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Analytical procedures for the determination of selected major (Al, Ca, Fe, K, Mg, Na, and Ti) and trace (Li, Mn, Sr, and Zn) elements in peat and plant samples using inductively coupled plasma-optical emission spectrometry

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Abstract

A simple, robust and reliable analytical procedure for the determination of Al, Ca, Fe, K, Li, Mg, Mn, Na, Sr, Ti, and Zn in peat and plant materials by inductively coupled plasma-optical emission spectrometry (ICP-OES) was developed. A microwave heated high pressure autoclave was used to digest powdered sample aliquots (approximately 200 mg) with different acid mixtures including nitric acid (HNO_3), tetrafluoroboric acid (HBF_4) and hydrogen peroxide (H_2O_2). The optimized acid mixture for digestion of plant and peat samples consisted of 3 mL HNO_3 and 0.1 mL HBF_4, in addition to H_2O_2 which was sub-boiled into the PTFE digestion tubes during heating of the autoclave. Using HNO_3 alone, recoveries of Al and Ti were too low by 40 and 160%, respectively, because HNO_3 could not fully liberate the analytes of interest from the silicate fraction of the plant and peat matrix. However, for all other elements (such as Mn, Sr, and Zn), the use of HBF_4 was less critical. The accuracy of the analytical procedure developed was evaluated with peat and plant reference materials of different origin and composition. The ICP-OES instrument was optimized using solutions of plant reference materials considering RF power, nebulizer pressure, auxiliary gas flow and rinse time. Scandium was used as an online internal standard (IS) as it provided accurate results and showed less than 3% drift in sensitivity over time which was lower compared to other potential IS such as Rh (20%) and In (6%). The combination of most sensitive and less sensitive wavelengths allowed to obtain low detection limits and highest possible dynamic range. The achieved procedure detection limits ranged from 0.05 $\mu g\,g^{-1}$ (Li) to 15 $\mu g\,g^{-1}$ (Ca) and allowed a precise quantification of all elements. Comparative X-ray fluorescence spectrometric measurements of solid peat and plant samples generally agreed well with results obtained by digestion/ICP-OES. To overcome interferences caused by Na, K, and Li, a solution of 10 $\mu g\,g^{-1}$ $CsCl_2$ was successfully used as an ionization buffer. The good agreement between the found and certified concentrations in plant and peat reference materials indicates that the developed analytical procedure is well suited for further studies on the fate of major elements in plant and peat matrices.

Keywords: Microwave digestion; ICP-OES; Plant; Peat; Major elements

1. Introduction

Major and trace elements have widespread implications in industrial, geological, geochemical and environmental studies. Studies of major and trace elemental composition of mineral dust are necessary to better understand geochemical cycle of these dusts and their relationship to climate changes [1–3]. The transport and deposition of mineral dust from arid and semi-arid continental regions has been investigated since many years [1,2,4]. There is a growing interest in the use of plants as bioindicators and peat bogs as archives of atmospheric mineral dust deposition [3,5–7]. Ombrotrophic peat bogs are the most appropriate medium for that purpose as they receive mineral dust particles exclusively from air.

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However, precise and accurate analytical procedures for the reliable determination of major and trace elements are needed to reconstruct atmospheric mineral dust deposition rates, and to quantify possible changes due to weathering and diagenesis.

To this end, peat samples have to be digested prior to multi-elemental analysis by most instrumental techniques. At present, sample digestion is commonly carried out by heating the samples with acids in open or closed vessels, increasingly by means of microwave irradiation. This method involves the total or partial decomposition of the sample, destroying most of the organic matter. Sample preparation for subsequent elemental analysis is always a crucial step of the analytical procedure. Many factors such as level of contamination, homogeneity of samples, reproducibility and completeness of digestion, suitability of the analytical technique employed, time needed for sample preparation and economic aspects should be considered [8–11]. In comparison to open vessel microwave-assisted digestion, closed vessel microwave-assisted acid digestion has been extensively used for sample digestion [8,9]. Closed vessel microwave- assisted digestion techniques are superior sample pretreatments allowing shorter heating time, reducing cross contamination and minimizing loss of volatile analytes. However, simply employing a closed pressurized digestion system will not give accurate and precise results. Digestion efficiency largely depends on various parameters such as the method of heating, working pressure as well as kind and volume of acids specifically required to dissolve the sample matrices. Several studies dealing with closed vessel microwave acid digestion of peat and plant matrices have been reported [8,9,11]. Various authors showed that the digestion procedure, specifically, the composition of the acid mixture, has a dominant influence on the results obtained when determining major and trace elements [8,9,11,12]. The main reagents used for digestion of sample matrices such as plant, peat and air particulates are different combinations of nitric acid (HNO_3), hydrofluoric acid (HF) and hydrogen peroxide (H_2O_2). Common practice for the digestion of plant matrices is the addition of H_2O_2 to HNO_3. Addition of H_2O_2 to the digestion mixture increases the oxidation power of HNO_3 during digestion and enhances the attack of organic material present in the sample. However, mixtures of HNO_3/H_2O_2 alone cannot dissolve all of the siliceous material present in the sample, thus leading to poor recoveries for many elements [8,9,13]. Other elements such as As and Se are not bound to the silicate fraction of peat or plant materials and consequently do not require complete dissolution of the siliceous matrix for their accurate quantification [14,15]. Hydrofluoric acid in combination with boric acid (H_3BO_3) is commonly used in the acid mixtures to dissolve silicates present in the samples and to complex “excess HF” in the digestion solutions. In the past few years, however, comparative studies clearly demonstrated the advantages of using tetrafluoroboric acid (HBF_4) over the combination of HF and H_3BO_3 for complete digestion of peat [8,9].

Inductively coupled plasma-optical emission spectrometry (ICP-OES) has been widely used for multielemental analysis [11,16,17]. Analytical qualities such as relatively low detection limits, capacity for simultaneous, rapid and precise determinations over wide concentration ranges have made ICP-OES the method of choice for multielemental analysis and preferred instrumentation over other techniques such as atomic absorption spectrometry (AAS), flame atomic emission spectrometry (FAES), instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF) spectrometry. Even though several previous studies reported on the multielement analysis of plant and airborne particulate materials using ICP-OES [11,15,18], no modern investigations of peat samples can be found in the literature. The analytical procedures used to determine major elements developed for plant and particulate matter might not be successfully applied to dissolve peat samples as their composition frequently differs. Besides the plant derived organic material in various stages of decay and humification, the presence of an inorganic mineral fraction, predominantly derived from atmospheric soil dust, makes peat a difficult-to-digest matrix.

The aim of this study was to develop and evaluate an analytical procedure for the digestion of peat materials elucidating the potential of HBF_4, followed by the determination of selected major elements by ICP-OES. In order to evaluate the digestion and ICP-OES procedures, the seven major (Al, Ca, Fe, K, Mg, Na, and Ti) and four trace (Li, Mn, Sr, and Zn) elements were determined in several certified peat and plant reference materials. Additional measurements of the investigated elements in the solid samples by XRF helped to evaluate the completeness of the digestion procedure and the suitability of the developed analytical procedure.

2. Experimental

2.1. Determination of elements by ICP-OES

ICP-OES measurements were carried out using a Vista MPX instrument with charge coupled devices (CCD) simultaneous detection systems (Varian Inc., Victoria, Australia). Plasma torch alignment was performed by using a Mn solution ($5\,\mu g\,g^{-1}$) at emission line 257.61 nm. During measurements, chemical attack of instrumental parts such as nebulizer, spray chamber and plasma torch as well as residue formation should be minimized. As the sample solutions contained HBF_4 which is corrosive to quartz, an HBF_4 resistant Inert V-groove nebulizer (Varian Inc.) was used. Similarly, an inert Ertalyt® (Polyetlylene Terephtalate) Sturman-Masters spray chamber (Varian Inc.) was employed to improve plasma stability and to minimize matrix interferences.

2.2. Reagents and standards

All solutions were prepared with high-purity water of $18.2\,M\Omega\,cm$ resistivity obtained from a MilliQ-system