



A simple and automated sample preparation system for subsequent halogens determination: Combustion followed by pyrohydrolysis

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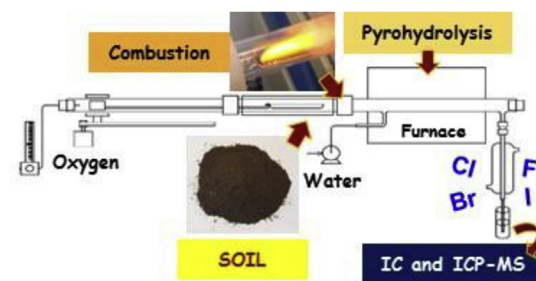
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HIGHLIGHTS

- A simple and automated sample preparation system.
- Combustion and pyrohydrolysis steps combined in the same system.
- Volatilization of halogens using microcrystalline cellulose as a combustion aid.
- The use of diluted solutions was compatible with both IC and ICP-MS analysis.
- Halogens determination in soils containing variable organic matter.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple and automated system based on combustion followed by a pyrohydrolysis reaction was proposed for further halogens determination. This system was applied for digestion of soils containing high (90%) and also low (10%) organic matter content for further halogens determination. The following parameters were evaluated: sample mass, use of microcrystalline cellulose and heating time. For analytes absorption, a diluted alkaline solution (6 mL of 25 mmol L⁻¹ NH₄OH) was used in all experiments. Up to 400 mg of soil with high organic matter content and 100 mg of soil with low organic matter content (mixed with 400 mg of cellulose) could be completely digested using the proposed system. Quantitative results for all halogens were obtained using less than 12 min of sample preparation step (about 1.8 min for sample combustion and 10 min for pyrohydrolysis). The accuracy was evaluated using a certified reference material of coal and spiked samples. No statistical difference was observed between the certified values and results obtained by the proposed method. Additionally, the recoveries obtained using spiked samples were in the range of 98–103% with relative standard deviation values lower than 5%. The limits of quantification obtained for F, Cl, Br and I for soil with high (400 mg of soil) and low (100 mg of soil) organic matter were in the range of 0.01–2 µg g⁻¹ and 0.07–59 µg g⁻¹, respectively. The proposed system was considered as a simple and suitable alternative for soils digestion for further halogens determination by ion chromatography and inductively coupled plasma mass spectrometry techniques.

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1. Introduction

Soils can present a high variability of composition ranging from very low to high organic matter (OM) content [1]. Soils are

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considered as complex matrices composed by a mixture of mineral and organic compounds and are formed by the action of physical, chemical and biological agents on the source rock. Variable environmental conditions, such as weather, topography, microorganisms action, among others, result in soils with different structure, color, texture and nutrients [1,2]. In the last years, halogens concentration in soil has been recognized as providing important information for geochemical and environmental studies [3–6].

Fluorine, chlorine, bromine and iodine have an important role in the biogeochemical cycles in natural environment [7,8] and are present in organic and inorganic natural compounds [2]. Depending on the soil type, the fluorine concentration found in worldwide soil ranges from 300 to 1200 mg kg⁻¹ [2,9], this high concentration associated with phosphatic rocks [9,10]. Regarding chlorine, the concentration of this element in soil has been estimated at around 100–1000 mg kg⁻¹ and it is found as NaCl or halides due to saline deposits present in subsoil [9,10]. There are a very few reports in literature mentioning about bromine concentration in soil. Among the other halogens, bromine is considered the element more easily leached from the soil [10–12]. Studies have shown iodine association with OM, as well as hydroxides (mainly Al and Fe) and clays [10,12]. Iodine has the lowest concentration in soils, ranging from 0.1 to 10 mg kg⁻¹ and methods allowing suitable iodine limits of quantification (LOQs) are still required [9].

The sample preparation step is still considered a challenging task for soil analysis, especially in the case of further halogens determination. In this sense, few sample preparation methods allowing further halogens determination in these matrices are available in literature [13–18]. Pyrohydrolysis [19–22], extraction [15,23,24] and microwave-induced combustion (MIC) [25–27] have been successfully proposed for overcoming the limitations of sample preparation methods using conventional systems. Pyrohydrolysis and MIC are especially suitable because they are very efficient for the oxidation of OM from the sample and allow the use of diluted alkaline solutions for halogens absorption, minimizing the high risk of contamination, analyte losses and allowing the determination by several techniques, such as ion chromatography (IC), inductively coupled plasma optical emission (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) [28]. However, these methods have some limitations related to inorganic matrices (MIC) [29] or to high OM content (pyrohydrolysis) [30] and some changes must be performed to allow their application for a more general use.

Recently, MIC has been applied for further halogens determination in soils with low OM (ranging from 8 to 50%) [18]. It was suitable for quantitative volatilization of halogens resulting in low relative standard deviation (RSD). However, considering that MIC method requires a high pressure system, the operational conditions are higher when compared to non-pressurized systems such as pyrohydrolysis. On the other hand, despite the restrictions for high OM content, pyrohydrolysis is a simple system where the sample is heated to approximately 1000 °C for analytes volatilization in the presence of water vapor [17,20].

The use of pyrohydrolysis system presents some advantages such as the use of relatively high sample mass and quantitative release of analytes from matrix [19]. However, pyrohydrolysis in the conventional system generally requires the use of an accelerator (e.g., V₂O₅) for assuring quantitative results, being prone to contamination and interferences in the determination step. Based on this, the development of an automated system, which could slowly introduce the sample in the furnace, instead of applying a temperature program, would be useful. This automation became feasible in recent years due to the spread use of open-source hardware system, such as the boards Uno and Mega 2560 from Arduino (Italy), which is accessible to virtually every research

groups with a basic knowledge of electronics and programming [31]. In addition, these systems are cheap, easy to use and can help in many laboratory operations [32,33].

In this sense, the aim of this study was to develop a sample preparation method based on the combination of combustion followed by pyrohydrolysis reaction. Soils with high and low OM (90 and 10%), were selected as an example of application in order to demonstrated the feasibility of the proposed system for matrices with very low or high organic matter content. Operational parameters (sample mass, the effect of heating time after soil combustion and the use of microcrystalline cellulose as an aid for the combustion process) were evaluated. The results obtained by MIC were used as reference values for optimization of the proposed method. In order to show the suitability of digests for a variety of analytical techniques, the determination of halogens was performed by IC and also by ICP-MS. Accuracy was evaluated using a certified reference material (CRM) of coal and also by spiked samples.

2. Experimental

2.1. Instrumentation

Samples were digested by the proposed method using a system based on a quartz tube (18 mm i.d., 450 mm length) with a lateral inlet that remained inside a tubular electric furnace (Sanchis, Brazil) during heating for steam production by water pumping through a peristaltic pump (IPC8, Ismatec, Switzerland). In order to insert the quartz boat (13 mm i.d., 40 mm length) containing the sample inside of the quartz tube, an automatic driving system was developed. It consisted of an aluminum chamber (130 mm length, 60 mm width and 40 mm depth) with a rectangular aperture at the top that allowed the positioning of the quartz boat into the driving system. A polycarbonate cover was placed over the top of the metallic chamber and a Viton™ O-ring was used to for sealing. Two hand screws were used for closing the system by pressing the cover against the chambers top containing the O-ring. The quartz boat containing the sample was moved inside the furnace by a quartz rod (4 mm o.d., 300 mm length) that contained, in the opposite side of the connection with the quartz boat, a metallic cylinder lined with polytetrafluoroethylene (PTFE).

The quartz rod and metallic cylinder were placed inside a glass tube (19 mm i.d., 450 mm length) that was connected to the metallic chamber, and, at the other end, to the oxygen inlet plug. The quartz rod was moved towards the furnace by the magnetic coupling of the metallic cylinder to an external neodymium magnet driven by a stepper motor. The stepper motor, the magnetic system and the glass tube were positioned in a metallic frame placed beside the furnace. A glass condenser was connected to quartz tube by a PTFE joint and it was used to cool down the products coming from the furnace. Water of the condenser was cooled at 4 °C by a chiller (Q-214U2, Quimis, Brazil). An open source microcontroller (Pro Mini, Arduino, Italy) was used to control the stepper motor through a microstepping driver (A4988, Pololu Robotics and Electronic, USA). The electrical components were placed in a plastic container and a 3" display and a rotary encoder were used to program and control the sample introduction system. This system also controlled the water flow during the heating program. The oxygen flow rate was controlled by a gas flow regulator (2A13, Key Instruments, USA). In Fig. 1 it is shown the scheme of the system developed with its respective components.

A Multiwave 3000 (Anton Paar, Austria) system equipped with high-pressure quartz vessels (internal volume of 80 mL) was used for samples digestion by MIC method for the reference values [18]. Quartz holders were used to introduce the samples inside the

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