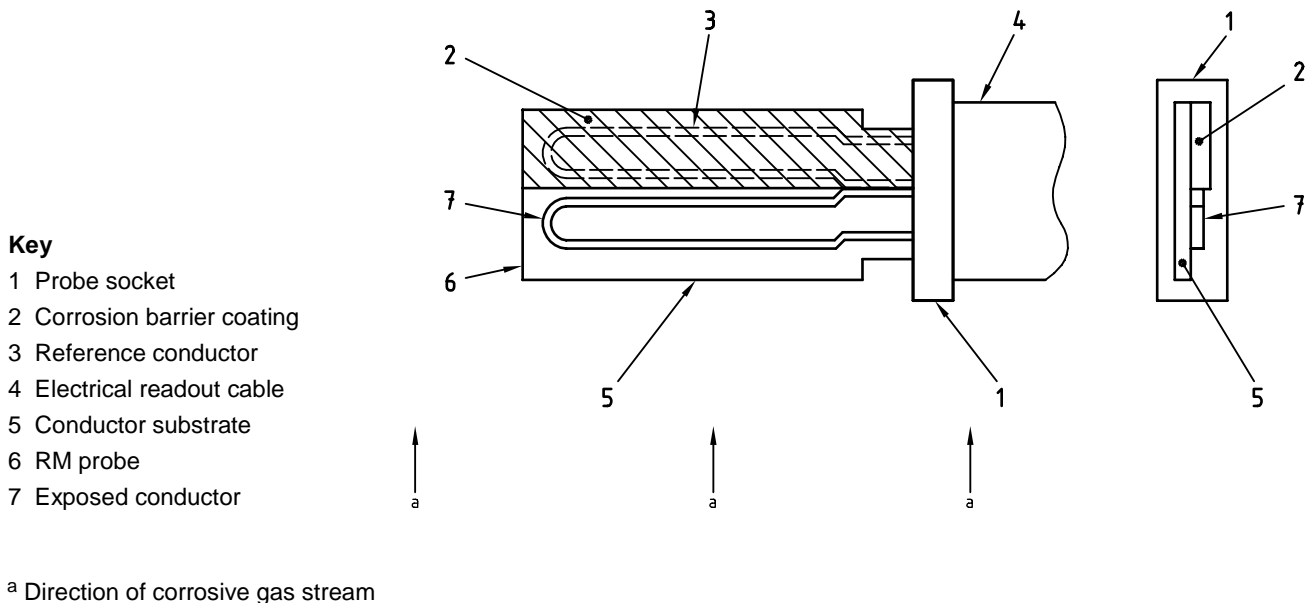

Key
1 Probe socket
2 Corrosion barrier coating
3 Reference conductor
4 Electrical readout cable
5 Conductor substrate
6 RM probe
7 Exposed conductor

a Direction of corrosive gas stream

Figure E.1 — Installation of RM probe in corrosive gas stream

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[6] Discussions of reference electrodes and their uses can be found by consulting the indices in most basic textbooks of physical chemistry or chemical analysis. Examples of such texts are:

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