Fast microwave-assisted sample preparation for further determination of halogens in medicinal plants

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Introduction

The use of medicinal plants for drugs manipulation is officially accepted by World Health Organization since 1978. In the sense, medicinal plants became important to the development and research of new drugs.[1] Halogens, can play different functions depending on the concentration in the organism. Iodine, for example, is essential for humans due to its contribution at the synthesis of thyroid hormones. However, excessive intake can result in some diseases, e.g. hyperthyroidism. Bromine is not essential although it has been reported as an anti-epileptic agent. In other cases it is believed to be carcinogenic.[2] In addition, the practice of fumigation with methyl bromide as pesticide can also increase the concentration of Br in plants.[3] Therefore, Expert Committee of US Pharmacopeia (USP) establishes 50 µg g^{-1} as the official limit for Br, in some pharmacopeial articles of botanical origin. Despite the necessity to determine halogens in medicinal plants, some difficulties are related to sample preparation for halogens determination at low concentration, mainly due to the risk of contamination and formation of volatile compounds.[2] In this sense, microwave-assisted alkaline extraction (MAE) was investigated for further halogens determination in medicinal plants (*Chamomilla recutita L., Zinziber officianallis* and *Phillanthus neruri*).

Results and Discusions

A microwave oven (Multiwave 3000 Anton Paar, Austria) equipped with 8 quartz vessels (80 mL) and maximum temperature and pressure of 280 °C and 180 bar, respectively, was used. Comparatively, microwave-assisted wet digestion (MAWD) using HNO_3 and microwave-induced combustion (MIC) were applied for digestion of samples. Results obtained by MIC using 50 mmol L^{-1} NH_4OH as absorbing solution were considered as reference values. The determination of Br and I was performed by inductively coupled plasma mass spectrometry (ICP-MS), in a spectrometer equipped with a concentric nebulizer and a cyclonic spray chamber (Elan DRC II, Perkin Elmer-SCIEX, Canada). The determination of Cl and residual carbon, was performed by inductively coupled plasma optical emission spectrometry (ICP OES) using an axial view spectrometer (Ciros CCD, Spectro Analytical Instruments, Germany). The determination of F was carried out by potentiometry using ion selective electrode (ISE, 6. 502.150, Metrohm, Switzerland) and by ion chromatography (IC, 850 Professional IC, Metrohm, Switzerland). Sample masses of 500 mg were used for both methods. The alkaline extraction was performed using H_2O, NH_4OH (1%) or TMAH (1%), following a 2^3 factorial design. The variables studied were: volume of extractor medium (6 and 10 mL), temperature (90 and 280 °C) and extraction time (5 and 20 min). When MAWD with HNO_3 was used, losses of halogens were observed and agreement with reference values was only about 29% (for Cl). For F, the extraction method showed interferences for the determination by ISE and IC. With regard to the extraction conditions, better results were obtained using TMAH (10 mL) at 90 °C, using only 5 min for Cl, Br and I and no statistical difference (test-*t*, confidence level 95%) was observed in comparison to the reference values. Under the same conditions, for extraction with H_2O, recoveries were of 102%, 90% and 26% for Cl, Br and I, respectively. Using NH_4OH, recoveries of 92%, 90% and 51% for Cl, Br and I were obtained. Limits of detection from 2.5, 0.01, and 0.009 µg g^{-1} were obtained for Cl (ICP OES), Br (ICP-MS) and I (ICP-MS), respectively. The accuracy was evaluated using certified reference materials (NIST 1572, Citrus Leaves and NIST 1547, Peach Leaves) and no statistical difference was observed between the results obtained by the proposed method and certified values for Cl, Br and I.

Conclusions

The proposed method was suitable for Cl, Br and I determination in medicinal plants using TMAH as extractor medium. However, for the determination of F, the method showed interferences by ISE and also IC. The method showed advantages, as the of use low amount of reagents, low risk of contamination, low detection limits and low extraction time. Furthermore, the sample preparation allowed the determination of halogens by ICP OES, ICP-MS and IC.

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