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Neutron activation analysis of essential elements in Multani mitti clay using miniature neutron source reactor

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HIGHLIGHTS

- ▸ Multani mitti clay has been studied for 19 essential elements for human adequacy and safety using INAA and AAS.
- ▸ Weekly intakes for different consumer categories have been calculated and compared with DRIs.
- ▸ Comparison of MM with other type of clays depict that MM clay is a good source of essential elements.

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ABSTRACT

Multani mitti clay was studied for 19 essential and other elements. Four different radio-assay schemes were adopted for instrumental neutron activation analysis (INAA) using miniature neutron source reactor. The estimated weekly intakes of Cr and Fe are high for men, women, pregnant and lactating women and children while intake of Co is higher in adult categories and Mn by pregnant women. Comparison of MM clay with other type of clays shows that it is a good source of essential elements.

1. Introduction

Multani mitti (MM) clay is classified as sedimentary clay of Pakistani origin that is famous for its benevolent use in the daily lives of people from every class and age group. Its plentiful deposits are located near "the Land of Mystics", the city of Multan is Fullers earth and scientifically classified as bentonite and montmorillonite: smectite clay mineral. Clays are basically rocks formed by the accumulation of less than 2 μm fine particles (Luiz et al., 2009). Awareness and use of various types of clays and their beneficial effects can be traced down to the ancient Mesopotamians, Chinese, Indian and Egyptian civilizations to as far back as three to five hundred years ago (Finkelman, 2006). In the recent past clays have been rediscovered for their beneficial uses and curative properties. Clays are being used as dietary supplements, in aesthetic medicine, for healing purposes, as therapeutics and as cleaning agents (Carretero, 2002). Our life cannot exist without some basic minerals as our body cannot manufacture its own minerals and the absence or deficiency of these minerals humans and other living beings are prone to develop various health problems. Clays are rich in these minerals with high amounts of Ca, Fe, K, Mg, Mn, Si and Zn, and accordingly have been routinely ingested by humans in various cultures. In many parts of the world clays are being used as dietary supplement for general weakness, in anti-aging products, for longevity, for the treatment of diabetes, gastro-intestinal disorders, colds, bleeding gums, healing of wounds and fractures, arthritis, weight control and detoxification (Slamova et al., 2011). The impact of geological materials on human health has initiated interest in medical geology focusing on the health issues pertinent to exposure and ingestion of essential and toxic minerals.

It has been reported that due to various mineral deficiencies humans crave and ingest edible clays which help them overcome these deficiencies. This intake of clays is referred to as "geophagy" in Greek meaning "eating earth" (Kawai et al., 2009). Clay eating

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is more common for children, pregnant, lactating and middle aged women. It has been found that geophagy helps the intake of some essential elements (especially Ca, Mg, Zn, Fe, Cu, Mn, and Se) that help to diminish mineral deficiencies in women (Carretero, 2002; Kawai et al., 2009; Abrahams et al., 2006). MM is considered a natural cleanser and astringent therefore it is used in face and body and hair wash, face mask and many other cosmetic products to help the body in the removal of dirt and in oil balancing (Carretero and Pozo, 2009). It is also used to reduce arthritic pain, strengthen fingernails, teeth and gums. Clay also acts as a bleaching agent due to the presence of hydrated aluminum silicates that contain magnesium, sodium and calcium within their structures to absorb impurities like oils, fats and petroleum-based dirt residues as well as fungus (Luiz et al., 2009). This property of MM has been used by archaeologists for cleaning and conservation of the world famous marble wonder, the Taj Mahal (National and International Council for Scientific Research, 2010–2011).

The present study was initiated due to the common use of unprocessed MM clay by the general populace of Pakistan as dietary supplement, in beauty care products and as a therapeutic agent. Instrumental neutron activation analysis (INAA) using miniature neutron source reactor, together with atomic absorption spectrometry (AAS) was used in this work to quantify essential and other trace minerals. The work presents characterization of essential nutrients in MM clay to check the adequacy and safety of the material for human consumption. The data obtained can be utilized to establish certain baseline values of these minerals in this clay that can help to monitor any health problems related to its excessive and prolonged intake.

2. Experimental

2.1. Sampling and sample preparation

Representative MM clay samples were collected from the excavation site from Raki stream, Gazige formation near Dera Ghazi Khan District in Pakistan. Samples were packed in clean plastic bags and transported to the sample preparation laboratory at the Pakistan Institute of Nuclear Science and Technology (PINSTECH) in Islamabad. Here the samples were first crushed and then grounded to fine powder. The ground material was then passed through a stainless steel sieve of 120 mesh ASTM that separated 0.125 mm particles size as a fine powder for homogenization. All sieved MM samples were finally stored in pre-cleaned bottles fitted with airtight screw capped polyethylene bottles. Moisture content of the MM sample was determined by taking about 10 g of the processed sample in a dry and clean pre-weighed container and dried for about 24 h in an oven at 105 °C. Six randomly selected aliquots of approximately 100 mg from the processed MM material were taken for homogeneity test. These samples were analyzed for their Mn and K content and were found to be homogeneous as the variation in these measurements was less than 6% around the mean values.

2.2. INAA methodology

Multiple MM samples of approximately 100 mg each and the International Atomic Energy Agency (IAEA) reference materials (IAEA S-7 and IAEA SD-M-2/TM) as control materials were separately packed and sealed in pre-cleaned polyethylene capsules. Four different batches of the samples were prepared corresponding to different irradiation schemes. All capsules were properly labeled; heat sealed and packed in reactor rabbits. The targets were irradiated in the periphery of the reactor core of the 27 kW tank-in-pool type Miniature Neutron Source Reactor (MNSR) with a thermal neutron flux of $1\times10^{12}\,cm^{-2}\,s^{-1}$. The cooling and counting times were adjusted in accordance with the half-life of the isotope of the desired element. After different irradiations and desired cooling of the irradiated targets the active samples were transferred to pre-cleaned and pre-weighed polyethylene counting capsules and subjected to the optimized radio-assay scheme.

High purity germanium detector (Canberra Model AL-30) linked to a PC-based Intertechnique Multichannel Analyzer (MCA) was used for counting of the irradiated samples. "Intergamma, version 5.03" software was used for data acquisition. The resolution of the system is 1.9 keV at 1332.5 keV peak of ^{60}Co and peak to Compton ratio is 40:1. The data files were subjected to calculations on our validated in-house computer programs (Wasim, 2010). All necessary corrections (background subtraction etc.) were applied and the final results obtained on dry weight basis. Error propagation rules were applied at each stage of the calculations and accounted for the uncertainties in peak area, uncertainties in weighing and uncertainties in certified values of RMs used for calibration. The calculation programs have been validated through their application to IAEA RMs and participation in IAEA Proficiency Test (PT) exercises.

2.3. AAS methodology

1 g of MM clay sample was weighed and transferred to 100 ml digestion flask fitted with 30 cm long air condenser and 10 ml of aqua regia was added. Instead of total digestion it is more usual in soil and clay samples to perform pseudo total digestion with boiling aqua regia under reflux. A further advantage is that aqua regia digestions can be analyzed by Flame Atomic Absorption Spectrometry (FAAS) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS) relatively free of problems. The content was heated on hot plate at 85 °C for leaching to 2 h. After cooling it at room temperature 1.5 ml H_2O_2 was added drop wise at 60 °C until reaction completes (Sastre et al., 2002). The leachate was filtered and solution was made up to 10 ml in volumetric flask up to mark with deionized water. All the samples were analyzed in triplicate. In order to validate the accuracy of the proposed procedure certified reference materials soil-7 was digested using the same procedure and was analyzed for Cu and Ni. The determined values of these elements in Soil-7 were in good agreement with certified values. Quantification was carried out using Hitachi model Z-2000 Polarized Zeeman Atomic Absorption Spectrometer (AAS) coupled with software based data handling facility.

3. Results and discussion

Seventeen essential major, minor and trace elements (Ba, Co, Cr, Cs, Fe, K, Mg, Mn, Mo, Na, Rb, Se, Sn, Sr, Ti, V and Zn) have been determined in MM clay using instrumental neutron activation analysis (INAA) technique, while Cu and Ni were quantified using atomic absorption spectrometry (AAS). For elements determined by INAA four different radio-assay schemes were adopted and are presented in Table 1. This suitable variation in irradiation and cooling times minimized the spectral interferences and few that were experienced were carefully dealt with as mentioned in our previous studies (Waheed et al., 2007; Sabiha-Javied et al., 2010).

Elemental content of IAEA-RMs were also determined using the irradiation and radio-assay scheme optimized for this work, to help ensure the trueness and bias of the adopted methodology in accordance with ISO-5725 standards (Kane, 2001). IAEA-RMs (IAEA S-7 and IAEA SD-M-2/TM) were employing to check the