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Evaluation of sample pretreatment methods for analysis of polonium isotopes in herbal medicines

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ABSTRACT

Herbal infusions like ayurvedic aristas are widely consumed by Indian population for good health. With increasing awareness about radiological assessment, an effort was made to assess the radioactivity concentration of naturally occurring radionuclides in herbal medicines. ^{210}Po is an important alpha particle emitter contributing to internal dose to man from ingestion. Though ^{210}Po can be spontaneously deposited on silver disk for alpha spectrometric measurements with less radiochemical step, great care has to be taken during the sample pretreatment step owing to the high volatility of polonium even at low temperatures. Aim of the study was to evaluate an appropriate sample pretreatment method for estimation of polonium in herbal medicines. ^{209}Po was used for radiochemical yield calculation. Conventional open vessel wet ashing, physical evaporation, freeze-drying and microwave digestion in a Teflon vessel were examined. The recovery ranged between 9 and 79%. The lowest recovery was obtained for the samples that were processed by open vessel digestion without any volume reduction. The recoveries were comparable for those samples that were freeze dried and subjected to $HNO_3 + HClO_4 + H_2O_2 + HF$ acid digestion and microwave digested samples. ^{210}Po concentration in the samples ranged from 11.3 to 39.6 mBq/L.

1. Introduction

In India, herbal medicines are used according to different medical traditions like ayurveda, sidha and unani. Ayurveda, meaning science of life, is the most ancient tradition originated thousands of years ago. Use of ayurveda medicines have increased not only in Asian countries but also in western countries. Ayurveda formulations are prepared using herbs, minerals and other materials (Chopra and Doiphode, 2002). In Indian Market, Ayurveda medicines are available in various forms like herbal infusions, decoctions, tinctures, capsules, powders, infused oils, ointments, creams, fermented decoction and infusions. Aristas, are fermented decoctions that are widely used for both preventative and therapeutic purposes. These medicines are prepared by allowing the herbal decoction to ferment with addition of sugar in the form of jaggery, honey or raisin paste (Mishra et al., 2010). Dasamoolaristam is prepared from the extracts of at least ten different herbal roots (Kalaiselvan et al., 2010; Linga Rao and Savithramma, 2011). The extracts in the form of decoction are soaked in a solution of sugar or jaggery, for a specified period of time during which fermentation occurs to generate alcohol facilitating the extraction of the active components contained in the medicine. They are usually consumed for good health. There are literatures reporting the trace element composition in the herbal medicines and in herbs itself. Many researchers have also investigated on the microbial content and phytochemical properties. But little work is done on radionuclide content in these medicines. Hence an attempt was made to analyze the natural radioactivity in these medicines as they are prepared from herbal plants. Radionuclide content in the leafy plants or herbs is due to uptake from soil and direct aerial deposition on leaves (foliar uptake) (Persson and Holm, 2011). The uptake may vary from plant to plant based on the chemical form of the radionuclide, type of soil and ground water. Radionuclides from uranium and thorium series and ^{40}K are the major contributor to internal dose from intake of plants. In terrestrial environments, the naturally occurring radionuclides ^{210}Pb and ^{210}Po are present through atmospheric deposition, following the decay of emanated ^{222}Rn and via the in situ decay of ^{238}U in the soil. Karunakara et al. (2000) reported that 84% of the α activity in plants is due to ^{210}Po, either by direct absorption from soil or deposition on the leaves. The main route of intake of ^{210}Po is by ingestion and inhalation.

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Analysis of ^{210}Po in herbal medicines especially arista involves sample pretreatment, coprecipitation, auto deposition and alpha spectrometry. Due to high organic content because of the herbal roots and jaggery, sample digestion for ^{210}Po analysis is complex. Adequate care is needed owing to high volatility of polonium isotopes. Pretreatment steps involve volume reduction by means of evaporation, dry ashing and freeze drying followed by sample dissolution and organic matter destruction. Considering the high volatility of Po isotopes, volume reduction by physical means has a restriction on the maximum temperature that can be used. During dry ashing in muffle furnace, loss of Po isotopes starts at a temperature of 100 °C, by approximately 90% will be lost at 300 °C and at 800 °C entire polonium is lost (Martin and Blanchard, 1969). Hence we have used open vessel evaporation at 90 °C or freeze drying technique for sample volume reduction. The next step in sample pretreatment is sample digestion for dissolution and organic matter destruction (decomposition). In sample digestion, the main purpose of sample pretreatment is to decompose the sample matrix to a point where the elements of interest present are brought completely into the solution without loss. Dissolution or digestion is achieved by wet ashing with acids in open system and microwave digestion. In both cases combination of HNO_3, HCl, H_2O_2, HF and $HClO_4$ was used in different proportions. Dissolution was achieved using only HNO_3 (Lin and Wu, 2009), $HNO_3 + H_2O_2$ (Cunha et al., 2001), $HNO_3 + H_2O_2 + HClO_4$ (Swift, 1998) or HNO_3 + aqua regia (HCl:HNO_3, 3:1) (Ham et al., 1997), HNO_3 + HF (Martin et al., 1998). Wet ashing in open vessel is time consuming and has greater chances of external contamination. Microwave digestion enables us for a rapid and temperature controlled dissolution process. Murray et al. (2007) have published an extensive review report on determination of Polonium in different matrix. In this paper, different physical and chemical treatment methods were attempted to standardize an appropriate pretreatment procedure for the analysis ^{210}Po in herbal medicines.

2. Materials and methods

2.1. Reagents

Electronic grade reagents were used for radiochemical procedure. A working ^{209}Po tracer solution (8.8 mBq/ml) was prepared from ^{209}Po Tracer obtained from NPL.

2.2. Samples

Dasamoolaristam bottled samples were purchased from Ayurveda pharmacy shop in Mumbai. All the samples were stored carefully in a cool area away from sunlight. Each bottle contained 450 ml Arista. Though the same generic name medicines were purchased the packing dates and batch number were different hence the samples were named as B1 and B2 based on the batch numbers.

2.3. Radioanalytical method

To each 450 ml sample known amount of ^{209}Po was added as radiochemical yield tracer and continuously stirred for 2–3 h. These samples were subjected to the following physical and chemical pretreatment methods: a) conventional open vessel evaporation on a hot plate; b) freeze drying; c) Digestion using classical open vessel acid digestion on a hot plate; d) microwave reaction system. Combination of various mineral acids and oxidizing agents like aqua regia, ConHNO_3, H_2O_2 and $HClO_4$ were used.

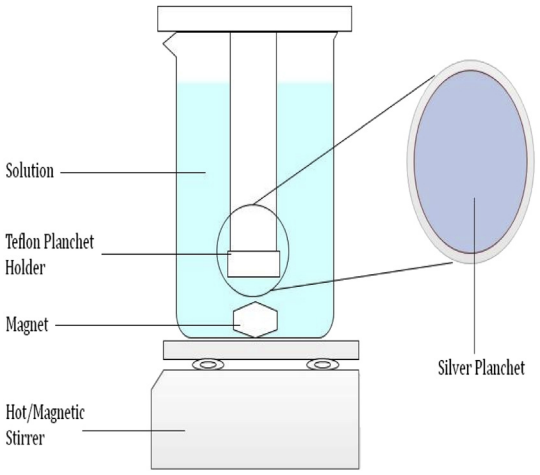

Fig. 1. Schematic diagram of polonium auto deposition setup.

After sample digestion, the samples were filtered through a Whatman-542 filter paper. 200 mg calcium carrier and 10 ml phosphoric acid were added to the filtered sample. Polonium isotopes present in the sample were pre-concentrated by coprecipitation with calcium phosphate at 8–9 pH with addition of ammonia. The precipitate was centrifuged and the supernatant was discarded. The precipitate was dissolved in conc. nitric acid and evaporated to dryness. The residue was redissolved in 65% hydrochloric acid and evaporated to dryness. The residue was again dissolved in conHCl and diluted to a concentration of 0.5 M hydrochloric acid.

To prevent interferences of competing ions in the deposition process, particularly Fe^{3+} that can otherwise cause heavy deposits on the plating discs and subsequent loss of counting efficiency and resolution during the alpha spectrometry measurement, 0.8–1 g ascorbic acid was added to the above solution (0.5 N HCl) to reduce Fe^{3+} to Fe^{2+}. Polonium was spontaneously deposited onto silver disk (25 mm ⌀) screwed to a Teflon holder at 90 °C with constant stirring for 3 h (Fig. 1). After plating the disc was washed with distilled water and ethanol before counting (Lin and Wu, 2009). The activities of ^{209}Po and ^{210}Po on the silver disk were measured using a high resolution alpha particle spectrometer equipped with 450 mm^2 PIPS semiconductor silicon detectors interfaced with 1024 channel MCA (Fig. 2). The counting efficiency of the silicon detectors was about 23% and background was about 1–2 counts for 86,400 s in the region of interest. Table. 1 provides the relevant decay data for polonium isotopes.

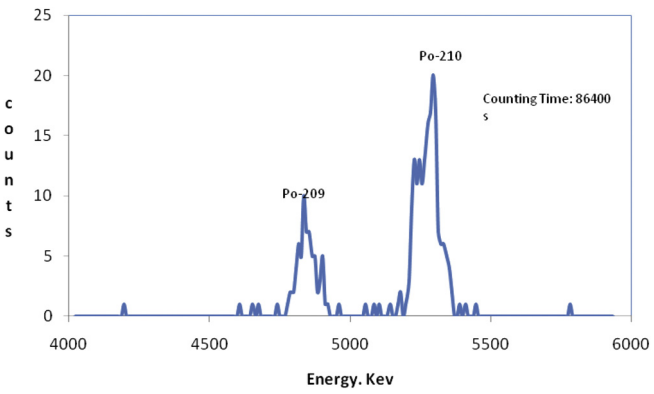

Fig. 2. A typical alpha spectrum of polonium isotopes in herbal medicine.