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Summary of ISO standard 20289-Total reflection X-Ray Fluorescence analysis of water

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Abstract

The International standard ISO 20289 provides a method for determining the elemental concentration of impurities dissolved in water samples. It exploits Total reflection X-Ray Fluorescence Spectroscopy (TXRF) to measure a dried residue on an X-Ray reflector. The scope is to provide a chemical metrology for quantitative analysis to obtain traceable results within a defined degree of accuracy and precision according to good practice and in compliance with ISO 17025. Target users include technicians working in laboratories who perform routine analysis of large numbers of samples. The method is specifically focused on determining elements dissolved in drinking, surface and ground water, but it can be also extended to waste waters and eluates if dilution steps are considered. The standard includes the description of all reagents, standards and materials, including suitable reference materials, which are needed to prepare the sample and ensure quality assurance and control protocols. In addition, the standard presents a detailed description of sample preparation, contributions factors affecting the uncertainty budget, the general procedure to check instrumental calibration, determining limits of detection and quantification as well as methods for spectra fitting.

Keywords: water, TXRF, experimental calibration, ISO, accuracy, precision.

1. Introduction

Elemental analysis of water seems a relatively easy task as it is routinely performed in chemical laboratories all around the world as part of water quality control measures. However, detailed analysis is often complicated by the presence of dissolved salts, gases, non-soluble fine particulate matter, colloids and organic compounds that can all interact with analytical signals leading to erroneous results.

Contamination by solubilized elements is often present in drinking water but is often considered less important than any microbial residues due to their significantly lower health effects, usually associated with long-term exposures. However, the presence of potentially toxic elements is an important factor in identifying available water resources, environment impact and can even cause socio-economic imbalances. For this reason, water monitoring regulations now include elemental analysis as a decisive component in determining water quality levels¹. Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), and ICP Optical Emission Spectroscopy (ICP-OES)²⁻⁵ are currently the main approaches employed for elemental analysis of water. However, the demand of simultaneous multi-elemental analysis across a wide concentration range as a sensitive and convenient analytical technique for water quality monitoring has increased, especially in fast developing countries and so new accurate and traceable approaches are needed.

Over several years, Total reflection X-Ray Fluorescence (TXRF) spectroscopy has become known as a versatile tool for elemental analysis across many application fields^{6,7}. TXRF is an advanced technique for surface chemical analysis which, within ISO, was originally applied to measure and control the contamination of silicon wafers to support the semiconductor industry⁸⁻¹⁰. It was then further exploited in other application fields where there was a demand for measuring low mass volumes where the sample was then deposited onto X-ray reflective surfaces. Material surface analysis remains at the heart of TXRF, but more recently, the availability of commercial benchtop TXRF instrumentation has increased the use of TXRF for analysing many different types of samples: nowadays TXRF is used widely to perform elemental analysis of water^{6,11-15}, soils¹⁶⁻²⁰, bio-monitors²⁰⁻²⁵, food^{26,27}, and biological matrices²⁸⁻³¹. In these contexts, the community has so far been focused on developing specific sample preparation protocols to ensure the analytical performance of the method^{32,33}. These generally assume instrumental features and that the total reflection conditions are fulfilled during measurements. A lack of detailed instrumental knowledge makes direct modelling of the data difficult, especially for non-expert users and this may cause strong biases and variable accuracy in attempts at quantification of elemental concentrations. To this end, TXRF analysis of residues is performed routinely by adding an internal standard of known concentration and doing comparative studies. Under such conditions the effects of instrument and sample geometry along with the specifics of the detector, which would otherwise introduce significant uncertainties in the collected spectra, are mostly compensated for. However, care is still needed to ensure any instrumentation is reproducible and that a suitable internal reference is selected with a concentration which is known precisely.

The sensitivity of the TXRF measurement, in this scenario, is set by the internal standard, meaning that it is “relative” sensitivities that are determined for the other elements. Absolute sensitivities are determined by spectrometer calibration, which is mainly performed by the manufacturer, with the element concentration and quantification mostly elucidated via automatic software analysis and spectral fitting. It is worth noting that this automated approach is often performed without checking the validity of the “thin film like” conditions required for the linear response regime and simply applies Eq. 1:

$$C_i = \frac{C_{IS} \times N_i \times S_{IS}}{N_{IS} \times S_i} = \frac{C_{IS} \times N_i}{N_{IS}} \times \frac{1}{S_{rel i}} \quad (1)$$

Here C_i is the concentration, N_i the net area of the selected peak, and S_i the sensitivity of element i with the subscript IS referring to the same parameters for the internal standard. $S_{rel i}$ is the sensitivity ratio S_i/S_{IS} . Indeed, the linear relationship between the fluorescence signal of an element, N_i and its concentration, C_i , is only valid under the condition that defines the validity of TXRF, i.e. that the residue mass and thickness are lower than critical values³⁴. The exact critical threshold depends on both the atomic number of the element and the total amount of sample, so it is difficult to calculate *a priori*, especially for samples with an unknown

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3 composition. However, the validation of appropriateness can be revealed by checking the shape of the
4 angular response, in particular for the qualification of reliable calibration samples ³⁵. By building on the
5 approaches developed for solid state analysis and incorporating internal reference standards we believe that
6 TXRF has the potential to become a robust technique for reliable elemental analysis of both solids and liquids.
7 This motivated our commitment to develop a dedicated standard in the field of environmental and biological
8 analysis to support quantitative elemental analysis and provide a route for physically traceability of data.
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10 Reference to TXRF in documents of the International Standard Organization (ISO) dates back to 2004 with
11 ISO 17331:2004 which is devoted to quantification methods for silicon wafer surface analysis, followed by
12 ISO 14706:2014 on a similar topic devoted to surface contamination. The development of ISO documents
13 dedicated to TXRF applications in biological and environmental analysis begun in 2011 with a project for a
14 dedicated technical specification which was finally published in 2015 as ISO TS18507. TS18507 laid the
15 groundwork for developing standards dedicated to specific samples and/or application fields. Water was
16 selected as the first sample due to its relevance in multiple contexts, and thus TXRF analysis of water is the
17 subject of ISO 20289:2018.
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19 Method validation, including intra and inter laboratory comparisons, form the basis of standard documents.
20 To compare the quantification and control protocols then in place, the first round-robin test for TXRF analysis
21 of water was executed amongst many laboratories during 2012. In this exercise, six different water matrices
22 were analysed according to the usual procedures in place in each laboratory ⁶. The data yielded significant
23 variance between laboratories and highlighted that fitting of the spectra, the quantification method itself
24 along with choice of instrumental parameters and settings were the main source of sample independent
25 error (if reproducibility of the instrumentation was assumed to be negligible). A not insignificant contribution
26 to the uncertainty budget also arose from sample dependent spatial distributions of matrix effects, especially
27 at high concentrations. Both factors contributed to the errors in quantification and gave rise to a systematic
28 underestimation of concentrations in some cases. These initial data demonstrated the need for a more
29 detailed and robust method for sample preparation if TXRF could be used as a metrology tool for the analysis
30 of water.
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33 A major identified issue in the initial round-robin exercise was deleterious matrix effects which at high
34 concentration levels results in a non-linear relation between fluorescent intensity and concentration. The
35 analytical chemistry approach to compensate for matrix effects is through the use of calibration factors
36 and/or modifying the relative sensitivities conformed to the linear relationship between fluorescent intensity
37 and composition is demonstrated and maintained within a set degree of confidence. It was based on this
38 approach that the sample preparation procedures were developed and tested to validate the proposed
39 method for TXRF analysis of water in ISO 20289. The entire experimental procedure to validate the method
40 and define the linear calibration range has been published ¹¹. The mass limit needed to confine the method
41 into a suitable range in which matrix effects are reduced to a manageable level was set to the upper end of
42 the linear calibration range. In every laboratory performing chemical analyses, current good practice
43 methodology provides the route for the calibration procedures and the related analysis method. This is the
44 first step for quality assurance of the data and constrains the specific experimental setup in use and for this
45 reason has been included in the published standard.
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48 The guidelines published within ISO 20289 have been developed taking into account the results of round
49 robin tests that were performed in the framework of a VAMAS TWA 2 Project A10c) entitled "Inter-laboratory
50 comparison of total reflection X ray fluorescence spectroscopy of environmental and biological samples" ^{6,36}.
51 Results of the two inter-laboratory tests define honestly the status of the analytical capabilities of
52 participants (more than 30 around the world) and shows clearly the importance of following a standard
53 method, not only in terms of the protocol for sample preparation and analysis but also in terms of specific
54 procedures aimed at ensuring wider quality checks and good practices. The lack of a laboratory capability
55 check and/or verification of performance were identified as contributing factors for the reported low
56 reproducibility and as such they are stressed in the standard. The developed sample and metrology
57 procedures articulated in ISO 20289 will hopefully lead to a significant performance improvement both within
58 and between laboratories after its adoption as a reference for trace elemental analysis in water samples.
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2. SCOPE AND MAJOR COMPONENTS OF ISO 20289:2018

2.1 Scope

The International standard ISO 20289 provides a method for determining the elemental concentration of content dissolved in water samples. It exploits Total reflection X-Ray Fluorescence Spectroscopy (TXRF) to measure a dried residue on the flat surface of an X-Ray reflector. The scope is to provide a chemical metrology tool for quantitative analysis in order to obtain traceable results within a defined degree of accuracy and precision according to good practice and in compliance with ISO 17025. For validation purposes of quality management work items in line with ISO 17025, or to qualify calibration samples, different traceability chains such as TXRF based on calibrated instrumentation³⁷ are available. Target users include technicians working in laboratories who perform routine analysis of large numbers of samples. The method is specifically focused on determining the elemental concentration of impurities dissolved in drinking, surface and ground water. However, it can be extended to include waste waters and eluates if suitable sample preparation steps are considered. The typical specified limit of quantification lies between 0.001 and 0.01 mg/l and the working range between 0.001 and 10 mg/L, depending on the element of interest and experimental configuration.

2.2 Major Components

ISO 20289 includes a general description of the apparatus (Clause 7) as well as the reagents, standards and materials (including reference materials) needed to perform the sample preparation and quality assurance/control procedures (Clause 8). The core components of the standard are included in clause 9, 10 and 11. Clause 9 describes the necessary steps for sample preparation recommending cleaning conditions of the reflectors and wider instrumental environment as well as checking parameters such as pH that may affect sample homogeneity and representativeness. Sub-clause 9.3 details specifications for the preparation of the sample which includes the amount of Internal standard required for quantification purposes. Reproducibility through trials/replicates of the sample residue on the reflector is given in sub-clause 9.5. In addition, the effect of residue mass, size and its position on the reflector is discussed within the framework of maintaining the TXRF conditions within the spectrometer³⁸. We propose that the limit of validity of the TXRF measurement is related to the threshold mass of the residue. Clause 10 defines the procedure for measurements (sub-clause 10.4) and analysis of the spectra (sub-clause 10.5) in order to extract concentration limits and other data for further processing. A general procedure to check instrumental calibration and limits of detection and quantification, to perform measurements as well as spectra fitting is also reported. Qualitative and quantitative analysis in terms of element identification, determination of concentration by internal standard calibration and comparison with limits of quantification are described in Clause 11. The results are to be reported based on averages of multiple replicates (sub-clause 11.3) and the evaluation of the uncertainties associated with the measurements are included in sub-clause 11.4 and are based on the Guide of Uncertainty Measurements approach (JCGM 100 series). A section is dedicated to quality control and is inserted in Clause 12 to harmonize this approach with ISO 17025 and to ensure accuracy. Regular checks of the instrumental calibration, detailed measurements of certified reference materials, and participation in proficiency and repeatability tests are strongly recommended for any laboratories conducting this work (Clause 13). The information needed to be reported when providing results of water analysis according the ISO 20289 method are detailed in Clause 14.

2.3 Informative annexes

Additional information is contained within the Annexes and include an approach to uncertainty estimation in TXRF measurements (Annex A)^{39–42} along with an example of the intra-laboratory method validation (Annex B)¹¹. Annex A specifies the relevant contributions to the uncertainty budget including: the internal standard concentration, the sample preparation apparatuses (weight and volume), net intensities from spectra fitting, and the relative sensitivities. The results should be reported at the 95% confidence level. Results from the validation performed within one laboratory using a commercial spectrometer equipped with Mo tube are shown in Annex B. A description of the instrumentation, the procedure to verify the range of linear calibration, the extraction of relative sensitivities from the fitting the experimental data and the derived of limits of detection and quantification are also reported. Results of a quality check for accuracy determination performed within the framework of an Italian proficiency test are reported in comparison with

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3 target values. The use of experimentally derived sensitivities as compared to instrumental ones are also
4 discussed.
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7 **3. OTHER STANDARDS RELEVANT TO THIS TOPIC**

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

10 ISO 17331:2004, *Surface chemical analysis — Chemical methods for the collection of elements from the*
11 *surface of silicon-wafer, working reference materials and their determination by total-reflection X-ray*
12 *fluorescence (TXRF) spectroscopy*

13 ISO 14706:2014, *Surface chemical analysis — Determination of surface elemental contamination on silicon*
14 *wafers by total-reflection X-ray fluorescence (TXRF) spectroscopy*

15 SEMI Standard M33-0998, 'Test Method for the Determination of Residual Surface Contamination on
16 Silicon Wafers by Means of Total Reflection X-Ray Fluorescence Spectroscopy (TXRF)', Semiconductor
17 Equipment and Materials International: San Jose, CA, USA (1998)

18 ASTM Standard F1526-95(2000) 'Standard Test Method for Measuring Surface Metal Contamination on
19 Silicon Wafers by Total Reflection X-Ray Fluorescence Spectroscopy', American Society for Testing and
20 Materials: Conshohocken, Pa, USA (2000)

21 **AUTHOR CONTRIBUTIONS**

22 (Please turn to the CRediT taxonomy for terms explanation.)

23 Conceptualization, L.B; Investigation, Writing – Original Draft, L.B., F.B.; Review & Editing: S.F., T.H., E.M.,
24 Y.H., B.B.; Funding Acquisition; Resources; Supervision: L.E.D.

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