PD ISO/TS 18507:2015

BSI Standards Publication

Surface chemical analysis — Use of Total Reflection X-ray Fluorescence spectroscopy in biological and environmental analysis

bsi.

...making excellence a habit.™

Document Sharing Hub

National foreword

This Published Document is the UK implementation of ISO/TS 18507:2015.

The UK participation in its preparation was entrusted to Technical Committee CII/60, Surface chemical analysis.

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

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

© The British Standards Institution 2015. Published by BSI Standards Limited 2015

ISBN 978 0 580 81543 0

ICS 71.040.40

Compliance with a British Standard cannot confer immunity from legal obligations.

This Published Document was published under the authority of the Standards Policy and Strategy Committee on 31 July 2015.

Amendments issued since publication

Date	Text affected

Documents
Document Sharing Hub

Full document details: PD ISO/TS 18507:2015

TECHNICAL SPECIFICATION

ISO/TS 18507

First edition
2015-07-15

Surface chemical analysis — Use of Total Reflection X-ray Fluorescence spectroscopy in biological and environmental analysis

Analyse chimique des surfaces — Utilisation de réflexion spectroscopie des rayons X de fluorescence totale dans l'analyse biologique et de l'environnement

Reference number
ISO/TS 18507:2015(E)

Documents
Document Sharing Hub

© ISO 2015

Full document details: PD ISO/TS 18507:2015

COPYRIGHT PROTECTED DOCUMENT

© ISO 2015, Published in Switzerland

All rights reserved. Unless otherwise specified, 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
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

© ISO 2015 – All rights reserved

Documents
Document Sharing Hub

Full document details: PD ISO/TS 18507:2015

Contents

Page

Foreword ... **v**

Introduction ... **vi**

1 Scope ... **1**

2 Normative references ... **1**

3 Terms, definitions, symbols, and abbreviated terms ... **1**
3.1 Terms and definitions ... 1
3.2 Symbols and abbreviated terms ... 2

4 Background ... **2**
4.1 Preliminary remarks ... 2

5 Instrumentation ... **4**
5.1 Instrumental requirements ... 4
5.1.1 X-ray sources of radiation ... 4
5.1.2 Monochromator ... 5
5.1.3 Detector ... 5
5.1.4 Sample station ... 6
5.1.5 Critical and glancing angle ... 6
5.2 Quality control of TXRF spectrometer ... 7
5.2.1 Stability check of X-ray beam ... 7
5.2.2 Spectroscopic resolution ... 7
5.2.3 Energy calibration ... 8
5.2.4 Sensitivity test ... 8

6 Specimen preparation ... **8**
6.1 Preliminary remarks ... 8
6.2 Sample carriers ... 9
6.2.1 Choice of sample carriers ... 9
6.2.2 Cleaning procedure for sample carriers ... 9
6.3 Sample treatment procedures for chemical analysis by TXRF ... 10
6.3.1 Liquid samples ... 10
6.3.2 Solid samples ... 12
6.3.3 Preparation of the Internal Standard solution ... 13

7 Data Collection and Storage ... **14**
7.1 Preliminary remarks ... 14
7.2 Data collection ... 14

8 Data Analysis ... **14**
8.1 Qualitative analysis ... 14
8.2 Quantitative analysis ... 14
8.2.1 Preliminary remarks ... 14
8.2.2 Background correction ... 14
8.2.3 X-ray intensities of each element ... 15
8.2.4 Experimental derivation of relative sensitivities ... 15
8.2.5 Quantification by means of internal standard ... 15
8.2.6 Statistical treatment ... 16

9 Information required when reporting TXRF analysis ... **16**
9.1 Preliminary remarks ... 16
9.2 Experimental details ... 16
9.3 Analysis procedures ... 17

Annex A (informative) **Comparison of detection limits of TXRF, AAS, and ICP-MS** ... **18**

Annex B (informative) **Case studies of TXRF analysis for environmental applications** ... **21**

Annex C (informative) **Case studies of TXRF analysis for biological applications** ... **24**

AVA Documents
Document Sharing Hub

© ISO 2015 – All rights reserved

Full document details: PD ISO/TS 18507:2015

Annex D (informative) **Theoretical derivation of relative sensitivity factors** **27**
Bibliography **29**

© ISO 2015 – All rights reserved
Documents
Document Sharing Hub
Full document details: PD ISO/TS 18507:2015

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 on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 201, *Surface chemical analysis*.

© ISO 2015 – All rights reserved

Documents
Document Sharing Hub
Full document details: PD ISO/TS 18507:2015

Introduction

Total Reflection X-Ray Fluorescence (TXRF) spectroscopy is a reliable technique for chemical analysis. TXRF today is employed in electronic industry quality control. TXRF is also a powerful multi-elemental method for trace and ultra-trace analysis of different kind of samples that can be grouped as follows: environmental samples (as water, soil, aerosols, deposits, plants), geological and mineralogical samples (as ore, crystals, mineral raw materials), technological samples (as petroleum and petroleum products, thin films, wastes, metals, polymers), biological samples (as blood, serum, urine, human tissue), food samples (as fish, fruit, meat, nuts, mushroom), pharma and biomedical samples (as pharmaceuticals, cell culture media), archaeological, art, and forensic samples. Sample preparation is critical for the quantitative analysis and depends on the sample and its aggregate state.

Because of its capability to analyse different kinds of samples, TXRF is suitable for chemical metrology at the nanoscale, both for heavy metals and light elements in environmental and biological analysis.

The key advantages of TXRF are the following:

a) simultaneous multi-element trace analysis including halogenides;

b) analysis of very small sample amounts (lower than nanograms to microgram range depending on sample preparation and condition);

c) simple quantification using an internal standard and possibility of reference-free quantification;

d) suitable for various sample types and applications;

e) theoretically low matrix or memory effects;

f) relatively short time is required for measurement collection;

g) high-sensitivity, low-detection limits depending on sample (elements) matrix, preparation method, and instrumentation.

© ISO 2015 – All rights reserved
Documents
Document Sharing Hub
Full document details: PD ISO/TS 18507:2015

Surface chemical analysis — Use of Total Reflection X-ray Fluorescence spectroscopy in biological and environmental analysis

1 Scope

This Technical Specification provides a framework on the uses of Total Reflection X-Ray Fluorescence (TXRF) spectroscopy for elemental qualitative and quantitative analysis of biological and environmental samples. It is meant to help technicians, biologist, doctors, environmental scientists, and environmental engineers to understand the possible uses of TXRF for elemental analysis by providing the guidelines for the characterization of biological and environmental samples with TXRF spectroscopy.

Measurements can be made on equipment of various configurations, from laboratory instruments to synchrotron radiation beamlines or automated systems used in industry.

This Technical Specification provides guidelines for the characterization of biological and environmental samples with TXRF spectroscopy. It includes the following: (a) description of the relevant terms; (b) sample preparation; (c) experimental procedure; (d) discussions on data analysis and result interpretation; (e) uncertainty; (f) case studies; and (g) references.

2 Normative references

No normative references cited in this document.

3 Terms, definitions, symbols, and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1.1
sample carrier
flat substrate where the specimen is deposited

Note 1 to entry: The reference surface corresponds to the flat surface of the sample carrier, where the residue lays. The most important feature of the sample carrier is to be a reflector/mirror for X-rays. Surface roughness, matrix, and contamination of the sample carrier have an impact on TXRF measurements.

3.1.2
residue
specimen that lays on the sample carrier to be measured

© ISO 2015 – All rights reserved

Documents
Document Sharing Hub

Full document details: PD ISO/TS 18507:2015

3.2 Symbols and abbreviated terms

ppm	concentration in part per million range
ppb	concentration in part per billion range
MW	Microwave [used to describe the method of digestion (acidic MW digestion)]
APDC	Ammonium pyrrolidine dithiocarbamate
MIBK	Methyl isobutyl ketone
AAS	Atomic Absorption Spectroscopy
GF-AAS	Graphite Furnace Atomic Absorption Spectroscopy
ICP-MS	inductively coupled plasma-mass spectroscopy
IS	internal standard
INAA	Instrumental Neutron Activation Analyses
LPME	liquid phase microextraction procedure
FWHM	full width at half maximum
IR	infrared
QC	quality control
SR	Synchrotron radiation
XRT	X-ray tube
XSW	X-ray standing wave

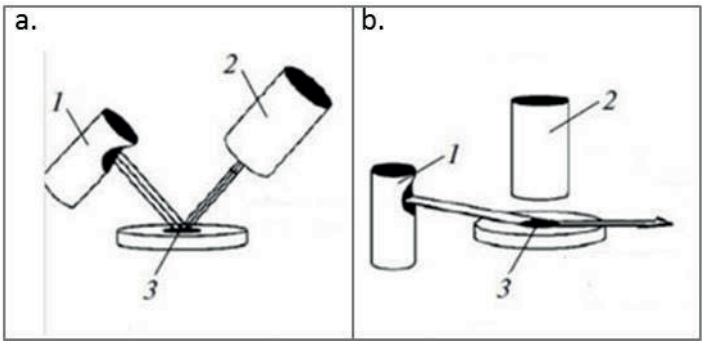
4 Background

4.1 Preliminary remarks

TXRF is a surface elemental analysis technique often used for ultra-trace analysis of particles, residues, and impurities on smooth surfaces. TXRF is currently a key tool for wafer surface contamination control in semiconductor chip manufacturing.

In the TXRF experiment, the monochromatic X-ray beam impinges on the sample holder carrying the sample at very small angle, causing total reflection of the beam. The glancing beam angle shall be below the critical angle of X-ray total reflection, differently from XRF method, where both the glancing beam and the detection angle are at 45°.[1] Figure 1 shows XRF and TXRF geometries.

© ISO 2015 – All rights reserved
Documents
Document Sharing Hub
Full document details: PD ISO/TS 18507:2015



Key

1 X-ray generator

2 energy dispersive detector

3 irradiated sample area

Figure 1 — a. XRF conventional instrumental geometry: X-ray incident beam angle and fluorescence detector angle are 45° with respect to the sample surface; b. TXRF instrumental geometry: X-ray incident beam angle is near to 0° and detector position is 90° with respect to the sample surface.[2]

Due to the low glancing beam angle, in TXRF the detector can be arranged close to the sample leading to a higher fluorescence yield with respect to the conventional XRF geometry. The monochromatic X-ray beam illuminates the sample and it is totally reflected. The great inherent advantage of TXRF is the double excitation of the sample by both the primary and the reflected beams, leading to a doubling in the fluorescence intensity.

TXRF detection limits are comparable or better of those that can be obtained by FAAS, while the former technique is more sensitive in terms of total sample amount.[1] Table A.1 and Table A.2 show the comparison of the detection limits of TXRF, AAS, and ICP analysis of environmental and biological samples, respectively. An advantage of TXRF over AAS and ICP-OES and ICP-MS is the possibility to detect halogenides.

TXRF can be used to perform qualitative and quantitative multi-element analysis. For quantitative analysis, an internal standard, i.e. an element absent in the sample (for example, V, Sc, Ga, Ge, Se, Y, or Co), is added to the sample aliquot. Reference free TXRF analysis for quantification and qualification is technically possible and has been proposed several times and is employed at some facilities.

Resulting benefits of TXRF are significantly reduced background noise and matrix effects. In addition, a sample preparation procedure without digestion allows more accurate analysis of some volatile elements, as Hg, As, or Se, which can be reduced by the sample preparation. Table 1 shows a comparison of some characteristics of TXRF, AAS, and ICP-MS.

Light elements (Z < 11) are not detected efficiently with commercial spectrometers because their fluorescence signals are absorbed before detection. However, using the vacuum chamber spectrometer, the proper excitation energy (e.g. Cr-Ka, Rh-L...), and the suitable detector with Ultra Thin window, the detection down to Carbon is possible.

The detection limits for specific element depend on the X-ray tube. For example, by using Mo X-ray tube, only the L-lines of some elements (such as Cd, Sn or Sb) can be detected. Because of the low energy of L-lines and their possible overlapping with K-lines of Cl, K, and Ca, the quantitative analysis for these elements is not reliable.

© ISO 2015 – All rights reserved

Documents
Document Sharing Hub
Full document details: PD ISO/TS 18507:2015

Table 1 — Comparison between TXRF, AAS, and ICP-MS

Property	TXRF	AAS	ICP
Technique used	Non-destructive technique	Destructive technique (digestion required)	Destructive technique (digestion required)
Calibration	Single-standard calibration (internal)	Multi-standard calibration (external)	Multi standard calibration (external)
Sample presentation	solutions, suspensions, particles, thin films	solutions[a]	solutions[a]
Multi-element analysis	Yes	Sequential only	Yes
Digestion procedure	Not necessary	Yes	Yes
[a] GF-AAS and LA-ICPMS allow the analysis of solid samples for special applications.			

5 Instrumentation

5.1 Instrumental requirements

The TXRF spectrometer consists of the following:

— sources of X-ray radiation like high-voltage generator and X-ray tubes or synchrotron radiation;

— a spectral modification element like a monochromator or a cut-off reflector, if necessary;

— sample station for handling the sample carrier;

— energy-dispersive detector;

— data acquisition unit.

Wavelength, voltage, and current of the X-ray tube, the presence of a spectral modification element (not always necessary), detector type, and glancing angle are the most relevant parameters. Today the performances of TXRF instruments are improving due to innovative X-ray optics.

5.1.1 X-ray sources of radiation

5.1.1.1 X-ray tubes

The X-ray tube is a device for the production of X-radiation via electrons striking an anode material. The electrons required are emitted from a heated cathode and are accelerated by a high voltage. Today, ceramic X-ray tubes cooled by air (low-power X-ray tubes) are also available.

X-ray tube voltage is the high voltage applied to the X-ray tube that determines the relative intensities of the characteristic X-ray lines. The maximum allowed high voltage is normally 60 kV. The optimum yield of characteristic X-ray lines is obtained when the tube voltage (in kV) is about 3 to 4 times the energy of the absorption edge of the anode material (in keV).

The anode material of the X-ray tube is the material that is struck by accelerated electrons. The anode material determines not only the characteristic X-ray lines emitted by the X-ray tube but also the intensity of the Bremsstrahlung. The latter is proportional to the atomic number of the anode material and to the square of the applied voltage.

Types of X-ray tubes that can be used:

— Side-window tube X-ray tube from which the X-radiation is emitted perpendicular to the axis of the tube.

— Fine-focus X-ray tube side-window tube with a fine, collimated, either point or line-shaped beam profile.

© ISO 2015 – All rights reserved
Documents
Document Sharing Hub
Full document details: PD ISO/TS 18507:2015

— Mixed anode X-ray tube: a fine-focus X-ray tube with an anode composed of two different metals, whose emitted spectrum consists of the spectra of the individual anode components.

The element of the XRT cannot be properly detected, and other elements (such as Cd, Sn, Sb, and Pb when Mo tube is used) can be identified only by means of their L lines. When the quantification of these elements is necessary, the XRT source shall be changed.[3]

5.1.1.2 Synchrotron radiation

The use of synchrotron radiation (SR) as primary excitation source can increase the overall sensitivity of TXRF. Compared to X-ray sources produced by electron bombarding on metal targets, SR is produced as a natural by-product of circulating or oscillating electrons in a storage ring. It contains all the wavelengths of the electromagnetic spectrum and is 100 or more times powerful than an X-ray generator of a commercial instrument.[4]

The advantages of SR are:

— High incidental flux combined with low divergence which results in higher fluorescence intensities and so lower detection limits.

— Reduced elastic scattering of the incoming beam due to its linear polarization in the orbital plane (Detector has to be placed in the orbital plane to make use of this).

— The spectral background, which is already reduced by total reflection, is further lowered.

— The tunability of SR allows improving the sensitivity for special elements (by increasing the photon absorption cross section when setting the excitation energy right above the absorption edge of the respective element).

5.1.2 Monochromator

A monochromator is a device for the selection of a narrow spectral region. A dispersive medium is the main constituent of the monochromator. It consists of an arrangement of two multilayers which select the X-ray radiation, according to the Bragg law. Low-pass filters can also be used as monochromator but they are less effective. Crystal monochromators are also used with synchrontron radiation, especially if TXRF is combined with XANES, as the high spectral resolution is required for XANES.

5.1.3 Detector

Detector is one of the key tool for TXRF analysis. It collects the characteristic X-ray radiation emitted by the sample, according to the drift chamber principle. The following materials are usually used in solid-state detectors: Li doped Si or Ge single crystals, high purity Ge single crystals. These detectors are described by the following acronyms respectively: Si (Li), Ge (Li), Si-PIN, Si drift, or HPGe detectors.

Detector parameters are: energy resolution, efficiency, and dead time.

Resolution is the capability of distinguishing between two nearly equal wavelengths. The energy resolution of a detector expressed as the full width at half maximum (FWHM) of a peak. For Silicon-based detectors, the FWHM of Mn-Kα line at 5,9 keV is taken as reference value. Typical values for the resolution lie in the range from 120 keV to 150 keV, depending on the size of the detector crystal.

Detector efficiency is the ratio of output signal (peak intensity) to the input signal (photon rate) at a given energy. The detector sensitivity only accounts for the photons that reach the detector. The overall sensitivity of system taking into consideration the system geometry is usually significantly lower. The sensitivity varies within the range 10 % to 100 %, depending on the energy of radiation and the type of detector. An important issue of the detector efficiency is also the absorption of the Be window. To improve the efficiency in the low-energy range, ultra-thin windows (UTW) are used; this allows the detection of low energy radiation of elements. Only in the high-energy regions the thickness of the crystal influences the efficiency.

© ISO 2015 – All rights reserved

Documents
Document Sharing Hub
Full document details: PD ISO/TS 18507:2015

The dead time is the time period following the arrival of a photon in the detector in which the pulse processing takes place and during which no new photons can be registered. The dead time (dead time loss) is given as the ratio of the dead time to total time.

Depending on the detector, artificial signals and background noise might be created. Escape peaks, pile–up peaks, shelf and tail will appear in the spectrum depending on the energy that is registered by the detector. Thus, when a photon with definite energy escape from the detector-active region, an escape line appears. For silicone-based detectors, the escape peak lies at an energy which is lower than the main peak by an amount corresponding to the Si-Kα energy (1,74 keV). Pile-up peak is caused by the simultaneous processing of two X-ray photons that the detector registers as a single event: it is a sum peak appearing to the sum of energies of two intense lines in the X-ray spectrum. The incomplete charge collection in the detector causes shelf and tail lines. All detector artefacts have to be considered during the analysis and compensated for electronically or via computer operations.

5.1.4 Sample station

A sample station is used for automatic and repeated measurements of multiple samples. It also separates the radiated measurement area from the sample interface and protects the operator.

The data acquisition unit is a stand-alone computer, which is connected to the apparatus for control of the data acquisition, data evaluation, and storage.

5.1.5 Critical and glancing angle

The choice of the glancing angle of the X-rays beam is critical for TXRF analysis. Figure 2 shows the reflectivity of X-rays for different glancing angles.

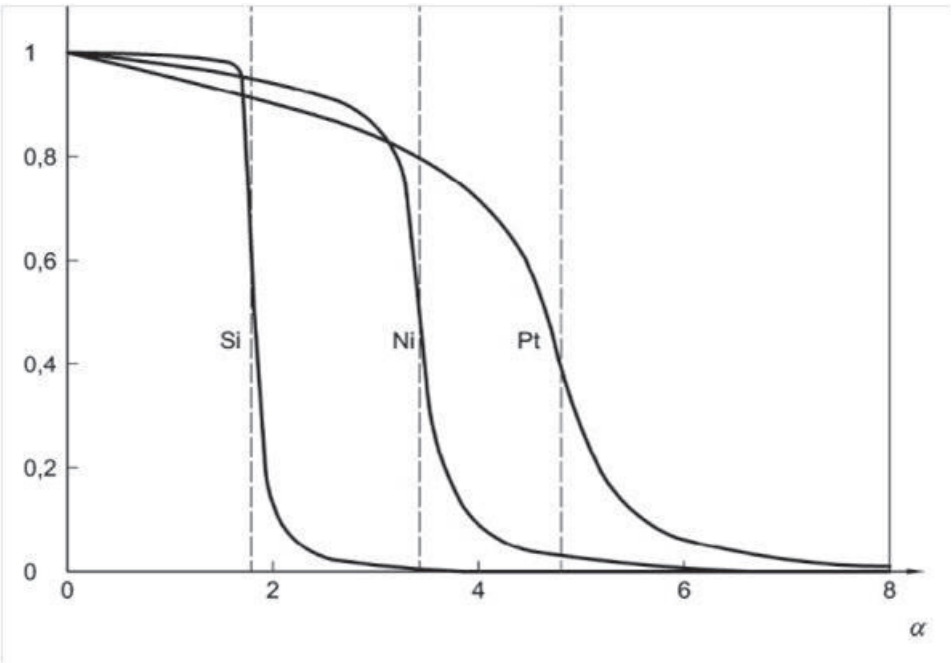


Figure 2 — Reflectivity curves of three different media calculated for *E* = 17,4 keV (Mo – Kα)

© ISO 2015 – All rights reserved
Documents
Document Sharing Hub
Full document details: PD ISO/TS 18507:2015