

## Application of total reflection X-ray fluorescence spectrometry for trace elemental analysis of rainwater

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**Abstract.** Applicability of total reflection X-ray fluorescence (TXRF) spectrometry for trace elemental analysis of rainwater samples was studied. The study was used to develop these samples as rainwater standards by the National University of Singapore (NUS). Our laboratory was one of the participants to use TXRF for this study. The rainwater sample obtained from NUS was analysed by TXRF and the trace elements Mn, Fe, Ni, Cu, Zn, V and Pb were determined as required by the NUS. The average precision was found to be within 16% and the TXRF-determined elemental concentrations of these elements were below 20  $\mu\text{g/l}$ . The average deviation of TXRF-determined values from the certified values were 20% (excluding the deviation for Fe and V which were comparatively high). Apart from the above elements, S, K, Ca, Rb, Sr, Ba and Br were also determined by TXRF and were found to be in the range of 0.2 to 191  $\mu\text{g/l}$ . TXRF-determined values of our laboratory played an important role in the certification of concentration of seven elements in this rainwater sample which was later developed as a rainwater standard.

**Keywords.** Rainwater; total reflection X-ray fluorescence; interlaboratory study; trace elements.

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### 1. Introduction

Determination of trace elements present in environmental samples is of considerable interest because of the increased awareness about environmental pollution and human health as some of the trace elements are toxic whereas some are considered as nutrients for living population. Monitoring and accurate determination of these trace elements are very important because some elements which are nutrients, can also act as a toxin if they are present above certain limits. Analysis of various environmental samples such as soil, rocks, vegetation, sea water, rainwater, ground water, etc., helps in studying the origin and nature of deposition of trace and major elements [1–3]. Determination of trace as well as major elements present in rainwater gives a direct indication about the nutrient and toxic elements present in the atmosphere. The presence of heavy elements indicates the level of pollution over that region. For monitoring rainwater quality, it is essential to ensure that the results produced from a particular laboratory by a particular technique

are sufficiently accurate and precise. This requires the availability of suitable certified reference materials (CRMs) [4]. Interlaboratory studies (ILS) play a major role in the development of these certified standards. The certification of trace element concentration in a particular CRM depends on the number of laboratories participating and the number of techniques used for the determination of a particular element.

As rainwater contains a number of elements at ultratrace levels it is seldom possible to detect and determine all the elements by a single technique. The sample collection and storage also play a vital role as there are great chances of contamination during these processes. Various techniques used for the elemental characterization of trace elements in rainwater are, inductively coupled plasma-mass spectrometry (ICPMS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS), X-ray fluorescence (XRF), total reflection X-ray fluorescence (TXRF), neutron activation analysis (NAA), electroanalytical techniques, etc. [5–7]. Total reflection X-ray fluorescence (TXRF) is an upcoming technique for trace and ultratrace analysis. In TXRF, the X-ray beam falls on the sample at an angle less than the critical angle and gets totally reflected after touching the sample and thus has a minimum interaction with the sample support over which a few microlitres/micrograms of the sample is deposited. This unique geometry makes TXRF an advanced variant of energy-dispersive X-ray fluorescence (EDXRF) and leads to excitation of the sample by incoming as well as totally reflected beams. Since the penetration of the beam inside the sample support is almost negligible, background in TXRF is very low. Both these features i.e., sample excitation by incoming and totally reflected beams and lower background result in comparatively better detection limits [8] in TXRF than in XRF by several orders of magnitude. Also, due to almost negligible matrix effects a single element can be used as internal standard for all elements. Moreover, since the sample is deposited on a limited area of the TXRF sample support, sample contamination can be controlled. All these features make TXRF a potential analytical technique for the analysis of environmental, biological and industrial samples [9].

Though monitoring of rainwater is very important, the number of rainwater standards available is limited. Moreover, because of the presence of trace elements in rainwater at ultratrace levels (ppt-ppb), quantification of these elements without much sample preparation is a challenging task. National University of Singapore conducted an interlaboratory study (ILS) to develop such rainwater CRM and Fuel Chemistry Division, BARC, participated in this ILS by determining trace elements in rainwater samples by TXRF [10]. In this paper we present the TXRF methodology and elemental analysis results obtained by the analysis of this rainwater sample.

## **2. Experimental procedure**

### *2.1 Instrumentation*

An Ital Structures TXRF spectrometer TX-2000 with Mo-W dual target tube was used for TXRF measurements. Mo  $K_{\alpha}$  radiation obtained from the tube operated at 40 kV and 30 mA and monochromatized by a W-C multilayer was used for the excitation of the elements in sample. The characteristic X-rays emitted from the samples were detected

### *Trace element determination in rainwater by TXRF*

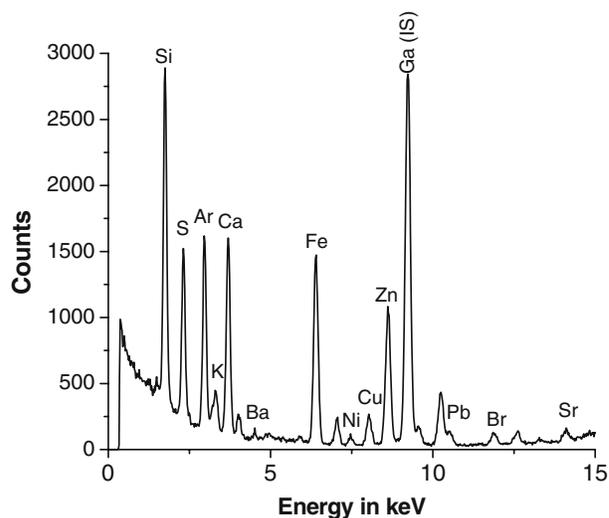
by a Si(Li) detector having a resolution of 139 eV at 5.9 keV. The TXRF spectra were recorded by TXRFACQ 32 and processed using the program EDXRACQ32 provided with the instrument.

#### *2.2 Sample preparation*

The collection and processing of rainwater samples are described elsewhere [10]. Homogeneity and stability tests were also performed on these rainwater samples and then distributed to various laboratories participating in this interlaboratory study. Our laboratory also received this processed sample to be analysed by TXRF. For TXRF determinations, the relative sensitivities of different elements were determined using a MERCK ICP multielement standard solution IV. All the standards were diluted in 1.5% suprapure HNO<sub>3</sub>. Five millilitres of rainwater samples were taken separately in two thoroughly cleaned glass bottles (SCHOTT DURAN). These glass bottles were earlier immersed in 1.5% suprapure HNO<sub>3</sub> solution overnight and then rinsed with the suprapure dilute nitric acid solution thrice. After this, 1 ml of the acid solution was put in the bottles and again left overnight. This solution was analysed for any trace impurity leaching out from the bottles. No impurity was found in any of the bottles. 50  $\mu$ l of Ga internal standard solution having 5  $\mu$ g/ml concentration was mixed with 5 ml of rainwater samples. Aliquots of 20  $\mu$ l were deposited ten times independently on six quartz sample supports so that 200  $\mu$ l of the above rainwater sample was deposited and dried under an IR lamp. The quartz sample supports were also cleaned with 1.5% suprapure nitric acid and checked for any contamination by measuring their TXRF spectrum before the sample deposition. The TXRF spectrum for each sample was recorded for 1000 s.

### **3. Results and discussion**

The excitation energy of Mo K $_{\alpha}$  (17.48 keV) from the Mo-W dual target tube was used for sample excitation as it can excite the K lines of medium and L lines of high Z elements very efficiently. In rainwater, major matrix is water which gets evaporated on the TXRF sample support after drying, leaving behind elemental constituents in concentrated form, so that it is fit for direct analysis by TXRF. The sample deposition on quartz support was done in steps of 20  $\mu$ l to avoid the uneven spreading of the sample on the sample support. This ensured less spreading and formation of a very thin film in about 2 mm radius and allowed the Si (Li) detector to receive almost all the excited X-rays. Depositing sample in this way also acted as a sample preconcentration step. A typical TXRF spectrum of such rainwater sample is shown in figure 1. As TXRF is a multielemental analytical technique applicable to metals and nonmetals equally, both metals and nonmetals present in the sample could be analysed simultaneously. The Si K $_{\alpha}$  peak in the spectrum is due to the sample support and Ar K $_{\alpha}$  peak is from the air. Gallium was chosen as internal standard as it was not present in rainwater. Trace elements S, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Br, Rb, Sr, Ba and Pb could be determined by TXRF and were found to be in the range of 0.2 to 191  $\mu$ g/l. The concentration of trace elements determined by TXRF is given in table 1 along with final certified concentrations [10]. The various techniques used in this ILS were ICP-MS, GFAAS, ICP-AES, DPASV and TXRF. One of the major



**Figure 1.** TXRF spectrum of 200  $\mu\text{l}$  rainwater sample measured after depositing on quartz sample support.

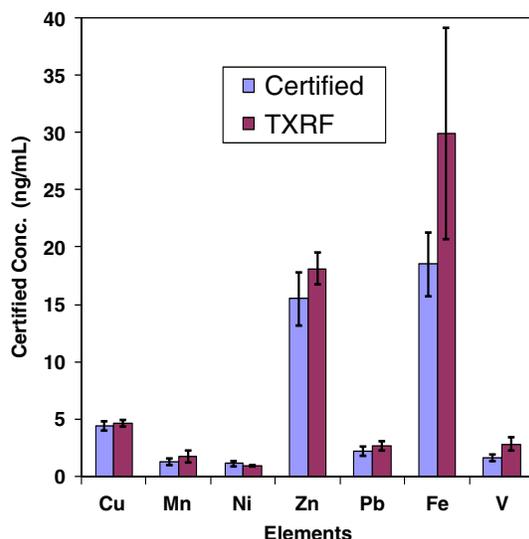
disadvantages of XRF/TXRF is their inability to determine low- $Z$  elements at ultratrace levels. Therefore, though Al was present in appreciable amount ( $15.0 \mu\text{g/l}$ ), it could not be determined by TXRF. Since Co and As concentrations are below  $1 \mu\text{g/l}$  (table 1) and have a strong interference with Fe  $K_{\beta}$  ( $7.06 \text{ keV}$ ), Co  $K_{\alpha}$  ( $6.93 \text{ keV}$ ), Pb  $L_{\alpha}$  ( $10.55 \text{ keV}$ ),

**Table 1.** A comparison of TXRF-determined and certified concentrations of some elements in the rainwater sample.

Elements	Certified values ( $\mu\text{g/l}$ )	TXRF-determined values ( $\mu\text{g/l}$ )
Cu	$4.4 \pm 0.4$	$4.6 \pm 0.3$
Fe	$19 \pm 3$	$30 \pm 10$
Mn	$1.2 \pm 0.3$	$1.7 \pm 0.5$
Co	$0.08 \pm 0.02$	ND
Ni	$1.10 \pm 0.15$	$0.9 \pm 0.1$
Zn	$16 \pm 2$	$18 \pm 1.4$
V	$1.6 \pm 0.3$	$2.8 \pm 0.6$
Al	$15 \pm 2$	ND
Pb	$2.2 \pm 0.4$	$2.7 \pm 0.4$
As	$0.14 \pm 0.03$	ND
Cd	$0.06 \pm 0.02$	ND

ND = Not detected.

Trace element determination in rainwater by TXRF



**Figure 2.** A comparison of certified and TXRF-determined concentrations of some elements.

As  $K_{\alpha}$  (10.54 keV), these two elements also could not be determined by TXRF. It is impossible to excite Cd  $K_{\alpha 1}$  (23.17 keV) using Mo  $K_{\alpha}$  (17.52 keV) excitation source. Cd  $L_{\alpha}$  (3.13 keV) can be excited with Mo  $K_{\alpha}$  but with very low excitation efficiency. In addition, the amount of Cd present in the water samples was so less that it could not be determined using Cd  $L_{\alpha}$  line as analytical line. Because of these limitations Cd also could not be determined by TXRF. Apart from the above elements, seven elements determined by TXRF were provided with certified values. These are V, Mn, Fe, Ni, Cu, Zn and Pb. The TXRF results obtained had an average precision of 16% (1 s). The agreement

**Table 2.** TXRF-determined values of other trace elements present in rainwater sample.

Elements	TXRF determined values ( $\mu\text{g/l}$ )
S	$190.7 \pm 26.9$
K	$26.9 \pm 2.7$
Ca	$176.2 \pm 21.1$
Cr	$1.7 \pm 0.4$
Rb	$0.24 \pm 0.06$
Sr	$0.76 \pm 0.2$
Ba	$9.1 \pm 2.9$
Br	$0.95 \pm 0.03$

between the TXRF-determined and the certified values is shown as a bar graph in figure 2. Except Fe and V all the elements are within the analytical uncertainty of the certified values. The average deviation of TXRF-determined values from the certified values are 20%. Hence, out of the 11 elements which were assigned the certified values, TXRF played an important role in the certification of the concentrations of seven elements. The analytical results of TXRF-determined values of other trace elements which were not assigned any certified values due to the lack of sufficient analysis data are given in table 2.

#### **4. Conclusions**

The role of TXRF in the development of rainwater standards was established. TXRF is one of the multielements analytical techniques which requires a very simple sample preparation method and uses a single internal standard for quantification of all the elements present in the sample. Out of the eleven elements which were assigned certified values, TXRF results from our laboratory for seven elements have a good agreement with the certified values.

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