

---

---

**Surface chemical analysis — Total  
reflection X-ray fluorescence analysis  
of water**

*Analyse chimique des surfaces — Analyse par fluorescence de rayons  
X en réflexion totale d'eau*

**iTeh STANDARD PREVIEW**  
**(standards.iteh.ai)**

[ISO 20289:2018](https://standards.iteh.ai/catalog/standards/sist/df84267d-cc69-470e-acb4-a23b070a79a1/iso-20289-2018)

[https://standards.iteh.ai/catalog/standards/sist/df84267d-cc69-470e-acb4-  
a23b070a79a1/iso-20289-2018](https://standards.iteh.ai/catalog/standards/sist/df84267d-cc69-470e-acb4-a23b070a79a1/iso-20289-2018)



**iTeh STANDARD PREVIEW**  
**(standards.iteh.ai)**

ISO 20289:2018

<https://standards.iteh.ai/catalog/standards/sist/df84267d-cc69-470e-acb4-a23b070a79a1/iso-20289-2018>



**COPYRIGHT PROTECTED DOCUMENT**

© ISO 2018

All rights reserved. Unless otherwise specified, or required in the context of its implementation, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office  
CP 401 • Ch. de Blandonnet 8  
CH-1214 Vernier, Geneva  
Phone: +41 22 749 01 11  
Fax: +41 22 749 09 47  
Email: [copyright@iso.org](mailto:copyright@iso.org)  
Website: [www.iso.org](http://www.iso.org)

Published in Switzerland

# Contents

	Page
<b>Foreword</b> .....	<b>iv</b>
<b>Introduction</b> .....	<b>v</b>
<b>1 Scope</b> .....	<b>1</b>
<b>2 Normative references</b> .....	<b>1</b>
<b>3 Terms and definitions</b> .....	<b>2</b>
<b>4 Symbols and abbreviated terms</b> .....	<b>3</b>
<b>5 Safety</b> .....	<b>3</b>
<b>6 Interferences</b> .....	<b>3</b>
<b>7 Apparatus</b> .....	<b>3</b>
7.1 General.....	3
7.2 Labware.....	4
7.3 Drying apparatus.....	4
<b>8 Reagents, standards and materials</b> .....	<b>4</b>
<b>9 Sample preparation</b> .....	<b>5</b>
9.1 Environment.....	5
9.2 Sample.....	5
9.3 Specimen.....	6
9.4 Sample carrier.....	6
9.5 Trials/replicates.....	6
9.6 Effect of residue mass, size and its position.....	7
<b>10 Procedure</b> .....	<b>7</b>
10.1 General.....	7
10.2 Instrument calibration.....	7
10.3 Detection limit.....	7
10.4 TXRF measurements.....	8
10.5 Spectra fitting.....	8
10.6 Unknown samples.....	8
<b>11 Qualitative and quantitative analysis</b> .....	<b>8</b>
11.1 Identification of elements.....	8
11.2 Quantification of elements.....	8
11.3 Calculations.....	9
11.4 Measurement uncertainty.....	9
<b>12 Quality control</b> .....	<b>9</b>
<b>13 Precision and accuracy</b> .....	<b>10</b>
<b>14 Test report</b> .....	<b>10</b>
<b>Annex A (informative) Uncertainty in TXRF measurements</b> .....	<b>11</b>
<b>Annex B (informative) Validation of the method</b> .....	<b>15</b>
<b>Bibliography</b> .....	<b>19</b>

## 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](http://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](http://www.iso.org/patents)).

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

For an explanation on the 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 the following URL: [www.iso.org/iso/foreword.html](http://www.iso.org/iso/foreword.html). (standards.iteh.ai)

This document was prepared by Technical Committee ISO/TC 201, *Surface Chemical Analysis*, Subcommittee SC 10, *X-ray Reflectometry (XRR) and X-ray Fluorescence (XRF) Analysis*.

ISO 20289:2018  
<https://standards.iteh.ai/catalog/standards/sist/df84267d-cc69-470e-acb4-a23b070a79a1/iso-20289-2018>

## Introduction

Total reflection X-ray fluorescence (TXRF) spectroscopy is a surface sensitive technique which can be used to obtain compositional information about different kinds of samples. ISO/TS 18507 provides the guidelines for the characterization of biological and environmental samples with TXRF.

TXRF is suitable for quantitative elemental analysis of liquid samples deposited as thin films on clean and well-polished reflectors, by means of internal standard calibration<sup>[1]</sup> <sup>[2]</sup>.

This document provides guidance and requirements for the quantitative elemental analysis of water by means of TXRF instrumentation.

## iTeh STANDARD PREVIEW (standards.iteh.ai)

[ISO 20289:2018](https://standards.iteh.ai/catalog/standards/sist/df84267d-cc69-470e-acb4-a23b070a79a1/iso-20289-2018)

<https://standards.iteh.ai/catalog/standards/sist/df84267d-cc69-470e-acb4-a23b070a79a1/iso-20289-2018>

**iTeh STANDARD PREVIEW**  
**(standards.iteh.ai)**

ISO 20289:2018

<https://standards.iteh.ai/catalog/standards/sist/df84267d-cc69-470e-acb4-a23b070a79a1/iso-20289-2018>

# Surface chemical analysis — Total reflection X-ray fluorescence analysis of water

## 1 Scope

This document provides a chemical method for technicians working with Total Reflection X-ray Fluorescence (TXRF) instrumentation to perform measurements of water samples, according to good practices, with a defined degree of accuracy and precision. Target users are identified among laboratories performing routine analysis of large numbers of samples, which also comply with ISO/IEC 17025.

This document specifies a method to determine the content of elements dissolved in water (for example, drinking water, surface water and ground water). Taking into account the specific and additionally occurring interferences, elements can also be determined in waste waters and eluates. Sampling, dilution and pre-concentration methods are not included in this document.

Elements that can be determined with the present method may change according to the X-ray source of the instrument. No health, safety or commercial aspects are considered herewith.

The working range depends on the matrix and the interferences encountered. In drinking water and relatively unpolluted waters, the limit of quantification lies between 0,001 mg/l and 0,01 mg/l for most of the elements. The working range typically covers concentrations between 0,001 mg/l and 10 mg/l, depending on the element and predefined requirements.

[Annex B](#) reports, for example, the complete validation of the method of TXRF analysis of water performed with instrumentation that has Mo as the X-ray source and uses Ga as the internal standard for calibration.

Quantification limits of most elements are affected by blank contamination and depend predominantly on the laboratory air-handling facilities available, on the purity of reagents and the cleanliness of labware.

## 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 14706, *Surface chemical analysis — Determination of surface elemental contamination on silicon wafers by total-reflection X-ray fluorescence (TXRF) spectroscopy*

ISO 17331, *Surface chemical analysis — Chemical methods for the collection of elements from the surface of silicon-wafer working reference materials and their determination by total-reflection X-ray fluorescence (TXRF) spectroscopy*

ISO/TS 18507:2015, *Surface chemical analysis — Use of Total Reflection X-ray Fluorescence spectroscopy in biological and environmental analysis*

JCGM 100 series, *Guides to the expression of uncertainty in measurement (GUM series)*

### 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 3696, ISO 5667-1, ISO 5667-3, ISO 5725-1, ISO 5725-2, ISO 14706, ISO 17331, ISO/TS 18507, the JCGM 100 series and the following apply.

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

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

#### 3.1 calibration standards

known standard solutions, prepared from the primary dilution solution or stock solutions, containing the elements of interest or the internal standard element

#### 3.2 linear calibration range

concentration range over which the instrument response is linear

#### 3.3 sensitivity

slope of the linear fitting of the analytical curves, functional relationship between fluorescence intensity and concentration

#### 3.4 detection limit

minimum element concentration that can be identified with 99 % confidence that the element concentration is different from the blank

Note 1 to entry: See 10.3.

[SOURCE: ISO 18115-1:2013, 4.168, modified.]

#### 3.5 instrument performance sample

single element or multi-elemental calibration standard used to evaluate the performance of the instrument with respect to a defined set of criteria

Note 1 to entry: See 8.1.6.

#### 3.6 sample

water solution to be analysed

#### 3.7 specimen

solution containing internal standard prepared for TXRF analysis

#### 3.8 trial/replicate

sample carrier with deposited residue



**3.9****internal standard content**

known amount of an element used to normalize the variation in the fluorescence X-ray intensities of the other elements in a residue

**3.10****quality control sample**

reference material obtained from an outside source, with known element concentrations used to check accuracy and precision

Note 1 to entry: See [Clause 12](#).

**3.11****limit of quantification**

smallest concentration of an element that can be reliably quantified

Note 1 to entry: See [11.2](#).

**4 Symbols and abbreviated terms**

C	concentration (or mass per volume density) in mg/l
DL	detection limit
LOQ	limit of quantification
PT	proficiency test
RSD	relative standard deviation
S	sensitivity
TXRF	total reflection X-ray fluorescence

ITeH STANDARD PREVIEW  
(standards.iteh.ai)  
ISO 20289:2018  
<https://standards.iteh.ai/catalog/standards/sist/df84267d-cc69-470e-acb4-a23b070a79a1/iso-20289-2018>

**5 Safety**

This test method uses X-ray radiation. Consequently, it is important to avoid exposing any part of the body to the X-rays produced by the apparatus. A reference file of material risk handling sheets should be available for the personnel involved.

**6 Interferences**

The electrical conductivity of the water sample to be analysed should be lower than 2 mS/cm. The presence of particles and suspended solids could affect accuracy and precision of TXRF analysis due to self-absorption effects. Sea water or matrix rich wastewaters may be diluted or filtered to reduce possible interferences (see [9.2](#)) and background contributions (see [10.3](#)). All the reagents shall be analysed to check the possible presence of impurities. Interferences could be caused by contaminant elements due to uncleaned glassware (see [7.1](#)), sample preparation environment (see [9.1](#)) or reflectors (see [9.4](#)). Pile-up or sum peaks could arise if some elements are present in high concentration. Peaks overlap should be considered.

**7 Apparatus****7.1 General**

For reagents and specimen preparation, use ordinary laboratory glassware or plasticware unless otherwise stated. The apparatus for preparation of the samples shall be calibrated and cleaned.

Check periodically the accuracy of micropipettes and volumetric flasks used in the volumetric method, by taking an exact volume of water with the micropipette and weighing it on a high-precision calibrated

balance. The corresponding relative standard deviation (RSD) of all the micropipettes and glassware used shall be indicated and considered for the calculation of the overall method RSD.

## 7.2 Labware

The use of uncoloured material is preferable.

**7.2.1 One-mark volumetric flasks**, 10,00 ml  $\pm$  0,02 ml, made of glass, PE, PFA or PP.

**7.2.2 Plastic micropipettes**, from 1  $\mu$ l to 10  $\mu$ l and from 100  $\mu$ l to 1 000  $\mu$ l (minimum accuracy 2 %), made of PE, PFA or PP.

**7.2.3 Plastic beakers**, 100 ml and 1 000 ml, made of PE, PFA, PP or PTFE.

**7.2.4 Plastic test tubes**, 1,5 ml, 50 ml and 100 ml, made of PE, PFA, PP or PTFE.

**7.2.5 Syringe** with 0,2  $\mu$ m pore size filters.

**7.2.6 Carrier-stand** made of PFA or PTFE.

## 7.3 Drying apparatus

Use one of the following.

**iTeh STANDARD PREVIEW**  
**(standards.iteh.ai)**

**7.3.1 Infrared lamp.**

**7.3.2 Glass ceramic heating plate** with a power controller.

ISO 20289:2018  
<https://standards.iteh.ai/catalog/standards/sist/d84267d-cc69-470e-acb4-a23b070a79a1/iso-20289-2018>

**7.3.3 Vacuum vessel** fitted with gas flow equipment.

**7.3.4** Drying temperature should be lower than 60 °C to avoid the loss of volatile elements and compounds. Due to heat treatment, some elements might evaporate or diffuse into the X-ray reflector. Therefore, the recovery rate for elements has to be determined especially for fast diffusers, for example Cu or Ni, or for most volatile elements and/or compounds, such as As, Cl, Hg or SiF.

## 8 Reagents, standards and materials

Use only reagents of recognized analytical grade and only bi-distilled water or water of equivalent purity. The level of contamination of blanks shall be periodically checked, and taken into account for quantification.

**8.1 Ultra-pure water**, for example water with conductivity less than 0,05  $\mu$ S/cm, commercially available or obtained by purification systems.

**8.2 Ultra-pure nitric acid**, for example nitric acid (CAS 7697-37-2) solution with concentration from 65 % to 70 % wt.

**8.3 Cleaning solution**, for example liquid detergent, concentrated, alkaline and foaming, suitable for manual cleaning, soaking, ultrasonic baths and brushes systems (CAS 1310-73-2).

**8.4 Silicon solution in isopropanol**, for example silicon solution (CAS 67-63-0) in isopropanol if the level of contamination is acceptable.

**8.5 Internal standard solution**, for example 1 000 mg/l standard solution in 0,5 M nitric acid (CAS 69365-72-6) specified for AAS or ICP.

**8.6 Multi-element standard solution**, for example 1000 mg/l standard solution in nitric acid specified for AAS or ICP containing elements of interest.

### 8.7 Diluted internal standard solutions

The internal standard content in the specimen should be comparable to the amount of element to be quantified. Diluted internal standard solutions may be necessary to add a defined sample amount to prepare the specimen. Prepare fresh diluted internal standard solutions, either by volume or, preferably, by weight starting from internal standard solutions (8.5). Select the right dilution steps required to obtain the final defined concentration of internal standard element in the specimen. Take into account the accuracy of all the steps involved. Check the contamination level of the prepared solutions and take it into account for quantification.

EXAMPLE Diluted gallium internal standard solution 100 mg/l gallium solution

Prepare diluted gallium standard solution using either method a) or method b) below:

- a) Transfer 1 000 µl of gallium standard solution (8.5) to a plastic or glass 10 ml one-mark volumetric flask (7.2.1) with a plastic micropipette (7.2.2), add under 9 ml of ultra-pure water (8.1), finally make up to the mark with ultra-pure water (8.1) and mix.
- b) Weigh a 10 ml plastic beaker (7.2.3) to the nearest 0,001 g. Transfer 1 000 µl of gallium standard solution (8.5) to the beaker with a plastic micropipette (7.2.2), add under 9 ml of ultra-pure water (8.1), finally add ultra-pure water (8.1) to make the mass up to 10 g (plus the mass of the beaker) to the nearest 0,01 g and mix.

### 8.8 Validity of reference material

ISO 20289:2018  
<https://standards.iteh.ai/catalog/standards/sist/df84267d-cc69-470e-acb4-336070e70e1/iso-20289-2018>

The validity of the reference material (for example the expiration date) should also be checked.

The use of calibrated balances is recommended. Precision should be indicated and considered for the overall method uncertainty estimation (for example  $10,0 \pm 0,5$  mg).

## 9 Sample preparation

### 9.1 Environment

Cabinets meeting the requirements for ISO class 4 or better are recommended, but not compulsory, both for sample preparation and measurements. The use of a vertical laminar flow cabinet is strongly suggested for sample preparation. For reasons of cleanliness and operator safety, clean air shall be passed over the specimen-handling area and exhausted outside the cabinet.

Depending on the purpose of water analysis the environment of sample preparation has to be checked for contamination.

### 9.2 Sample

When the pH value of the sample changes drastically, precipitation and other phenomena affecting the homogeneity and representativeness of the sample may occur, and this should be avoided. If water samples have been previously stabilized, dilution effects and contamination levels of the blanks used should be considered for quantification. Where appropriate, samples with high turbidity may be filtered through 0,2 µm pore size filters. Only clean, uncoloured and, preferably, sterile plastic test tubes shall be used to keep and store water samples, to avoid contamination. Samples, specimens and trials/replicates should be handled in a clean environment (see 9.1).