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Surface chemical analysis — Total reflection X-ray fluorescence — Principles and general requirements

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Foreword

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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 document 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).

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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 201, *Surface chemical analysis*, Subcommittee SC 10, *X-ray Reflectometry (XRR) and X-ray Fluorescence (XRF) Analysis.*

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.

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Introduction

Through general technical developments, total reflection X-ray fluorescence analysis (TXRF) has been developed into a robust independent physical method of instrumental analytical chemistry. TXRF is a distinct multi-element micro-method and a method of surface analysis. It is used for the simultaneous qualitative detection of the elements and quantification of the element masses. Notably, only small quantities of material are used for the analysis to benefit from all the advantages inherent to the procedure and thus to achieve correct analysis values. TXRF is used alongside other atomic spectroscopic methods, such as atomic absorption spectrometry (AAS) or inductively coupled plasma-based techniques (ICP-AES and ICP-MS) that are also established in the field of element analysis. In addition, TXRF is used in surface analysis and complements techniques such as Auger electron spectroscopy (AES), Rutherford backscattering spectrometry (RBS) or secondary ion mass spectrometry (SIMS). The rapid and in part non-destructive measurement process of a TXRF configuration allows screening or qualitative analysis of unknown flat, film-like and particulate samples and is therefore a valuable addition to other analytical techniques.

The main difference between TXRF and conventional X-ray fluorescence spectrometry (XRF) is the efficient way to excite the material to be examined to fluoresce which is achieved by a special geometrical arrangement in the spectrometer. The spectral background is drastically reduced, the fluorescence intensity increased resulting in a significant enhancement of the signal to noise ratio. Special sample treatment and sample presentation are required for this purpose. If these boundary conditions are met, TXRF achieves a high degree of accuracy and repeatability of the analyses, although a simplified calibration and quantification is used. The detection limits currently achievable with TXRF are approximately 10^{-12} g or 10^{10} atoms/cm^2 and are thus orders of magnitude lower than for XRF. The relative element concentrations are, depending on the matrix or the main components of the sample and for the elements to be examined, between 0,1 % and up to 10^{-9} for the low concentrations.

This document describes the physical principles and instrumentation required for TXRF analysis assuming that the conditions for total reflection are met, without referring to the samples' specificity. As a demonstration of the good reproducibility of the TXRF instruments, data from a round-robin test performed using centrally prepared and optimized samples are presented (see Annex B).

Other standards focussing on specific case studies and procedures are available for silicon wafers (see ISO 14706 and ISO 17331), environmental and biological samples (see ISO/TS 18507), and water (ISO 20289).

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Surface chemical analysis — Total reflection X-ray fluorescence — Principles and general requirements

1 Scope

The document provides the physical principles and specifies instrumental requirements for total reflection X-ray fluorescence analysis (TXRF) spectrometers. This document specifies general procedures for calibration, method development and verification of TXRF measurements and quality control.

The document describes measurements with TXRF conditions having a fixed glancing angle below the critical angle of total reflection and considerably enhanced excitation radiation intensity. Although certain definitions of grazing incidence geometry are shown for clarification, this document is not applicable to measurement setups working under such conditions.

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 18115-1, *Surface chemical analysis — Vocabulary — Part 1: General terms and terms used in spectroscopy*

ISO 20289, *Surface chemical analysis — Total reflection X-ray fluorescence analysis of water*

JCGM 100, 2008, Joint Committee for Guides in Metrology, *Evaluation of measurement data - Guide to the expression of uncertainty in measurement*

3 Terms, definitions and abbreviations

For the purposes of this document, the terms and definitions given in ISO 18115-1 apply.

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/

3.1 Abbreviated terms

AAS	Atomic Absorption Spectroscopy
FWHM	Full Width at Half Maximum
GIXRF	Gracing Incidence X-ray Fluorescence
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
ICP-AES	Inductively Coupled Plasma –Atomic Emission Spectroscopy
SDD	Silicon Drift Detector
XRF	X-ray fluorescence

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XRR X-ray reflectometry

XSW X-ray Standing Wave

TXRF Total Reflection X-ray Fluorescence

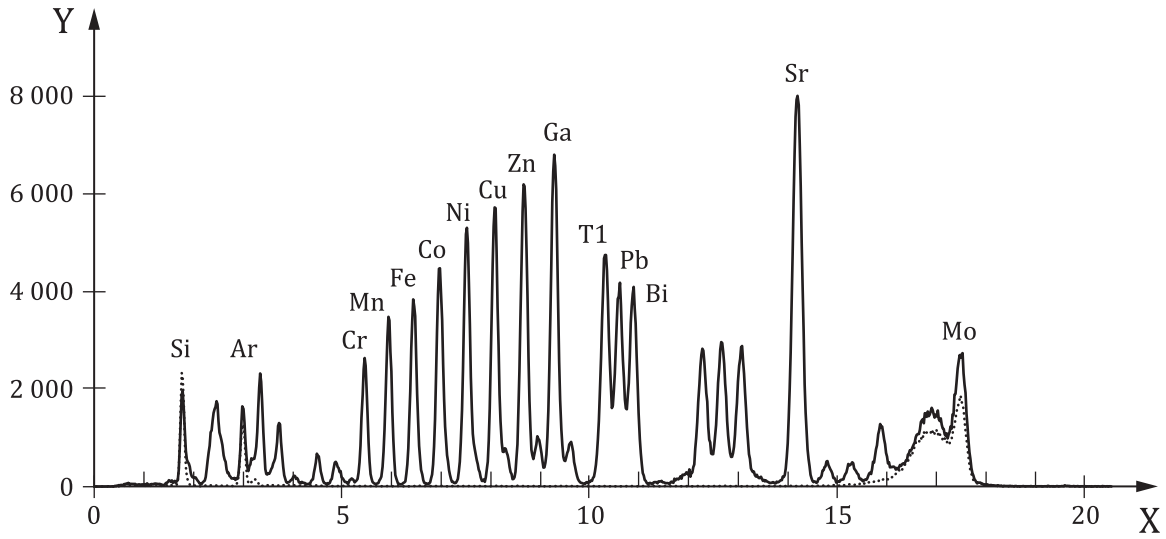
4 Physical background of TXRF

4.1 General

TXRF is based on the excitation (and detection) of element-specific X-ray fluorescence radiation at a very small glancing angle (smaller than the critical angle of the total reflection of the sample carrier, see Figure 3 and 4.2) of the incident radiation[1].

Total reflection has two beneficial effects on the measurement.

a) Since the primary beam penetrates only a few nanometres into the sample carrier, the proportion of radiation generated and detected by scattering and fluorescence excitation of the carrier material is significantly lower than, e.g. in classic XRF, which enables a lower background signal and thus better detection limits (Figure 1).



Key

X photon energy/keV

Y recorded counts

——— MES ICP-IV 1 mg/kg

..... blank

Figure 1 — Illustration of typical TXRF spectra. TXRF spectrum of a clean quartz carrier generated by excitation with a Mo X-ray tube (dashed line); TXRF spectrum of a reference material with 23 elements of the same concentration (solid line)

b) With a well collimated beam (for details refer to [2]) and a sufficiently good substrate surface as well as a suitable structure of the analyte, X-ray standing waves (XSW) with a location-dependent intensity distribution (typically between 0 and 4 I_0) are formed above the sample carrier surface, which on average lead to an excitation of X-ray fluorescence which is about twice as strong (see detailed discussion in 4.4). If no standing wave field occurs, the radiation passes through the analyte twice as an incident and a reflected beam, which also leads to doubled fluorescence intensity.

The attenuation length is defined as perpendicular distance from the sample surface within the reflecting medium at which the amplitude of the electric field associated with the propagating wave field is reduced

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