



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

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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 μm) gave a 3.7 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 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 μL 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 μg 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 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 analy-

sis (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

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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 (Strel, 2006). To perform analyses under total reflection conditions, samples must be provided as thin films. This is done by depositing 5–50 μL 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 (Marguí 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 (Marguí 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 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 $\text{M}\Omega$ (Millipore Corp., Bedford, MA). The commercial non ionic detergent Triton[®] 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 $3 \text{ mm} \pm 0.1 \text{ mm}$; 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- μm 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), NCS-DC73309 (“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 (CCRMP)).

2.3. Total bromine determination in soil suspensions

The best sample preparation conditions for soil suspensions analyzers 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[®] X-110 in water). Then Rh was added to the slurry sample for internal standardization (final Rh concentration of 15 mg kg^{-1}). Next the resulting solution was thoroughly homogenized (Vortex device) and an aliquot of 10 μL was transferred to a quartz glass sample carrier and left to dry under an IR lamp before the TXRF analysis.

2.4. Bromide determination in soil extracts

After the pretreatment, 1 g of soil (sieved at 0.125 mm) came into contact with 25 mL of MilliQ water (1:25 ratio). After 24 h of equilibration, the extract solutions were filtered (0.2 μm cellulose acetate filter) before the TXRF and IC analyses (Abderrahim et al., 2011).

The best sample preparation conditions for the soil extract analysis by TXRF were carefully evaluated (see Section 3.2.1). Briefly, an aliquot of 1 mL of soil was standardized using an adequate volume of Rh (final Rh concentration of 0.5 mg kg^{-1}). Then the resulting solution was thoroughly homogenized (Vortex device) and an aliquot of 10 μL was transferred to a quartz glass sample carrier and left to dry under an IR lamp before the TXRF analysis.

2.5. Instrumental conditions

Analyses of soil suspensions and extracts were performed with a commercial benchtop TXRF system, equipped with a low-power W X-ray tube (S2 PICOFOX, Bruker AXS Microanalysis GmbH, Berlin, Germany) that operated at 50 kV and 1 mA. In order to compare the obtained TXRF results for the soil suspension and soil extract analyses, a benchtop EDXRF system (S2 RANGER, Bruker AXS, GmbH, Germany), under the same conditions of voltage, current and detector as those for TXRF, and an Ion Chromatograph (IC5000, Dionex, Thermo Scientific, Inc., Spain), were respectively

used. The instrument specifications and final measurement conditions used for TXRF, EDXRF and IC are summarized in Table 1.

2.6. Quantification by TXRF

For TXRF, quantification can be performed directly by internal standardization (external calibration is not needed). This method is based on the addition of an element, named the internal standard (IS), which is not present in the sample (see Expression 1):

$$C_i = \frac{(N_i C_{pi} S_{pi})}{(N_{pi} S_i)} \quad (1)$$

where C_i is the analyte concentration, N_i is the analyte net peak area, C_{pi} is the IS concentration, S_{pi} is the instrumental sensitivity for IS, N_{pi} is the IS net peak area and S_i is the instrumental sensitivity for the analyte.

Medium-heavy elements with K lines detection are preferred for use as internal standards over heavy elements with L lines detection due to the lower number of peaks. Lighter elements with $Z \leq 21$ are not suitable as standards because of particle size-effects that are problematic within a low-energy range $E < 4$ keV (Klockenkämper and Von Bohlen, 2015). Appreciable amounts of Ga and Y were found in the analysis of the target soil samples. Therefore, these elements, which are commonly used in TXRF analyses as internal standards, could not be employed, which is why Rh was finally selected as the internal standard.

For both soil suspension and extracts, a measuring time of 1500 s was selected as a trade off between an acceptable repetitiveness of the results (RSD~6%) and the total analysis time.

Table 1
Instrumental parameters and measurement conditions.

TXRF benchtop spectrometer (S2 PICOFOX, Bruker AXS)	
X-Ray tube	W
Rating	50 kV, 1 mA (maximum power 50 W)
Optics	Multilayer Ni/C, 17.5 keV, 80% reflectivity
Detector	XFLASH™ Si drift detector, 10 mm ² , <160 eV resolution
	Mn-K _α
Working environment	Air
Sample station	Cassette changer for 25 samples
Size, weight	600 × 300 × 450 mm, 37 kg
Measurement time	1500 s
EDXRF benchtop spectrometer (S2 Ranger, Bruker AXS)	
X-ray tube	Pd
Rating	50 kV, 1 mA (maximum power 50 W)
Primary filter	Al 500 μm
Detector	XFLASH™ Silicon Drift Detector, <129 eV resolution Mn-K _α
Working environment	Vacuum
Measurement time	300 s
Ion chromatograph (IC5000, Dionex)	
Column	IonPac® AS18 anion-exchange column (4 × 250 mm) with the AG Guard column (4 × 50 mm)
Eluent flow rate	1 mL/min
Injection volume	25 μL
Detector	Conductivity detector (suppressed conductivity)
Eluent generation of mobile phase	22–40 mM KOH
Data system	Chromleon 6.8

3. Results and discussion

3.1. Analysis of soil suspensions

3.1.1. Selecting the sample preparation strategy for soil suspension analyses

One of the most interesting features of TXRF in the analytical field is the possibility of the quantitative direct analysis of solid samples with no prior chemical treatment. A direct solid analysis can be accomplished by means of adequate suspension, followed by internal standardization.

In the present work, a study of the best sample preparation strategy for Br determination in soil suspensions was conducted. Experimental tests were performed by analyzing the certified reference material LKSD-4 ([Br] = 49 mg kg⁻¹). Two dispersant agents (MilliQ water, 1% Triton® X-114 in water) and different amounts of sample were tested for soil suspension preparation. As seen in Fig. 1A, the best results were obtained by suspending 20 mg of soil sample in 1 mL of 1% Triton® X-114 in water.

The aim of the sample preparation process in TXRF is to obtain the target sample as a thin layer (<100 μm) on a carrier with a high reflectivity sample support. Therefore, the choice of an adequate sample deposition volume is crucially important to obtain a thin layer and to ensure the total reflection conditions. The influence of the suspension deposition volume (5 μL, 5 + 5 μL, 10 μL, 20 μL) on the Br content determination is shown in Fig. 1B. In view of the obtained results, a volume of 10 μL was established for further experiments.

3.1.2. Analytical figures of merit

The LOD (calculated using Expression 2) for Br was 3.7 mg kg⁻¹ when using the best analytical conditions studied to prepare the suspension.

$$LOD = \frac{3C_i \sqrt{N_{bkg}}}{N_i} \quad (2)$$

where C_i is the concentration of a given analyte, N_{bkg} is the background area and N_i is the net area of the analyte. This equation is analogous to the 3σ definition of the LOD.

Therefore, this fast and relatively simple methodology can be successfully applied to analyze Br content in most soils by taking into account that the bromine content range in soils is 5–40 mg kg⁻¹ (Reimann and De Caritat, 1998). In order to check the accuracy of the method, different certified reference materials were analyzed under the above-described analytical conditions (see Table 2 for the results). As we can see, a good agreement with the certified/indicative values was generally achieved over the whole studied concentration range. Global precision was also tested by analyzing eight replicates of the certified reference material LKSD-4 ([Br] = 49 mg kg⁻¹). The calculated relative standard deviation (RSD), with a value of 6%, was acceptable.

3.1.3. Effect of soil particle size

It has been demonstrated that the appearance of microscopic mountain agglomeration effects when depositing the sample on the reflector can result in large deviations in the nominal TXRF result values (Fernández-Ruiz, 2009). Agglomeration effects in TXRF analyses of solid samples are related to solid particle size. Therefore, studying the solid sample particle size effect is highly recommended

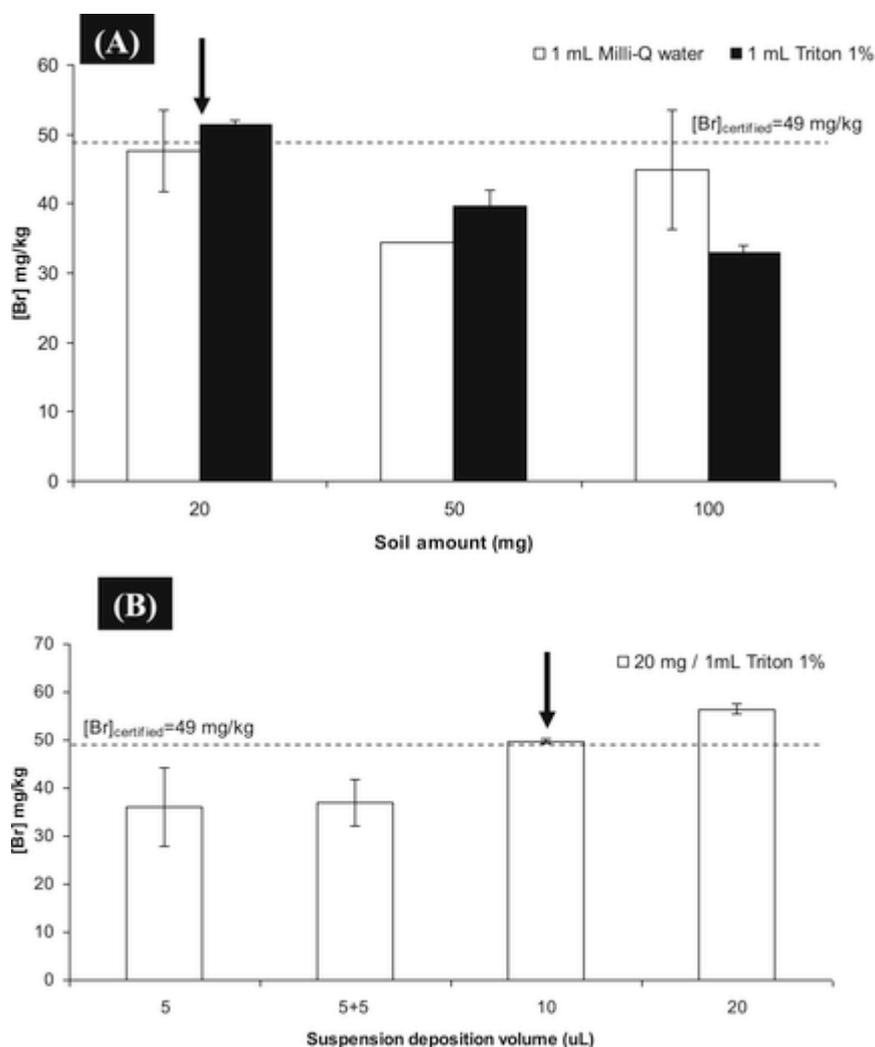


Fig. 1. Influence of: (A) soil amount and disperser agent and (B) suspension deposition volume on Br content determination by the TXRF method. Error bars represent the standard deviation of two replicates. Arrow indicates best sample preparation conditions.

Table 2

Br concentrations (mg kg^{-1}) in the certified reference materials after suspension sample preparation and a subsequent TXRF analysis (analytical conditions: 20 mg of sample, 1 mL of Triton 1%, sample deposition volume: 10 μL , 1500 s measuring time).

Sample	Solid suspension TXRF method		Certified
	Mean (n = 2)	SD (n = 2)	
LKSD1	13.1	0.1	11
LKSD2	16	2	18
LKSD3	15.7	0.2	16
LKSD4	51	2	49
SO-1	n.d	n.d	2
SO-2	22	2	17
SO-3	8	0.3	6
SO-4	5.6	0.2	5.2
NCSDC73309	n.d	n.d	2.2
STSD-1	45	2	40
STSD-3	26.6	0.4	24
STSD-4	15	3	13

n.d: not detected.

when analyzing solid samples by TXRF using suspension preparation. Usually, the particle size of soil and sediment certified reference

materials is lower than 70 μm . At this particle size level, sample suspension homogeneity is acceptable and the TXRF results are not biased (see Table 2).

In order to study the influence of particle size on Br determination in real soil samples, six soils samples of different particle sizes were prepared as suspensions and analyzed following the procedure described in Section 2.2. The obtained Br results were compared with those obtained by energy dispersive X-ray spectrometry. As shown in Fig. 2, particle size greatly affects the Br concentration determined by the proposed TXRF methodology. The obtained results indicated that soil particle size had to be reduced from 125 μm to 63 μm in order to obtain statistically similar values compared to the EDXRF ones.

3.1.4. Application to total bromine determinations in agricultural soils

By taking into account the expected Br levels in the two target agricultural soil profiles, soil suspension was selected as sample treatment before the TXRF analysis. Fig. 3 illustrates the Br concentrations obtained according to depth for the two target soils; in both cases, the Br concentrations in upper soil layers (up to 30 cm) are significantly higher than those obtained when analyzing deeper layers. This fact can be related to the repeated use of methyl bromide as a

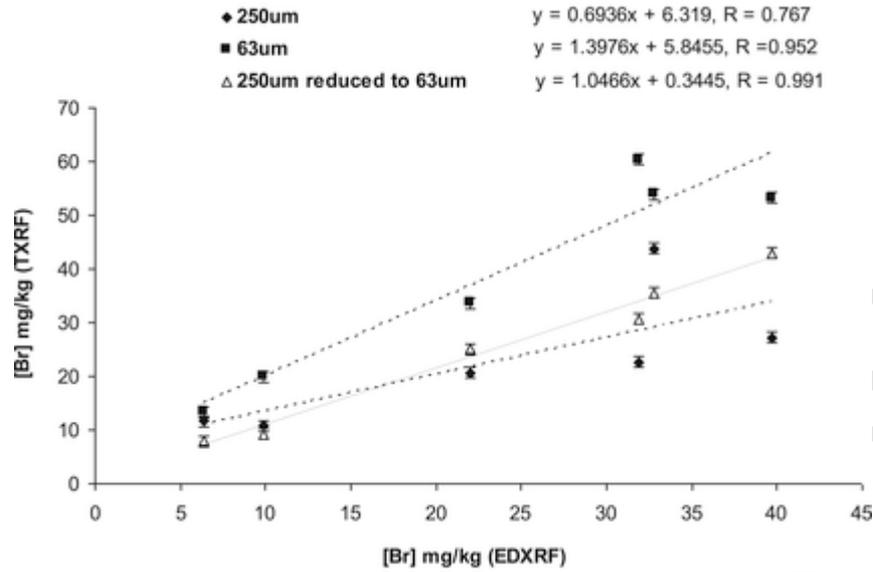


Fig. 2. Influence of soil particle size on Br determination using suspension preparation and a subsequent TXRF analysis (error bars represent the standard deviation of two replicates). Sample preparation for the EDXRF analysis consists of a powdered pellet (10 g soil ground to pass through a 0.250-mm sieve + 0.8 g Elvacite as the binding agent).

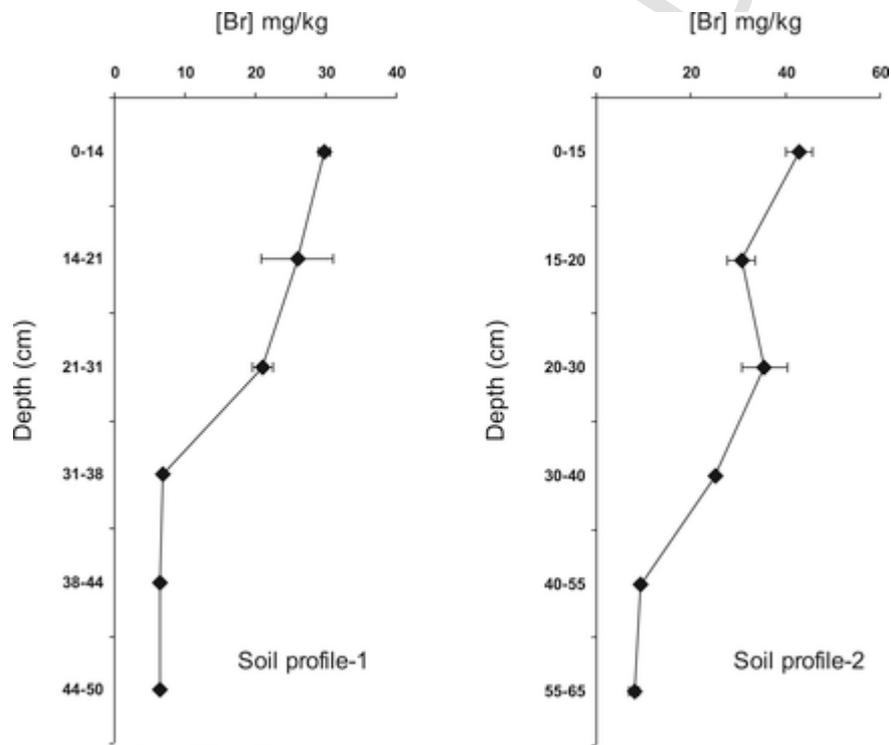


Fig. 3. Br concentrations in two agricultural soil profiles according to depth. (The analytical conditions were 20 mg of soil suspended in 1 mL of Triton 1% in water, 10 μ L of deposition volume, 1500 s measuring time).

pesticide, and also to the use of treated wastewater for irrigation purposes. As previously pointed by Zaccone et al., (2008), Br has a high affinity to organic matter, which usually accumulates in upper layers of agricultural soils.

By way of example, the TXRF spectrum obtained for one of the surface soil samples (0–15 cm, Soil profile-2) is displayed in Fig. 4. An examination of the X-ray fluorescence lines revealed that the

characteristic Br line (Br-K_{α}) clearly resolved, and no other element peaks from the soil matrix overlapped the analyte peak. As shown in Fig. 4, a clear advantage of the TXRF analyses is that multielemental information about the soil sample can be obtained. Therefore in addition to Br determination, direct measurements of soil slurries can be applied to also obtain a rough overview of soil composition.

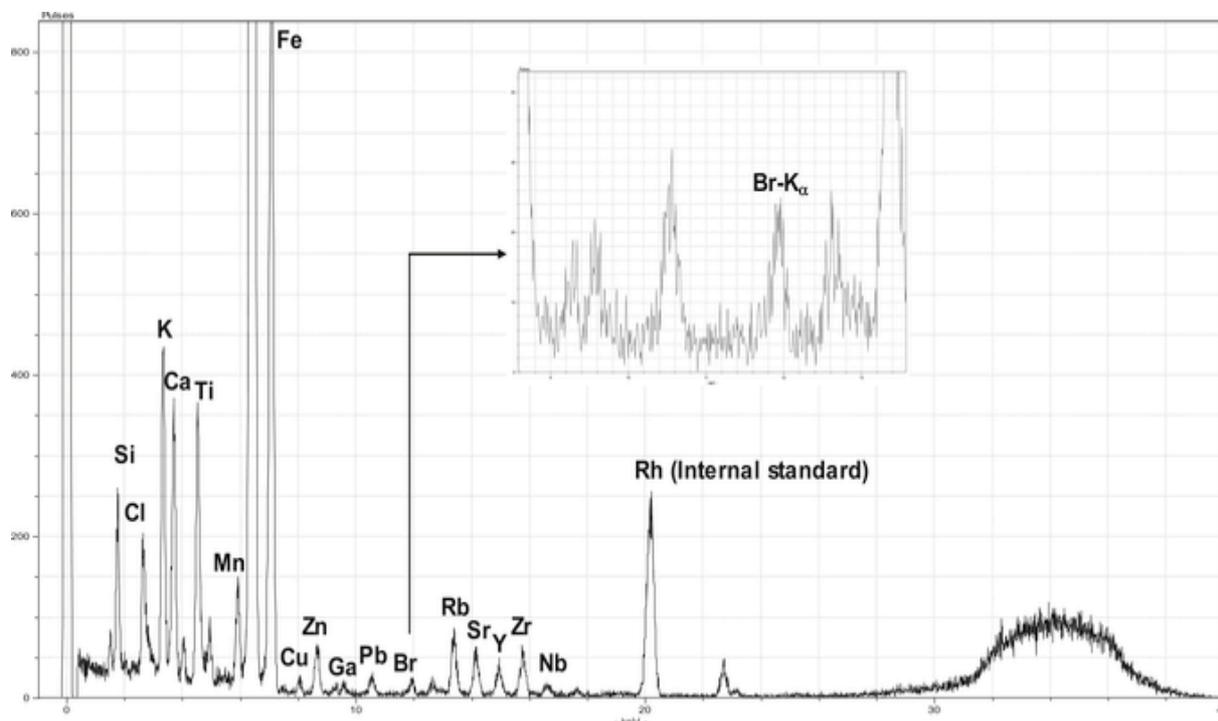


Fig. 4. TXRF spectrum for a surface soil sample (0–15 cm, Soil profile-2). (The analytical conditions were 20 mg of soil suspended in 1 mL of Triton 1%, 10 μL of deposition volume, 1500 s measuring time).

3.2. Analysis of soil extracts

An evaluation of the possibilities of TXRF to determine Br in soil extracts was made. Bromide extraction was based on the procedure usually employed for determining bromide by ionic chromatography (see the details in Section 2.3).

3.2.1. Selection of the sample preparation strategy for soil extract analyses

For soil extracts, the influence of the sample deposited volume on Br determination was studied. To this end, different sample volumes (from 5 to 40 μL) of a soil extract that contained 500 $\mu\text{g L}^{-1}$ of Br (corresponding to 12.5 mg kg^{-1} of Br in soil) were analyzed using the best previously reported conditions. In view of the obtained results, a sample deposition volume of 10 μL was selected since sensitivity was higher and the deviation between replicates was lower compared to other tested volumes (for details, see Fig. 1 in the Supporting Information).

3.2.2. Analytical figures of merit

The LODs for Br in soil extracts were also calculated (using Expression 2) by analyzing a soil extract that contained 500 $\mu\text{g L}^{-1}$ of Br. The LOD for Br was around 10 $\mu\text{g L}^{-1}$, which corresponded to 0.25 mg kg^{-1} of Br in soil. Therefore, the LOD for Br determination in soil extracts was around 15-fold lower compared to that obtained for the direct soil suspension analysis. This fact can be related with a lower background compared to a solid sample analysis.

In order to study the applicable Br concentration range, several soil extracts were spiked at different bromide concentration levels (from 50 to 500 $\mu\text{g L}^{-1}$, which corresponded to 1.25–12.5 mg kg^{-1} of Br in soil) and analyzed by the proposed TXRF method. As shown in Fig. 5, a clear linear relationship is seen between the real bromide

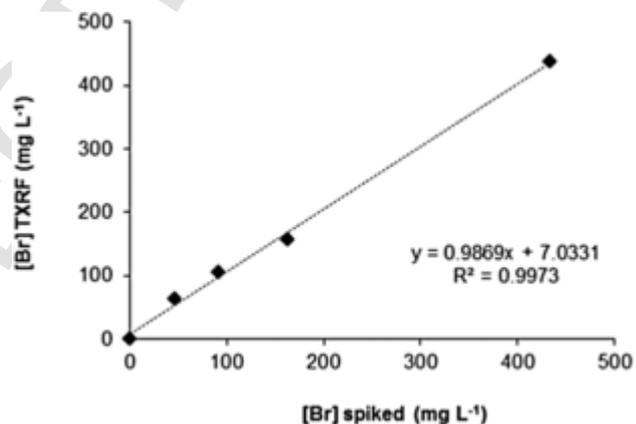


Fig. 5. TXRF Br concentration vs. bromide concentration for the spiked soil extract samples at different concentration levels.

concentration in the extract and the Br concentration obtained by the TXRF method. No statistical differences were found at the 95% confidence level.

Finally, the TXRF method was applied to determine Br content in two real soil extracts. The obtained results were compared with those obtained by ionic chromatography (the reference technique). As the results display in Table 3 show, the Br concentrations determined by the two methods are in good agreement. No significant differences were found at the 95% confidence level.

Global precision was also tested by analyzing five different soil extracts of the same soil sample (containing 500 $\mu\text{g L}^{-1}$ of Br) and the calculated RSD was around 11%. In order to estimate the uncertainty associated with the TXRF measurement, one of the soil extracts was measured 5 times. In this case the calculated RSD was

Table 3

Comparison of the mean Br concentrations in the soil extracts analyzed by the TXRF method and by ion chromatography. Concentrations are expressed as mg kg^{-1} with the relative standard deviation of two replicates.

Sample	TXRF method	IC method	t_{calc}^a
Extract soil-1	5.6 ± 0.9	5.0 ± 0.2	0.9
Extract soil-2	10.3 ± 0.8	11.4 ± 0.6	1.6

^a Students "t"-test. t_{calc} = calculated absolute value, $t_{\text{critic}} = 4.30$ ($P = 0.05$).

around 6%, which indicated that a significant part of uncertainty was due to sample preparation (the Br extraction procedure).

4. Conclusions

This work demonstrated the possibilities of several analytical approaches combined with TXRF spectrometry for Br determination in soil.

The use of direct analysis of soil suspensions by TXRF can be an interesting, fast and relatively simple methodology to obtain total Br concentrations in soils, provided that Br content is higher than 4 mg kg^{-1} . It can also be successfully applied to obtain a preliminary idea of the multielemental composition of soil. However, in order to obtain quality analytical results, it is mandatory to ensure that the soil particle size to prepare the soil suspension is lower than $63 \mu\text{m}$. This method has been successfully applied to study bromine accumulation in two agricultural soils fumigated with methyl bromide pesticide and irrigated with treated waste water. It could also be interesting to extend this application to other soil types with similar bromine levels, such as soils in which bromine is used as a tracer (water transport along unsaturated zone studies).

The data presented herein also indicate the versatility of benchtop TXRF instrumentation for bromide determination in 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 attained results are comparable to those obtained by ionic chromatography, which is the reference technique to monitor bromide in this type of samples.

To summarize, the TXRF methods proposed herein for bromine and bromide determinations entail less sample manipulation and smaller amounts of reagents compared with the most widespread techniques. Other advantages of the TXRF methods include the possibility of acquiring multielemental information about the sample, easy quantitation through internal standardization, and also low operating costs since the benchtop system does not require cooling media and gas consumption to operate.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2016.04.136>.

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Belova et al., 2013; Quiao et al., 2015.

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