



Research Article

USING TOTAL REFLECTION X-RAY FLUORESCENCE (TXRF) TO ANALYSE TRACE ELEMENTS IN SURFACE WATER OF XUAN HUONG LAKE – DALAT CITY

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ABSTRACT

The regular assessment of a water source has been important for safety and pollution warning. Specifically, the concentration of trace elements in water reflects the pollution level. Urbanization, industrialization, fertilizers and other plant protection products have negatively affected the environment; in particular, water and air quality. The main objective of this study was to evaluate the trace elements contained in surface water from Xuan Huong Lake – Dalat city by using the technique of Total Reflection X-ray Fluorescence (TXRF). The results show that the concentrations of some metal elements, such as Iron and Bromine, exceeded the limits by the Vietnamese standards as well as others in many countries.

Keywords: TXRF, trace elements, surface water, Xuan Huong Lake.

1. Introduction

Water plays an important role in our life. Water is one of the most important substances on earth (Alrakabi, 2017). Water from original natural resources which is indispensable to our life. Nowadays, the use of chemicals arbitrarily in the production of agriculture environment has increased the risk to water sources. Polluted surface water has impacted human beings either directly or indirectly (Do, 2015).

Xuan Huong Lake is located in the middle of Dalat city which is highland. Many water sources flow into this lake, including agriculture water, rain water, and surface water. Recently, water pollution in Xuan Huong Lake has reached an alarming level.

There have been many methods used to analyze trace minerals in water such as chemical method, neutron activation analysis, and TXRF technique. The trace element

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TXRF technique is one of the best analysis methods because of its accuracy (ppb), ability to analyze multiple elements with limited destruction of the sample (Do, 2015).

2. The experiment

2.1. Chemicals and equipment

Galium with amount of $1000 \pm 10 \text{ mg L}^{-1}$ is the internal standard solution was obtained from Merck. A silicone solution in isopropanol was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany).

Qualitative and quantitative TXRF analyses were performed with the benchtop S2 PicoFox TXRF spectrometer from Bruker Nano (Germany) (see Fig. 1.). All TXRF measurements were operated with X-ray tube at 50 kV, 1mA and a multilayer monochromator at 17.5 keV for $K\alpha$ line of Mo.

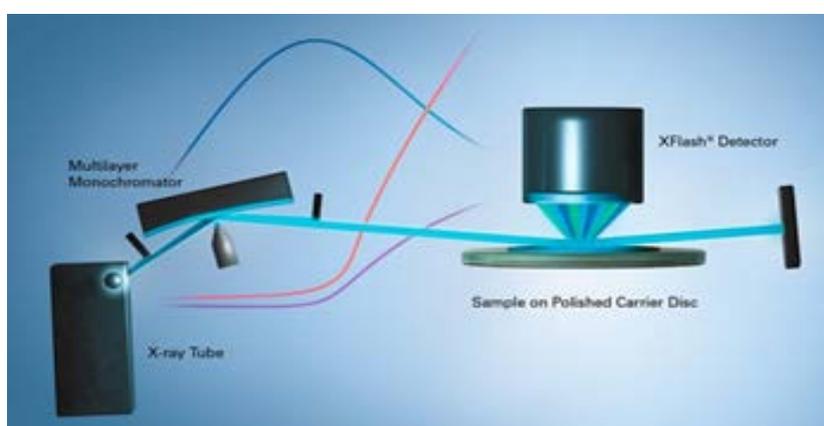


Fig. 1. Schematic working principle of TXRF

2.2. Sample collection

Samples were collected weekly in a rainy season from May 01, 2018 to April 31, 2019 at five different sites from Xuan Huong Lake (Fig. 2).



Fig. 2. Five different sites from Xuan Huong Lake

Samples were taken in the places which are the flows in and out of the lake. Site 1 and 2 are the flows in from other places which are called system deposit's lake. They are considered as a "mechanic filter" of all water flows before going to Xuan Huong Lake. Many canals flow in Site 1 which has been polluted and affected by agricultural activities (Dalat Hasfarm) (EPA, 2001). Site 3 is predicted less polluted than other sites, and it flows out to Cam Ly water fall. Water in Site 4 was polluted by pipes from Cu Hill (Hoang, 2018). Site 5 is considered to be 'medium' polluted of all the sites above.

2.3. Preparation of liquid samples

Gallium of 10 ppb which were internal standard, were added to all samples. For the optimization of the sample amount, the sample carriers were pretreated with 10 μ l of silicone solution and dried for 20 minutes in the oven at 60 °C.

Following the standard procedure, 10 μ l of a solution containing Ga of 10 ppb and lake water was disposed on a quartz sample carrier and dried on a heating plate at about 60°C in 20 minutes (Fig. 3).

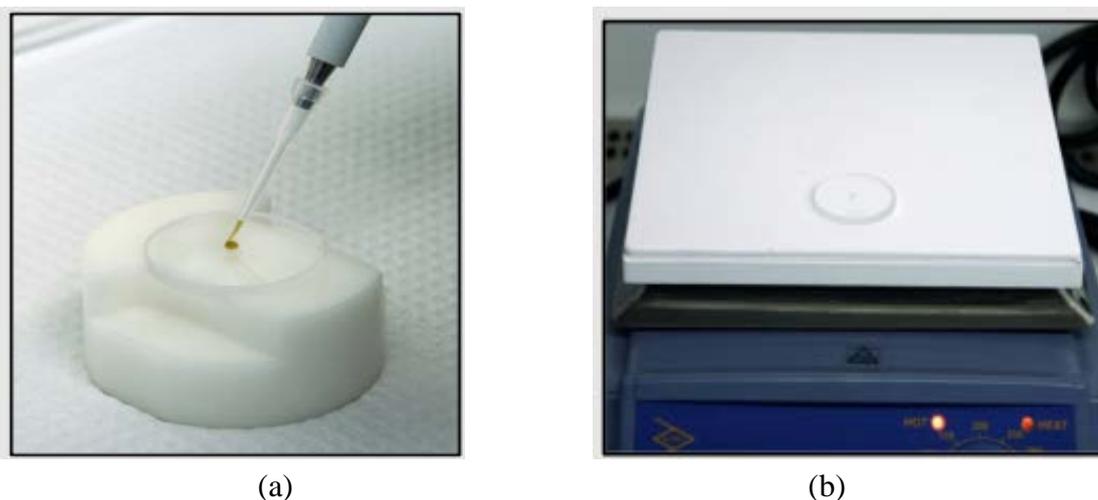


Fig. 3. Transfer of the sample onto the sample carrier (a) and drying of the sample (b)

For statistical evaluation, three samples were prepared for each of the two referenced standards. The measurement time was 600 seconds per each sample.

3. Results and discussion

The results demonstrate how TXRF can be used to analyze trace elements in fresh water samples in five different sites at Xuan Huong Lake. The results were averaged for all samples at the same site. Table 1 describes the quantitative analysis of the results with the TXRF. Spectrum of TXRF at different sites from Xuan Huong Lake is shown in Fig. 4.

Table 1. Comparison of trace elements contents from various sampling sites with the standards

Element	Concentration [ppb] / Error [%]										QCVN 08-MT:2015/BTNMT [ppb]	Ireland Standard [ppb]
	Site No.1		Site No.2		Site No.3		Site No.4		Site No.5			
Cl	161	6	185	4	159	7	145	7	127	7	250000	250000
Cr	n.d.	n.d.	6	8	3	6	11	8	n.d.	n.d.	50	50
Mn	60	3	52	4	34	4	41	6	24	3	100	50
Fe	1237	2	1059	4	306	2	544	4	258	2	500	200
Cu	94	2	92	3	69	3	72	4	74	2	100	50
Zn	87	3	135	3	84	2	86	4	116	2	500	3000
As	9	5	14	5	7	5	6	8	6	5	10	50
Br	123	2	73	3	110	2	137	4	106	2	25*	10
Hg	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1	1
Pb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	50

Note: n.d is symbol of none detection.

*: QCVN 01:2009/BYT – National technical regulation on the drinking water quality

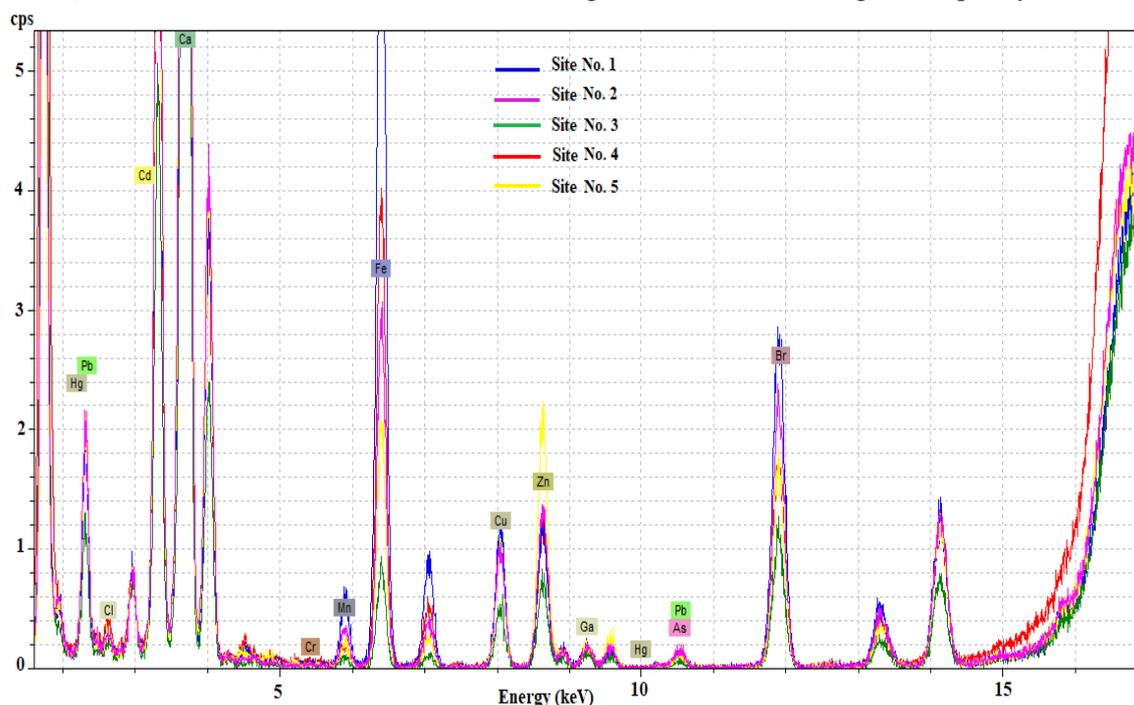


Fig. 4. Spectrum of TXRF at different sites from Xuan Huong Lake

All water samples in Xuan Huong Lake contained Cl, Cr, Mn, Fe, Cu, Zn, As, and Br. The concentrations of Cl, Cr, Mn, Cu, Zn have acceptable limits according to Vietnam standards (Huynh, 2018).

The amount of Br from different locations exceeded about 10 times of acceptable limits comparing with the standards (Lenntech, 2018; QCVN01: 2009 / BYT, 2009] and about 10 times comparing with the standard of drinking water in Vietnam (QCVN 08-MT: 2015 / BTNMT, 2015). Bromine is corrosive to human tissue in a liquid state, and its vapors irritate eyes and throat. Bromine vapors are very toxic when inhaled.

Humans can absorb organic bromines through the skin, with food and during breathing. Organic bromines are widely used as sprays to kill insects and other unwanted pests. However, they are not only poisonous to the animals that they are used against, but also to larger animals. In many cases they are also poisonous to human beings. The most important health effects that can be caused by bromine-containing organic contaminants are the malfunctioning of the nervous system functions and disturbances in genetic materials. In addition, organic bromines can also cause damages to organs such as liver, kidneys, lungs, and milt. They can cause stomach and gastrointestinal malfunctioning. Some forms of organic bromines, such as ethylene bromine, can even cause cancer (S2 PICOFOX™) Bromine is contained in agrochemicals, pesticides, dyes, disinfectants, petroleum, and plastic coatings of electronic devices. The reported high bromine in the water at the investigated sites is due to the agricultural waste stream containing pesticide residue which has chemical formula as CH_3Br (methyl bromide).

The findings of the study show that the water of Xuan Huong Lake is not safe to use for drinking (WHO, 2004).

The concentration of Fe at Site 1 and 2 was double than the limits by the Vietnamese standards. Because the two sites are the flows in Xuan Huong Lake and were affected by agriculture activities, domestic waste, and sewage sludge. When the high concentration of iron will make the water yellowish with a foul odor.

At Site 3, the concentrations of the investigated elements are smaller than the rest because this place is the flow out of Xuan Huong Lake. At site 4, the iron concentration is 1.1 times higher than the standard because this water drains from the Cu Hill. Site 5 in the middle of the household is the neutral place of the four remaining positions, the concentrations of the investigated elements there is at the average level between the surveyed locations.

4. Conclusions

Based on the findings of the study, it is concluded that water from Xuan Huong Lake is not safe for drinking due to the reported high contents of bromine and iron. Moreover, the water from the drinking water schemes from the river needs to be monitored for the presence of bromate ions.

Bromate content exceeds that of the standard due to chemical residues in agriculture (pesticides, disinfectants) from agricultural specialities to the lake. Therefore, it is necessary to re-organise the agricultural production area and build a water treatment

system before pouring into the reservoir. At the same time, it is necessary to propose appropriate measures to improve the water quality at the lake. The findings are from a preliminary survey only; thus, further studies are necessary to assess specific pollution levels of the lake.

❖ **Conflict of Interest:** Authors have no conflict of interest to declare.

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**ỨNG DỤNG KỸ THUẬT HUỖNH QUANG TIA X PHẢN XẠ TOÀN PHẦN (TXRF)
TRONG PHÂN TÍCH CÁC NGUYÊN TỐ VẾT CỦA NƯỚC HỒ XUÂN HƯƠNG,
THÀNH PHỐ ĐÀ LẠT**

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TÓM TẮT

Việc đánh giá nguồn nước là việc làm rất quan trọng cần thực hiện thường xuyên nhằm đảm bảo an toàn khi sử dụng và cảnh báo ô nhiễm nếu có. Nồng độ các nguyên tố vi lượng trong nước phản ánh mức độ ô nhiễm. Quá trình đô thị hóa, công nghiệp hóa, sử dụng phân bón và thuốc bảo vệ thực vật trong việc sản xuất nông nghiệp làm ảnh hưởng đến môi trường, đặc biệt là môi trường nước và không khí. Mục tiêu chính của nghiên cứu này đánh giá hàm lượng các nguyên tố vết trong nước ở hồ Xuân Hương, thành phố Đà Lạt bằng kỹ thuật phân tích huỳnh quang tia X phản xạ toàn phần (Total Reflection X-ray Fluorescence – TXRF). Kết quả cho thấy nước tại hồ Xuân Hương có một số nguyên tố như sắt, brom vượt tiêu chuẩn Việt Nam cũng như thế giới.

Từ khóa: TXRF, nguyên tố vết, nước mặt, hồ Xuân Hương.