



## Analytical Note

# Feasibility of wavelength dispersive X-ray fluorescence spectrometry for a simplified analysis of bromine in water samples with the aid of a strong anion exchange disk



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## ABSTRACT

The feasibility of wavelength dispersive X-ray fluorescence spectrometry (WDXRF) for a simplified analysis of bromine (Br) in water samples with the aid of strong anion exchange (SAX) disk was assessed in this study. Dissolved Br in the water sample was pre-concentrated on the SAX disk and directly analyzed by WDXRF without an elution step. The SAX disk was capable of fully adsorbing both bromide ( $\text{Br}^-$ ) and bromate ( $\text{BrO}_3^-$ ) on its surface owing to their anionic properties, regardless of the pH level of environmental samples. The SAX-WDXRF system was examined using calibration standards (i.e., SAX disks with specific amounts of Br retained; 1, 10, 50, 100 and 500  $\mu\text{g}$ ), and a determination coefficient of  $R^2 = 0.9999$  was yielded. The system had a low detection limit for Br (limit of detection = 0.253  $\mu\text{g}$  for Br on the SAX disk) with good reproducibility (relative standard error (RSE) = 4–7%). Spike and inter-comparison tests were performed to confirm the accuracy of the proposed SAX-WDXRF method. Both tests exhibited reasonable accuracy (RSE = 3–6%). The method is simple and easy, indicating a great possibility of application in various environmental sample types, especially for which a simplified analytical system for the determination of Br is urgently required.

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## 1. Introduction

There has been considerable interest in bromine (Br) in recent times because of its potential risk to human and environmental health. In particular, bromate ( $\text{BrO}_3^-$ ) has been classified as a potential carcinogen for humans, and can be formed from bromide ( $\text{Br}^-$ ) under highly oxidizing conditions [1,2]. For instance, ozonation and/or chlorination of disinfection processes in a water treatment plant can facilitate the formation of  $\text{BrO}_3^-$  in  $\text{Br}^-$ -rich water [3,4]. The World Health Organization (WHO) has set the permissible levels of  $\text{BrO}_3^-$  in drinking water at 10  $\mu\text{g L}^{-1}$  [5]. Hence, dissolved Br in environmental samples, including  $\text{BrO}_3^-$  as well as its precursor  $\text{Br}^-$ , which itself is not classified as a toxic species, should be monitored urgently and accurately.

A variety of methods have been used for the analysis of halogens in environmental matrices. The most established approach involves ion chromatography (IC) equipped with a conductivity detector (CD) [6] owing to its superior sensitivity and separation ability. Although it enables the separate determination of  $\text{Br}^-$  and  $\text{BrO}_3^-$  based on their ionic properties, IC has had several issues such as the complicated pretreatment procedures (e.g., processes for the removal of ozone, sulfate, and carbonate from water samples) [7], lengthy separation procedures, and lack of decent analytical skills to assess the chromatogram. Meanwhile,

the total dissolved Br concentration has been determined by inductively coupled plasma mass spectrometer (ICP-MS) and atomic emission spectrometer (ICP-AES) in short analysis times [8]. However, the significant signal depression has been observed in the ICP-MS or ICP-AES analysis due to the high first ionization potential of Br (11.8 eV) [8,9]. The depression leads to a significant aggravation of the detection limit for Br compared to that for fully ionized elements [10]. Additionally, for the IC-CD and ICP-MS/AES analysis, some complex environmental samples such as leachate, seawater, and human serum need to be diluted (i.e., generally 100-fold dilution) and/or pretreated (e.g., preconcentration, matrix match) because their high salinities and organic carbon contents cause an increase in artifacts which are expected to hamper the Br detecting procedures. These issues are clearly demonstrating the necessity for developing a simplified and sensitive method to determine Br in various conditions of water samples.

In recent times, a preconcentration procedure with an appropriate sorbent followed by direct solid analysis (i.e., wavelength dispersive X-ray fluorescence (WDXRF), total reflection X-ray fluorescence (TXRF), and energy dispersive X-ray fluorescence (EDXRF) spectrometers) has been widely applied to determine various elements such as Se, Cd,  $\text{Cr}^{6+}$ , As, Mn, Fe, Co, Ni, Cu, Zn, and Pb in water samples [11–16]. Multiwalled carbon nanotubes, activated thin layer, and alumina have been employed as solid sorbents to preconcentrate the analytes in complex matrices [11–15]. These techniques combining preconcentration and detection procedures allow us to determine various elements in a simple process with a high sensitivity. Furthermore, the

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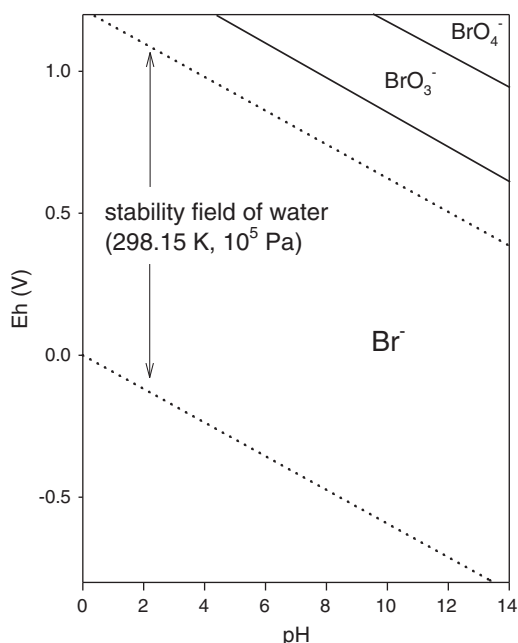


Fig. 1. Eh–pH diagram of the Br–O–H system [25]. Dotted lines indicate the stability field of water (temperature = 298.15 K, pressure =  $10^5$  Pa). Solid lines denote the boundary of each species.

elution step (i.e., the extraction of analyte from the solid sorbent) is not necessary, which considerably minimizes the use of solvents [11–15,17,18].

Herein, we describe a rapid, simple, and highly sensitive method for the analysis of dissolved Br in water samples, using the WDXRF with the aid of a strong anion exchange (SAX) disk. A disk-type sorbent was used as a specimen for the direct analysis techniques (e.g., WDXRF, accelerator mass spectrometry, and neutron activation analysis) [16–20]. Then, sample pretreatment steps were dramatically simplified since the preconcentration of analyte from the sample matrix and the preparation of specimen for the WDXRF analysis were concurrently completed by using the disk-type sorbent. The feasibility of the combined use of the SAX disk and WDXRF for the analysis of Br was investigated. As shown in the pH–Eh diagram (Fig. 1), dissolved Br generally consists of  $\text{Br}^-$ ,  $\text{BrO}_3^-$ , and  $\text{BrO}_4^-$ .  $\text{Br}^-$  is an abundant species in most water conditions while  $\text{BrO}_3^-$  and  $\text{BrO}_4^-$  mainly exist under highly oxidizing conditions. Hence, the SAX disk was selected as a sorbent for Br. The SAX–WDXRF system aims to eliminate the time-consuming and complicated sample-pretreatment procedures for the trace analysis of Br. It may be effectively applied for the continuous monitoring of dissolved Br as a precursor of disinfection byproducts (e.g.,  $\text{BrO}_3^-$ , brominated pollutants) in raw drinking water [21].

## 2. Materials and methods

### 2.1. Instruments

The WDXRF instrument (PW2404, Phillips, Netherland) was used to determine dissolved Br (i.e.,  $\text{Br}^-$  and  $\text{BrO}_3^-$ ) retained on the SAX disk. The Bragg angle of Br–K $\alpha$  was 29.923° when using the LiF200 crystal (thickness = 0.2014 nm). The X-ray pathway was maintained as vacuum state to avoid signal depression caused by air absorption. An aluminium sample holder with a diameter of 27 mm was used, so the diameter of the exposed surface area to X-ray was 27 mm. The ICP–MS system (Agilent 7700s, Agilent Technologies, Japan) was also employed for quantifying the Br contents in water samples. A tuning solution containing 1 ppb of Li, Ce, Y, and Tl was used to optimize the analytical conditions (i.e., intensity, resolution, and mass axis). The presence of Br

was monitored at an  $m/z$  ratio of 79 with the software Mass Hunter obtained from the manufacturer. Information of instrumental conditions of WDXRF and ICP–MS used in this study is presented in Table 1.

### 2.2. SAX disk

A resin-based SAX disk (3 M, St. Paul, MN, USA) with a diameter of 47 mm and a thickness of 0.5 mm was used. The SAX disk has a framework of a polystyrene divinylbenzene resin functionalized with a quaternary amine ( $\text{N}^+(\text{CH}_3)_3$ ). Its anion exchange capacity was reported to be 1.63 meq  $\text{g}^{-1}$  determined using the neutralization titration method [17]. The extraction procedure was followed by a simple vacuum filtration ( $\leq 20$  in. Hg). The pressure unit was converted as a conventional flow rate unit (about 60 mL  $\text{min}^{-1}$ ). The diameter of the surface area exposed to water samples was 37 mm. The SAX disk was conditioned using 10 mL of acetone, methanol, deionized water, and 1 N NaOH. Then, the dissolved Br, including  $\text{Br}^-$  and  $\text{BrO}_3^-$ , was collected on the SAX disk as the sample solution passed through it.

### 2.3. Effect of pH on the retention behaviors of $\text{Br}^-$ and $\text{BrO}_3^-$ on the SAX disk

Stock solutions (1000  $\text{mg L}^{-1}$ ) of  $\text{Br}^-$  and  $\text{BrO}_3^-$  were prepared by dissolving NaBr and  $\text{NaBrO}_3$  (Fluka, Switzerland) in deionized water with a specific resistance of 18.2  $\text{M}\Omega \text{ cm}$  obtained from a Milli-Q system (Millipore, Bedford, MA, USA). In order to assess the retention behaviors of  $\text{Br}^-$  and  $\text{BrO}_3^-$  on the SAX disks, 10  $\text{mg L}^{-1}$  solutions with different pH levels (i.e., 3, 6, and 9) were prepared and 10 mL of each solution was passed through the SAX disk. The pH was adjusted using 1 N  $\text{HNO}_3$  and NaOH. The difference between the Br concentrations of the initial solution and the effluent was taken by using the ICP–MS analysis, in order to obtain the amount of Br retained on the SAX disk.

### 2.4. Preparation of calibration standards

The SAX disks with varying Br contents (1, 10, 50, 100, and 500  $\mu\text{g}$ ) were prepared by preconcentrating 10 mL of the 0.1, 1, 5, 10, and 50  $\text{mg L}^{-1}$   $\text{Br}^-$  solutions to make the calibration standards. These disks were dried at 60 °C for 5 min and then directly analyzed by WDXRF to establish a calibration curve. The SAX disk preconcentrated with Br was coated with an X-ray film (Chemplex®, SE Waaler St. Stuart, FL, USA) to avoid deformation and fragmentation arising from X-ray irradiation [18].

Table 1

Instrumental conditions of WDXRF and ICP–MS for the dissolved Br analysis.

Parameter	Setup condition
(A)	Wavelength dispersive X-ray fluorescence spectrometry (WDXRF)
Diffraction crystal type	LiF200 (thickness = 0.2014 nm)
X-ray tube	Rhodium (Rh) target (60 kV, 50 mA)
Window	Be (thickness = 75 $\mu\text{m}$ )
Collimator	300 $\mu\text{m}$
Detector type	Scintillation
Peak angle	29.923 ( $2\theta$ ) for Br–K $\alpha$
Offset background <sup>a</sup>	0.547 ( $2\theta$ )
Analyzing time	100 s
(B)	Inductively coupled plasma mass spectrometer (ICP–MS)
RF power	1550 W
Carrier gas flow	Ar 1.07 L $\text{min}^{-1}$
Sampling depth	10 mm
Extract 1 and 2 lens voltage	0 V for extract 1 and –170 V for extract 2
Omega lens voltage	14.8 V
Torch	Standard Quartz 2.5 mm
Nebulizer	Micromist
Sampling and skimmer cone	Platinum
Integration time	0.33 s
Monitored mass	79 $m/z$

<sup>a</sup> Angular difference between peak and background.

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