INTERNATIONAL STANDARD

ISO 4968

Second edition
2022-03

Steel — Macrographic examination by sulphur print (Baumann method)

Reference number
ISO 4968:2022(E)

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

Published in Switzerland

Contents

Page

Foreword ..... **iv**
1 Scope **1**
2 Normative references **1**
3 Terms and definitions **1**
4 General **1**
5 Principle and aim of the test **1**
6 Test paper and reagents **2**
6.1 Photographic paper 2
6.2 Reagents 2
7 Fixing solution **2**
8 Test piece **3**
9 Sampling **3**
10 Machining **3**
11 Procedure **3**
12 Test report **4**
Annex A (informative) **Classification of sulphur print test results** **5**

Foreword

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

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

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

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

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

This document was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 7, *Methods of testing (other than mechanical tests and chemical analysis)*.

This second edition cancels and replaces the first edition (ISO 4968:1979), which has been technically revised.

The main changes are as follows:

— in the Scope, the applicable steels for this method are specified as from 0,005 % to 0,40 %, and this method may also be applied to cast irons;

— type and concentration of recommended reagents have been explicitly specified for steels with different sulphur content, respectively, to improve test effect and efficiency;

— method to remove extra acid solution and bubbles, and method to drain have been added in detail;

— classification of test results as positive segregation, negative segregation and central segregation, with examples in Annex, has been added.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Steel — Macrographic examination by sulphur print (Baumann method)

1 Scope

This document specifies a method (Baumann) for the macrographic examination of steel by means of contact printing using silver salts and acid.

The method is applicable to steels of which the sulphur content is less than 0,40 %. This method can also be applied to cast irons.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

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

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

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

4 General

4.1 The sulphur print test is essentially a qualitative test. It is inadvisable to evaluate the sulphur content of a given steel merely on the basis of its sulphur print.

4.2 Experience shows that the degree of darkening of the photo-sensitive emulsion is not always in proportion to the quantity of sulphides present in the metal. Certain factors may influence the macrographic attack to a greater or lesser extent; as examples, the following may be quoted:

— the chemical composition of the steel: the presence of certain elements modifies the type and shape of the sulphides and consequently the appearance of the image obtained, for example concentrations of titanium greater than 0,1 % give prints which do not reveal sulphides;

— the surface condition of the sample: the presence of surface cold working may alter the image obtained;

— the sensitivity of the photographic paper.

4.3 The use of the test, and the conditions for interpreting the results observed, depend on the particular case: details are laid down in product standards or shall be subject to special agreement.

5 Principle and aim of the test

5.1 The aim of macrographic examination by sulphur printing is to detect, by printing on photo-sensitive papers previously soaked in acid, the position of areas containing sulphur inclusions found

in the metal in various chemical forms and with various shapes: iron sulphide, manganese sulphides, mixed sulphides, oxy-sulphides etc.

NOTE The photographic paper can be replaced by a flat film. The positive and transparent prints obtained from the flat film can be used directly to produce negative proofs.

5.2 The distribution of the sulphur-rich areas is revealed by the local release of hydrogen sulphide, causing darkening of the sensitive emulsion due to the chemical conversion of the silver halides to silver sulphide.

5.3 By examining the distribution and size of the sulphur inclusions detected by this process it is possible to evaluate the degree of uniformity of the metal from the section examined. Thus, sulphur printing reveals chemical irregularities (segregations: for example those of a non-rimming free-cutting steel) and may reveal certain physical irregularities (for example cracks and porosity). Furthermore, sulphur printing may be used sometimes to distinguish rimming steel from killed steel and may also draw attention to certain areas where tests (for example, mechanical tests) or sampling for analysis may need to be carried out.

6 Test paper and reagents

6.1 Photographic paper

The sulphur print shall be made on the sensitive side of a sheet of photographic paper (or of a flat film) cut to suitable size.

In general, the paper used is thin matt paper with a thin layer of gelatine, for example bromide enlarging papers. The clear advantage of this type of paper is that there is less tendency to slip when it is applied.

NOTE A classification of sulphur print test results is given in Annex A, informative.

6.2 Reagents

Sulphuric acid, citric acid and acetic acid solution should be used as reagents. Type and concentration of recommended reagents according to the sulphur content of steel to be tested are shown in Table 1. If necessary, other reagents can also be used to get a clear sulphur print.

Table 1 — Type and concentration of recommended reagents

Sulphur content of steel [a, b] wt %	Reagent type	Reagent concentration
0,005 – 0,015	Sulphuric acid solution	(5 – 10) Vol %
0,015 – 0,035	Sulphuric acid solution	2 Vol %
0,10 – 0,40	Sulphuric acid solution	(0,2 – 0,5) Vol %
	Acetic acid solution	(10 – 15) Vol %
	Citric acid solution	(10 – 15) wt %

[a] Sulphur print test is rarely used for steel with 0,035 % - 0,10 % sulphur content. In such case, 2 % sulphuric acid solution should be used.

[b] For sulphur content less than 0,005 %, the choice of reagents is left to the discretion of testers.

7 Fixing solution

A commercial fixing solution or a 15 % to 20 % solution of sodium thiosulphate in water should be used.

8 Test piece

The test may be made on the product or on a test piece cut from the product. In general, this consists of a section perpendicular to the direction of rolling for products such as bars, billets and rounds, or of a surface suitably selected by agreement between the parties.

9 Sampling

In the absence of requirements in the product standards, the number and position of the surfaces examined shall be subject to agreement between the parties.

It is advisable, in particular, to locate the test surfaces away from the cut faces when cutting has been carried out:

— by hot shearing, which deforms the fibres as well as the inclusions and may greatly offset the segregates;

— by flame cutting, which, in the case of hard steels, may produce local hardening, shrinkage cracks or local tempering.

10 Machining

10.1 Preparation of the test-piece surface is of prime importance in obtaining a correct sulphur print. While rough machining, resulting in relatively coarse surfaces, may be sufficient in certain cases (routine inspection to reveal shrinkage holes, for example), it is generally required that the machining should be carried out as carefully as possible.

The following criteria shall be observed when machining:

a) cutting-tool marking should not be pronounced, for example as the result of incorrect adjustment, excessively deep cuts or heavy feeds on the lathe or the shaping machine; good results are generally obtained with a feed of approximately 0,1 mm;

b) there should be as little cold working of the surface as possible, due for example

  — to a type of tool which is not suitable for the metal, or which is badly sharpened;

  — to the use of unsuitable grinding wheels.

10.2 The main types of machining, generally used and leading to accurate prints which are more or less identical, are

— grinding, with or without preliminary machining;

— shaping or turning, provided that the lathe is fitted with a speed adjuster.

10.3 A too smooth finish (mirror-type finish) makes it easier for the paper to slip on the test piece. In general, it is recommended that a surface finish with an R_a of at least 3,2 µm be obtained after machining.

10.4 The surface of the test piece shall be properly cleaned by alcohol or acetone, to avoid generating dark spots which may be incorrectly interpreted as a gross sulphide segregation.

11 Procedure

11.1 Immerse the photographic paper (6.1) for approximately 5 min in a sufficient volume of the sulphuric acid (6.2) at ambient temperature.

11.2 After removing excess acid reagent, for example by draining, apply the sensitive side of the paper, still damp, to the surface to be examined, which should be clean and free from grease. As an alternative to this procedure, if the piece is small, it may be applied to the paper which has been impregnated beforehand. Ensure that there is firm contact between the piece and the paper, without any slipping, throughout the test. If necessary, weigh the piece down in order to aid contact.

11.3 To ensure firm contact, eliminate air bubbles and drops of liquid between the surface of the test piece and the sheet of paper, for example by means of rubber roller, squeegee or sponge.

11.4 Determine the time of application in advance from the available data concerning the metal to be examined (chemical composition, for example) and also by the type of irregularities to be detected. The emulsion side of the paper shall be kept in contact with the ground surface of the test piece. The contacting time is generally 30 s to 10 min, depending on the acid selected, the concentration of the acid solution, and the sulphur content of the steel. When comparing test results for relatively similar test pieces, it is best to standardize the acid selected, the concentration of the acid solution, the soak time and the contact time.

11.5 Remove the print and wash it in running water for approximately 10 min, after lightly rubbing it with a wad of wet cotton-wool. Immerse the print for at least 10 min in the fixing solution (Clause 7), then wash in running water for at least 30 min, and dry carefully.

11.6 In most cases, only one usable sulphur print can be made from the ground surface. Subsequent prints from the same surface usually turn out too light for practical use. For steels with a high sulphur content (above 0,10 wt % sulphur), the first print is generally so dark that the lighter second print may give a better result. If more than one usable sulphur print needs to be made from the same test piece, the testing surface shall be reground by at least 0,5 mm.

12 Test report

The test report shall include the following information:

a) the steel grade examined;

b) the cast number;

c) the position of the surface examined;

d) types and concentration of reagents;

e) the result of the test.

Annex A
(informative)

Classification of sulphur print test results

A.1 General

There are 5 types of sulphur print test results that are common in practice:

— positive segregation;

— negative segregation;

— central segregation;

— dispersed segregation;

— linear segregation.

A.2 Positive segregation

Sulphur content of the sample gradually increases from surface to centre. The density and size of the sulphides on the sulphur print photographic paper gradually increase from surface to centre, as is shown in Figure A.1.

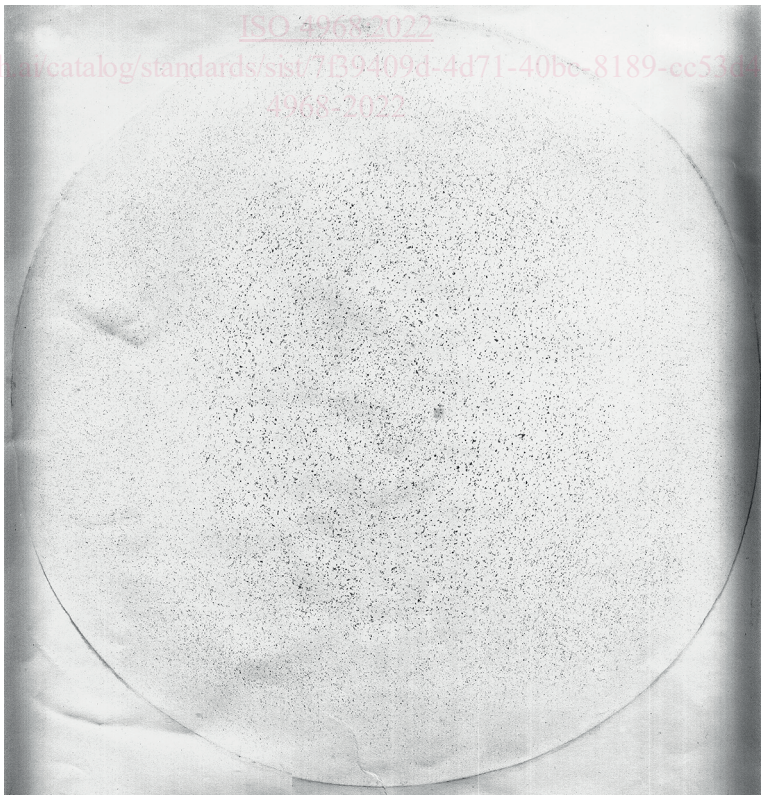

Figure A.1 — Positive segregation

A.3 Negative segregation

Sulphur content of the sample gradually reduces from surface to centre. The density and size of the sulphides on the sulphur print photographic paper gradually decrease from surface to centre, as is shown in Figure A.2.

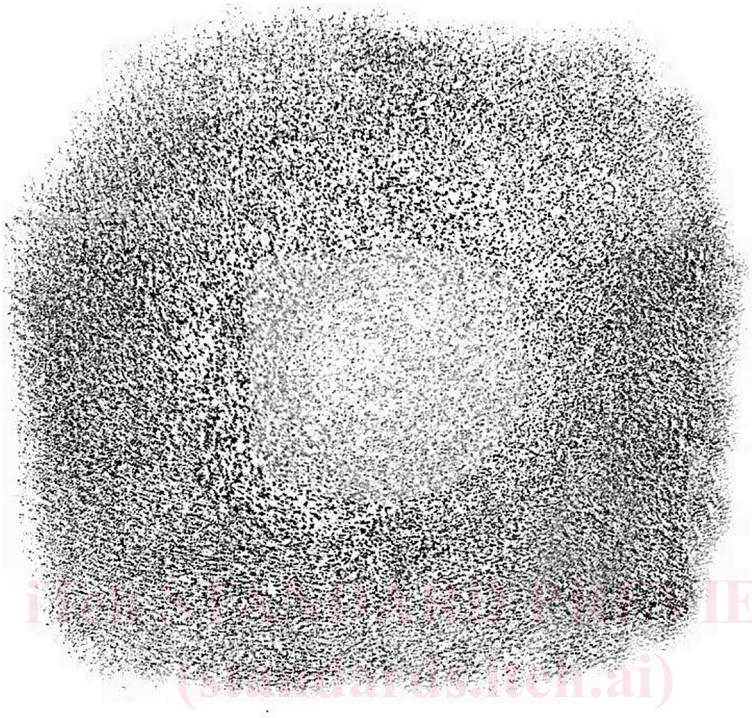

Figure A.2 — Negative segregation

A.4 Central segregation

Sulphur is concentrated in the centre of the sample. Most sulphides distribute in the centre of the sulphur print photographic paper, while sulphides in the rest part are not obvious, as is shown in Figure A.3.