



# Bromine and bromide content in soils: Analytical approach from total reflection X-ray fluorescence spectrometry



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## HIGHLIGHTS

- Evaluation of TXRF for the determination of bromine and bromide content in soils.
- Total bromine determination by solid suspension using 20 mg of powdered soil.
- Bromide determination by analyzing 10  $\mu\text{L}$  of the IS water soil extract.
- Good agreement with results obtained by other popular analytical techniques.

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## ABSTRACT

Monitoring total bromine and bromide concentrations in soils is significant in many environmental studies. Thus fast analytical methodologies that entail simple sample preparation and low-cost analyses are desired.

In the present work, the possibilities and drawbacks of low-power total reflection X-ray fluorescence spectrometry (TXRF) for the determination of total bromine and bromide contents in soils were evaluated.

The direct analysis of a solid suspension using 20 mg of fine ground soil (<63  $\mu\text{m}$ ) gave a 3.7  $\text{mg kg}^{-1}$  limit of detection for bromine which, in most cases, was suitable for monitoring total bromine content in soils (Br content range in soils = 5–40  $\text{mg kg}^{-1}$ ). Information about bromide determination in soils is also possible by analyzing the Br content in water soil extracts. In this case, the TXRF analysis can be directly performed by depositing 10  $\mu\text{L}$  of the internal standardized soil extract sample on a quartz glass reflector in a measuring time of 1500 s. The bromide limit of detection by this approach was 10  $\mu\text{g L}^{-1}$ .

Good agreement was obtained between the TXRF results for the total bromine and bromide determinations in soils and those obtained by other popular analytical techniques, e.g. energy dispersive X-ray fluorescence spectrometry (total bromine) and ionic chromatography (bromide).

As a study case, the TXRF method was applied to study bromine accumulation in two agricultural soils fumigated with a methyl bromide pesticide and irrigated with regenerated waste water.

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## 1. Introduction

Monitoring total bromine and bromide concentrations in soils is significant in many field and laboratory environmental studies. For instance, bromide and chloride ions have been widely used as

tracers to study water and solute transport along soil's non saturated zone because they do not adsorb to negatively charged soil minerals. As bromide occurs in much smaller background concentrations in soils than chloride, it is often preferred as a tracer in transport studies (Bero et al., 2015, Dusek et al., 2015). Other anthropogenic sources of bromine include agricultural fumigations using methyl bromide (MB) to control soil-borne pathogens, nematodes and weeds in many vegetable, fruit, nut and nursery crops worldwide (Klose and Ajwa, 2004). Despite the fact that MB

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was phased out in 2010 (European Community, 2009), high concentrations levels of Br are still found in some agricultural soils. Finally, the use of salty or regenerated waters for irrigation has promoted Br enrichment of surface layers of soils (Queralt et al., 2012). Given all these applications, fast analytical methodologies to monitor both bromine and bromide in soils are desired.

Total bromine content in soil samples is usually determined by solid-state techniques such as instrumental neutron activation analysis (INAA) (Muhammad et al., 2012) and X-ray fluorescence spectrometry (XRF) (Sandeep et al., 2014). Despite the high selectivity and sensitivity of INAA, expensive costs, the need for a nuclear reactor for irradiation, and the rather long analysis times imposed by long waiting (cooling) periods for short-lived radioisotopes to decay have restricted its application in some environmental studies. XRF, however, is a popular technique for major elemental analyses in geological samples as it helps avoid complicated acid-digestion procedures. In particular, the speed, accuracy and versatility of XRF are the most important features, among others, that have rendered it a very mature analytical tool in this field. For instance, the fast and direct wavelength dispersive XRF (WDXRF) analysis of total bromine in soil samples from the vadose zone has been successfully applied (Abderrahim et al., 2011) to estimate flux and transport along the unsaturated zone.

Some other analytical techniques have been used for the specific determination of bromide ions in soils (Crompton, 2012). In them all, bromide is first extracted from soil by a 24-h batch extraction procedure with deionised water (ASTM methods D4646-87, D5233-92 and D3987-85). The United States Environmental Protection Agency (US-EPA) proposes a potentiometric determination of bromide in the resulting soil extract using an ion-selective electrode (EPA Method 9211, 1996). Ionic chromatography (IC) has also been widely used to determine bromide ion in aqueous samples. One of the benefits of this technique is the possibility of obtaining simultaneous information about the different anions present in the target sample (Tirumalesh, 2008). However, it is a relatively expensive analytical tool. Other less used methods for bromide determination in soil extracts include flow injection potentiometry (Van Staden, 1987) and indirect determinations by a spectrophotometry method (Miller and Angui, 1991).

In the present work, we explored the analytical possibilities of total reflection X-ray fluorescence spectrometry (TXRF) for the determination of total bromine and bromide contents in soils. TXRF is a well-established analytical technique for multielement determinations in various sample types, especially liquids and powdered or microsamples (Strelí, 2006). To perform analyses under total reflection conditions, samples must be provided as thin films. This is done by depositing 5–50  $\mu\text{L}$  of sample on a reflective carrier and subsequently drying the drop. As X-ray photons are totally reflected at very low glancing angles of the primary X-ray beam ( $\sim 0.1^\circ$ ) with the TXRF system and, thus, the high background that would generally occur due to scatter from the sample support is absent, limits of detection (LODs) are better than in conventional XRF systems (Marguá and Van Grieken, 2009). In recent decades, most published TXRF analyses have been performed using large-scale instruments with high-power X-ray tubes, which demand water-cooling systems and liquid-nitrogen cooled detectors. In recent years, the development and commercialization of bench top TXRF instrumentation, which offers extremely simple operations with a low-cost compact design, have promoted its application in many environmental fields (Stosnach, 2005; Floor et al., 2013) and also in water quality control studies (Marguá et al., 2010a, 2010b).

After bearing in mind the possibility of analyzing solid suspension by TXRF, the application of this technique was studied for total Br determination in soils, and to also determine bromine in soil extracts. To our knowledge, very few papers about TXRF

investigations of geological samples exist, and there are none for Br determination in soils.

First, an evaluation of the best sample preparation and TXRF measurement conditions for Br determination in soils and soil extracts was made. The analytical figures of merit (LODs, accuracy and precision of results) for both methodologies (total Br and bromide determinations) were evaluated. The obtained TXRF results were compared with those obtained by other popular analytical techniques, e.g. energy dispersive XRF (total bromine) and IC (bromide). Finally as a study case, the TXRF method was applied to study bromine accumulation in two agricultural soils fumigated with a methyl bromide pesticide and irrigated with treated wastewater.

## 2. Experimental

### 2.1. Materials and reagents

A bromide stock solution of 1000  $\text{mg L}^{-1}$  was prepared from analytical grade NaBr salt (Sigma-Aldrich, Spain). An Rh stock solution of  $1000 \pm 0.5 \mu\text{g mL}^{-1}$  (Spectroscan, TECKNOLAB A/S, Norway) was used to standardize soil samples and soil extracts. The high purity water used for diluting stock solutions was obtained from a Milli-Q purifier system, which operated at 18.2 M $\Omega$  (Millipore Corp., Bedford, MA). The commercial non ionic detergent Triton<sup>®</sup> X-110 was purchased from Sigma-Aldrich (Spain). In the TXRF analysis the sample carrier plays an important role in achieving optimal analytical results. In most cases, the reflective sample carrier is made of quartz or acrylic glass. In this work, quartz glass discs (diameter of 30 mm and thickness of 3 mm  $\pm$  0.1 mm; Bruker Nano GmbH, Germany) were used as sample holders to introduce the sample into the TXRF equipment because of greater resistance to temperature and a lower background.

### 2.2. Samples

Two different agricultural soils were studied, taken from greenhouse cropped plots located in the alluvial plain of the Tordera river (40 km north of Barcelona, Spain). These soils have been treated with methyl bromide for the last 20 years and irrigated with treated wastewater. Incremental depth sampling (up to approx. 0.5 m, maximum yearly plough depth) in 5–10 cm lengths was carried out with a manual Eijkelkamp hand-auger sampler. After air drying, samples were passed through a 0.250-mm sieve and then ground in an agate mortar to pass through a 63- $\mu\text{m}$  sieve (see Section 3.1.3).

Several certified reference materials were employed to test the accuracy of the developed TXRF methodology for bromide determination: LKSD1-LKSD4 (“Lake sediment samples” from Natural Resources of Canada, Government of Canada), SO1-SO4 (“Soil samples” from CANMET Energy, Mines and Resources Canada), NCSDC73309 (“Stream sediment” from China National Analysis Centre for Iron and Steel), STSD-1, STSD-3 and STSD-4 (“Stream sediment” from Canadian Reference Material Project (CCRP)).

### 2.3. Total bromine determination in soil suspensions

The best sample preparation conditions for soil suspensions analysers by TXRF were carefully evaluated (see Section 3.1.1). Finally, the conditions selected for the soil suspension analysis were as follows: 20 mg of soil were suspended in 1 mL of the dispersant solution (1% Triton<sup>®</sup> X-110 in water). Then Rh was added to the slurry sample for internal standardization (final Rh concentration of 15  $\text{mg kg}^{-1}$ ). Next the resulting solution was thoroughly homogenized (Vortex device) and an aliquot of 10  $\mu\text{L}$  was transferred to a quartz glass sample carrier and left to dry under an IR lamp

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