Total Reflection X-Ray Fluorescence Spectroscopy

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Abstract

Total reflection X-ray fluorescence (TXRF) is widely used in trace elements, ultra-trace element, and multi-element analysis due to its low detection limit and low energy spectrum background count. This article studies the development and application of TXRF. The development of TXRF can be divided into three stages. The first stage: Total reflection was first presented in 1971 to the publication of the first monograph about TXRF in 1997, mainly the theoretical research of TXRF and the application in single element analysis; the second stage: 1998 to 2017, during this stage, TXRF has developed rapidly, from single element analysis to multi-element simultaneous analysis, mainly used in geology, environment, chemistry, medicine, etc. field; the third stage: based on the extensive application of TXRF, conduct in-depth research on its basic theory, further improve the performance of the instrument, and achieve more accurate analysis results.

Subject Areas

Nuclear Physics

Keywords

X-Ray Total Reflection, Critical Angle, Elemental Analysis

1. Introduction

Total-reflection X-ray fluorescence (TXRF) is a multi-element simultaneous analysis technology developed based on X-ray fluorescence (XRF) [1]. Different from the incidence angle of XRF, which is about 40°, the primary rays of TXRF are incident at an angle slightly less than the critical angle to illuminate a very small amount of samples on the optical platform (sample carrier) [2]. Due to the high reflectivity of the carrier, the rays are reflected. The primary rays are hardly

recorded by the detector, which greatly reduces the background count in the energy spectrum and improves the detection efficiency. In the analysis of ultra-trace elements [3], due to the ultra-low background count, the characteristic peaks will not be covered by the background count, to achieve the purpose of trace element analysis. Figure 1 shows the spectrum of XRF and TXRF. In the figure, the background interference of XRF is much greater than that of TXRF. Therefore, TXRF has the following characteristics [4]:

    1) High sensitivity;

    2) Low detection limit;

    3) No matrix effect;

    4) The quantitative analysis by the internal standard method is simple;

    5) The sample size is small (as low as ng to ug based on sample preparation);

    6) Non-destructive testing;

    7) Multielement simultaneous analysis.

2. The Principle of TXRF

X-ray fluorescence analysis uses the interaction of primary X-rays with substances to generate characteristic X-rays and analyze the characteristic X-rays [3]. Figure 2 shows how characteristic X-rays are generated.

The energy state of electrons in atoms is quantized [5], and characteristic X-rays generated by ionization or excitation correspond to specific atoms according to their energy. According to Moseley's law [6] and Sheman equation, the elements can be analyzed qualitatively and quantitatively. When total reflection occurs, the primary rays are emitted along the incident direction and can hardly be recorded by the detector, thus greatly reducing the background count. The wide incident wave and the wide reflected wave cause interference [3], forming a standing wave, which can generate in the thin samples on the sample stage and the total reflection surface of the sample stage. Figure 3 is the Schematic of total reflection and the generation of standing waves field.

At this time, the sample is excited by both incident radiation and total reflection
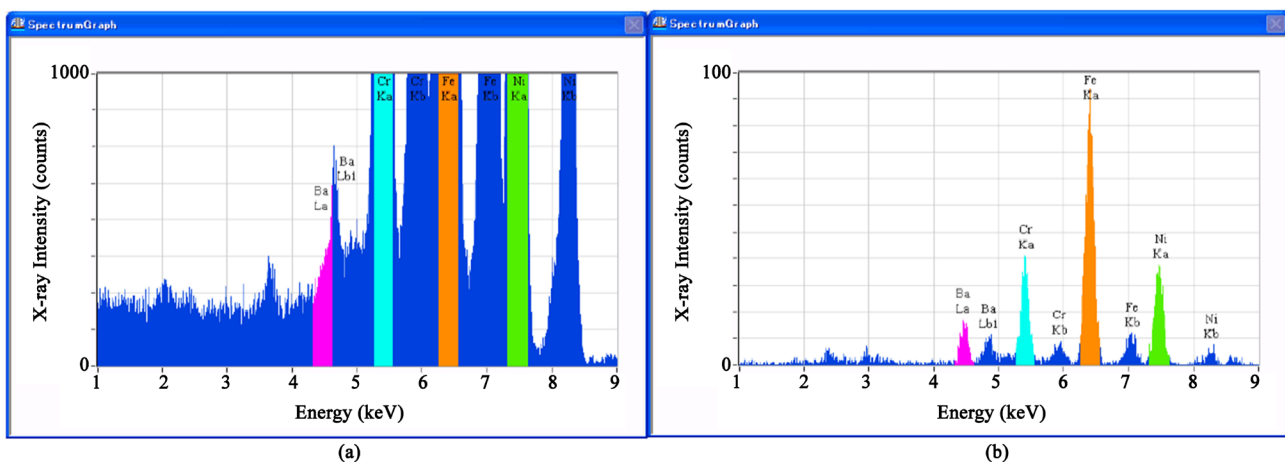

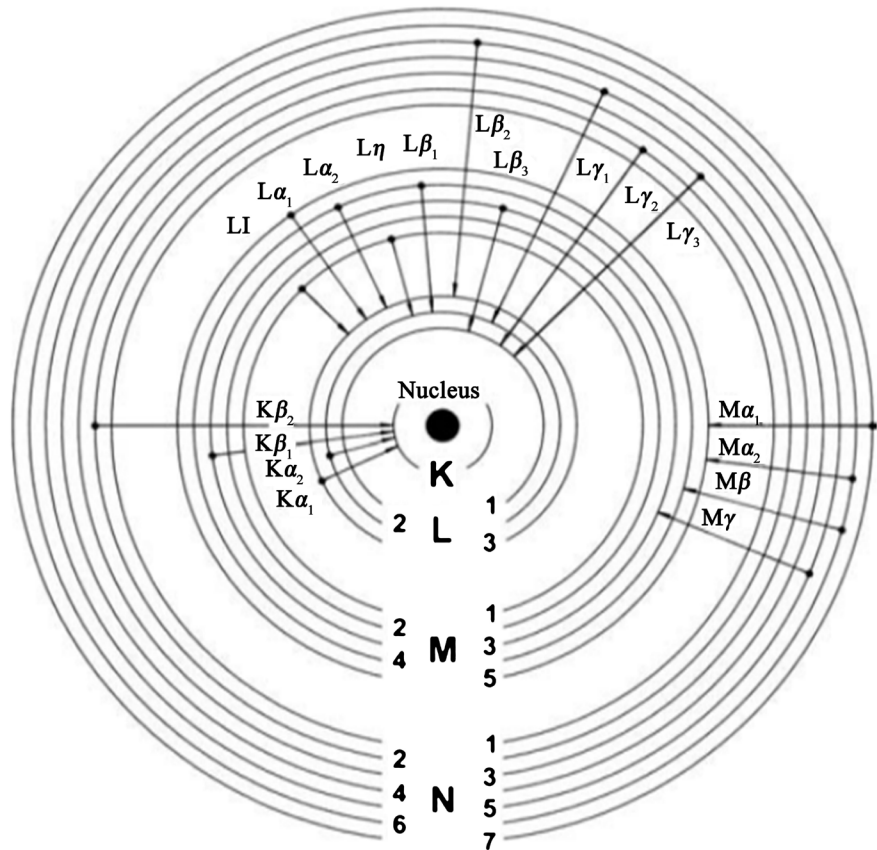**Figure 1.** (a) XRF Spectra; (b) TXRF Spectrum [4].

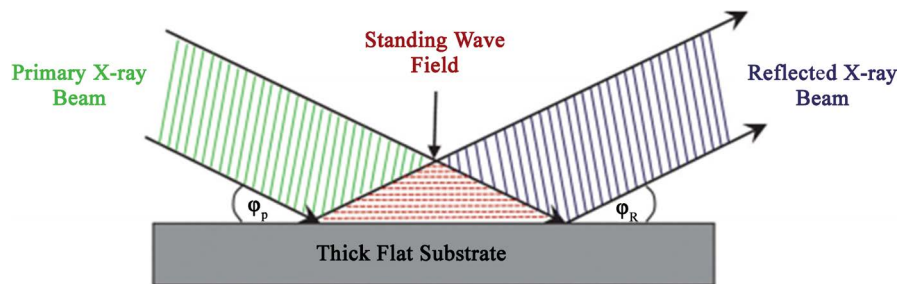**Figure 2.** The generation of characteristic X-rays.

Figure 3. Schematic of total reflection and generation of standing waves field [7].

radiation, and its fluorescence intensity shows a sudden increase trend [2]. **Figure 4** shows the geometric arrangement of XRF and TXRF.

The primary ray source is an X-ray tube, which irradiates the sample on the sample stage through a certain angle to generate secondary X-rays [9], and the secondary X-rays then recorded by the detector. When the resonance and quantum effects at the absorption limit are not considered [10], the critical angle is related to the reflector material and the wavelength of the incident ray. The critical angle [11] of X-ray total reflection is determined by Equation (1):

$$\alpha_c \approx \frac{1.65}{E} \sqrt{\frac{Z}{A} \times \rho} \tag{1}$$

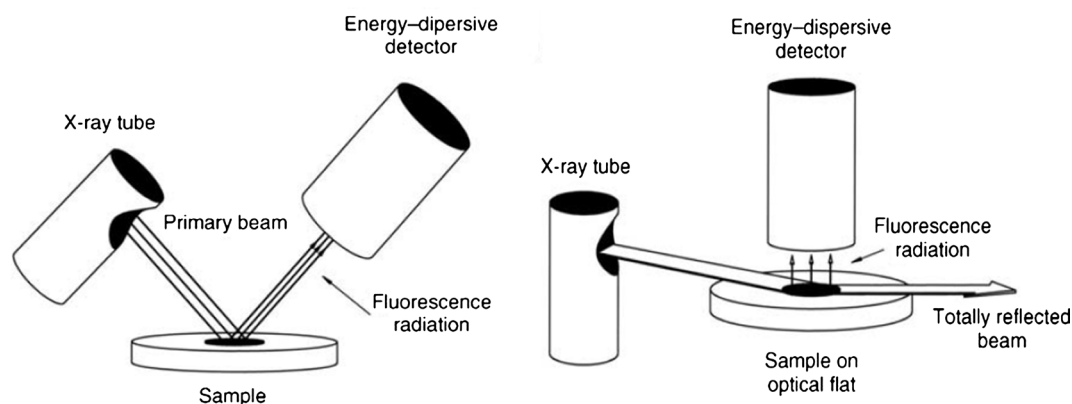In Equation (1), E is the energy of the primary ray;

Figure 4. Geometric arrangement of XRF and TXRF [8].

α_c is the critical angle;

A is the atomic weight of the sample stage;

Z is the atomic number of the sample stage;

ρ is the density of the sample stage.

The main differences between TXRF and XRF are the incident angle of the primary rays (XRF is generally about 40°, TXRF is generally less than 0.1°-critical angle [3] [12]); the smoothness of the sample stage, and the requirements of the sample (TXRF requires the reflectivity of the sample stage High to ensure the occurrence of total reflection, the sample thickness is generally less than 100 um [4] [13]); the position of the detector (due to the total reflection, the detector can be placed very close to the sample to improve the detection efficiency of the detector, generally 0.5 mm [4]).

3. Development and Application of TXRF

3.1. Initial Development of TXRF

Since 1971 Yoneda *et al.* [13] first application the total reflection technology to XRF, they determined uranium in seawater, iron in the blood, and rare earth elements in hot-spring water. The theoretical basis and experimental conditions were subsequently investigated. In Vienna, Austria, Wobrauschek wrote a Ph.D. thesis on the subject [14], and together with Aiginger, they reported detection limits of nanograms [15] [16]. In Geesthacht near Hamburg, Germany, Knoth, and Schwenke found element traces on the ppb-level [17] [18]. In the decade after 1980, a great variety of applications promoted a growing interest, the number of instruments in use increased to about 200 worldwide.

In 1981, the West German Rich Seifer Company successfully developed the first commercial total reflection X-ray fluorescence spectrometer. Since then, the development and application of the TXRF instrument have been rapidly developed and improved. Since 1984, several TXRF seminars have been held internationally [19]. Since the 1990s, China has been led by the Institute of High Energy Physics [10], the Institute of Modern Physics [20], and the Chinese Academy of Atomic Energy, which have successively carried out the development of TXRF

analysis devices and the research and promotion of analysis methods.

In 1983, the angular dependence of the fluorescence intensities in the range below the critical angle of total reflection was first observed by Becker *et al*. [21] It led to the nondestructive investigation of surface contamination and thin near-surface layers. In 1986, the X-radiation of a synchrotron was first used for excitation by Iida *et al*. [22]. At a first "workshop" in Geesthacht in 1986, the participants decided to call the new method "total reflection X-ray fluorescence analysis" and introduced the acronym "TXRF". In 1991, Wobrauschek, Aiginger, Schwenke, and Knoth won the distinguished Bunsen-Kirchhoff Prize of the DASp (Deutsche Arbeitskreis fur Angewandte Spektroskopie) for the development of TXRF. Table 1 shows several important stages of the initial development of the TXRF.

3.2. TXRF Mid-Development Application

In the years after first reviews and book contributions were published on the subject of TXRF (e.g. [24] [25]). The number of papers about TXRF grew explosively from some 3 to about 125 papers per year with large fluctuations [8]. TXRF is successfully applied all over the world. It is widely used in the analysis and determination of macro, trace elements in various fields such as chemical industry, food, environmental protection, biology, medicine, legal inspection, high-purity materials, geology and minerals, metallurgy, etc. [26]. In 1995, Tian Yuhong *et al*. [10] researched the structure of the secondary total reflection system. The minimum detection limit of the copper target under small beam conditions can reach 0.6×10^{-9}, and the platinum target can reach 2×10^{-9}. In 1996, when Christina Streli [27] used TXRF to analyze light elements, he compared the effects of possible x-ray sources such as standard x-ray tubes, special windowless x-ray tubes, and synchrotron radiation, and he using special excitation sources and special spectral correction components to reduce the detection limit and reduce the background count. C. Surely, Burba P, *et al*. have further studied the X-ray source, he found that detection limits depend upon the source. When

Table 1. TXRF several important stages of initial development.

Time	Representatives	Main work
1971	Yoneda Y, Horiuchi T	First proposed to apply total reflection technology to XRF
1978	Knoth, J. and Schwenke, H	Found element traces on the ppb-level
1981	Rich Seifer West Germany	Successfully developed the first commercial total reflection X-ray fluorescence spectrometer
1983	Becker	Studied the relationship between fluorescence intensity and angle below the critical angle
1986	Iida, A., Yoshinaga, A	Apply synchrotron radiation to TXRF
1991	Wobrauschek, Aiginger, Schwenke, and Knoth	Won the distinguished Bunsen–Kirchhoff Prize for the development of TXRF
1997	Klockenkamper [23]	Publication of the first monograph on TXRF

using synchrotron radiation as an X-ray source the detection limits are in the range of some hundred femtograms [28] while in the range of some pg when using a special windowless X-ray tube with a-Si anode [29].

TXRF is used everywhere. In terms of environmental protection, the TXRF analysis of environmental samples (such as water, soil, air particles, animals and plants, etc.) [30]-[37] can evaluate environmental changes. Erick K. Towett *et al.* [32] [33] used TXRF to study the element content in the soil, and compared with the ICP-MS measurement results after digestion, it showed the feasibility of TXRF measurement results in soil. Liu Guangya [34] used TXRF to measure atmospheric particles and evaluate air pollution. Through TXRF research on geological samples (such as ores, crystals, and mineral raw materials), geological and geochemical surveys and mineral census are realized. Cherkashina Ty *et al.* [38] used TXRF to study ore samples and proved that TXRF can quickly detect ore samples. In the chemical industry, product quality control can be achieved by analyzing the element or impurity content of chemical products (petroleum and petroleum products, fertilizers, wastes, films) [39] [40] [41] [42]. In foreign countries, I. De La Calle *et al.* [41] used TXRF to measure metal content in smelting slag to assess whether the smelting slag treatment process is appropriate and judge whether the slag can be recycled. F. M. Adebiyi *et al.* [39] used TXRF to analyze trace elements in Nigerian oil sands. In the field of medicine and food, Lankosz M W *et al.* [43] used TXRF to measure trace elements in human brain tissue to distinguish the disease level. Li Meng [44] studied the relationship between mineral elements and diseases through TXRF analysis of the hair of chronic hepatitis B patients and healthy people. In China, the use of TXRF is mainly concentrated in food (such as fish, fruits, nuts, pollen, tea) [45] [46] [47] [48] and the medical field, such as Yu Huichun *et al.* [45] for different types of wine grapes. Wang Shuxun [49] uses TXRF analysis Ganoderma lucid from different origins. Table 2 shows some applications of TXRF in mid-term development.

3.3. The Development of TXRF in Recent Years

In the past few years, many instrument improvements have been done, and elemental analysis has been done in the following applied research fields.

1) Minerals: feldspar, antimony oxide, gold ore, fluorite [50];

2) Metallurgy: nickel electrolyte, cast iron, bearings;

3) Environmental protection: pure water [51], mineral water, tap water, sewage, atmospheric dust, sludge, high salinity salt lake water; soil [52];

4) Chemical industry: catalyst formula for purifying automobile exhaust, sulfur in diesel, ceramic glaze formula;

5) Biology: teeth, marine animals, blood [53], cells and proteins, body fluids;

6) Legal inspection: Appraisal of samples at the crash site [54];

7) Material: glass, high purity quartz impurity content; medicine: trace elements in hair [46], nails, harmful trace elements in salvia;

Table 2. TXRF Some mid-term development applications.

Author	Related applications	Title of article
Erick K. Towett	Elemental content in soil studied with TXRF	Bromine and bromine content in soils: Analytical approach from total reflection X-ray fluorescence spectrometry
Liu Guangya	Measuring atmospheric particles with TXRF to assess air pollution	Analysis of the Concentration of Harmful Elements of Atmospheric Particulate Matter in Wuhan Based on Total Reflection X-Ray Fluorescence
Cherkashina T Y	A TXRF study of ore samples was used	Applicability of direct total reflection X-ray fluorescence spectrometry for multielement analysis of geological and environmental objects
I.De La Calle	Measurement of metal content in smelting slag using TXRF	Determination of residual metal concentration in metallurgical slag after acid extraction using total reflection X-ray fluorescence spectrometry
F. M. Adebiyi	Analysis of trace elements in Nigerian oil sands using TXRF	Characterization of Nigerian Oil Sands by TXRF Spectrometry
Lankosz M W	Identification of disease levels using TXRF measurements of trace elements in human brain tissue	Application of the total reflection X-ray fluorescence method to the elemental analysis of brain tumors of different types and grades of malignancy
Li Meng	Analysis of hair TXRF in patients with chronic hepatitis B and healthy population	Comparative analysis of the TXRF of 16 mineral elements in the hair of patients with chronic hepatitis B
Huichun	Different types of wine grapes	Determination of 16 mineral elements in different varieties of wine grape by TXRF method

8) Food: beneficial and harmful elements in beverages, rice [55], plant materials, leaf roots, and stems.

In 2017, Mercedes Radio [56] investigated the effect of an inorganic ($CaCl_2$) and an organic matrix on metals quantification by TXRF for liquid samples. In 2018, Tsugufumi Matsuyama [57] proposed a new methodology to evaluate uranium concentration in water containing many kinds of impurities by total reflection X-ray fluorescence analytical. Hikari Takahara [58] developed a non-dissolution preparation method for powder sample analysis by total reflection X-ray fluoresce spectrometry (TXRF). In 2019, I.Szaloki [12], *et al.* presented a new fundamental parameter model and calculation algorithm for quantitative analysis for total reflection X-ray fluorescence analytical technique. In 2020, Aleksandra Winkler [59] *et al.* determined the elemental composition of various herbal infusions and teas, including trace elements by using total reflection X-ray fluorescence (TXRF). Gruber Andreas [60] precisely quantify iron and other trace metals in a variety of biological samples by total reflection X-ray fluorescence (TXRF) analysis. Alex von Bohlen [7] explained that TXRF analysis is not working completely free of matrix effects if the thickness of the residue of matrix samples according to the results of TXRF analysis of the different components of beverages exceeds a certain margin. Table 3 is a number of applications TXRF in recent years.

4. Summary and Outlook

It has been 50 years since the first application of total reflection technology to XRF in 1971. During this period, TXRF has developed rapidly. Based on XRF, the background caused by scattering has been overcome, making it possible to analyze ultra-trace elements. It solves the measurement problem of multiple

Table 3. TXRF some applications in recent years.

Year	Author	Related applications	Title of article
2020	Aleksandra Winkler	The elemental composition of various herbal infusions and teas was determined by full reflection X-ray fluorescence analysis (TXRF)	Total reflection X-ray fluorescence analysis of the elemental composition of herbal infusions and teas
2020	Gruber Andreas	Determination of iron and other trace elements in various biological samples by full reflection X-ray fluorescence analysis	Total reflection X-ray fluorescence spectrometry for trace determination of iron and some additional elements in biological samples.
2020	Alex von Bohlen	TXRF analysis is not working completely free of matrix effects if the thickness of the residue of samples exceeds a certain margin according to the results of TXRF analysis of the different components of beverages notes	Experimental evidence of matrix effects in total reflection X-ray fluorescence analysis: Coke case
2019	I.Szaloki	presented a new fundamental parameter model and calculation algorithm for quantitative analysis for total reflection X-ray fluorescence analytical technique	Fundamental parameter model for quantification of total reflection X-ray fluorescence analysis
2018	Tsugufumi Matsuyama	proposed a new methodology to evaluate uranium concentration in water containing many kinds of impurities by total reflection X-ray fluorescence analytical	Determination of uranium in immersion liquid of demolition waste using total reflection X-ray fluorescence analysis
2018	Hikari Takahara	developed non-dissolution preparation method for powder sample analysis by total reflection X-ray fluoresce spectrometry (TXRF)	Method development for the analysis of poorly soluble solids by total reflection X-ray fluorescence spectrometry
2017	Mercedes Regadio	investigated the effect of an inorganic ($CaCl_2$) and an organic matrix on metals quantification by TXRF for liquid samples.	Direct Analysis of Metal Ions in Solutions with High Salt Concentrations by Total Reflection X-ray Fluorescence

elements in geological samples that have plagued the scientific community for many years. Due to the very small amount (μL or μg), the matrix effect can be almost eliminated, making the analysis results more accurate. Total reflection X-ray analysis technology can detect almost all elements in the periodic table (from (B) boron to (U) uranium), and even superheavy elements in the actinide series.

Since the amount of sample is very small, it is easy to be contaminated during sample preparation and testing. Sample preparation is a key process in TXRF analysis and is particularly important for the study of sample preparation. With the continuous improvement of the TXRF spectrometer, the more economical, portable and easy-to-operate TXRF spectrometer will continue to be marketed.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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