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Characterization of coal and charcoal by alpha-particle and gamma-ray spectrometry

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HIGHLIGHTS

- Determination of activity concentrations of radionuclides in coals and charcoals.
- Efficiency transfer method for calibration of an HPGe detector to study extended samples with wide ranges of densities.
- Leaching the carbon samples for the radiochemical procedure prior to alpha-particle spectrometry.

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ABSTRACT

Although coal and charcoal have similar physical and chemical characteristics, there are several crystallographic procedures used to distinguish and characterize them. But if the matrix is crushed, there is no standard procedure to distinguish coal from charcoal. In this work, a procedure to characterize coal and charcoal samples based on the radioactive content is proposed. The first assay is by gamma-ray spectrometry, which allows a part of the radioactive content to be determined rapidly and non-destructively. Then, alpha-particle spectrometry is applied to assay the content of those radionuclides which are difficult to determine precisely by gamma-ray spectrometry. This second technique requires prior chemical purification of the carbon sample in order to separate the corresponding radionuclides of interest.

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1. Introduction

Coal is a sedimentary rock formed by a geological process called carbonization in which organic materials are gradually transformed into materials with increased carbon content. The process of formation of coal needs to occur in wetlands for the organic matter to be degraded by bacteria. There are different types of coal according to the degree of coalification which they have undergone, depending on the age and depth of the deposit, and the pressure and temperature conditions it has been subjected to (Thomas, 2013). Trace elements, including radioactive isotopes, are incorporated into coal by water leaching them from surrounding rocks (Finkelman, 1999).

Charcoal is the result of the slow pyrolysis of organic material under air-limited conditions in a closed space. The material obtained is enriched in carbon. The raw materials used to make charcoal are usually wood chips, branches, sawdust, agricultural waste, forestry residues, or prunings. The properties of manufactured charcoal depend as much on the seasonal raw material used as on the production process conditions (Rubio Montero et al., 2009). Any radioactive content of charcoal comes from the incorporation of radionuclides in aqueous solution taken up by the roots of the plants that were subsequently used as the raw material in the pyrolysis process.

Coal and charcoal are formed under very different conditions of time, pressure, and temperature, but these processes result in carbon-enriched materials with similar physical and chemical properties. Traditionally, proximate and elemental analysis are two of the procedures used to classify coal and charcoal. The most important differences, however, are that carbonization is a much longer process that charcoal formation, and that the trace elements are incorporated through very different pathways. Significant differences in radioactive content between coal and charcoal can help differentiate them.

The radioactive content of coal is extensively studied in several industries, especially those related to power generation, to ensure radiological safety. ^{40}K and isotopes from natural series ^{238}U, ^{232}Th are frequently present in coals (Lu et al., 2006). Secular equilibrium is sometimes assumed, but various processes may disturb it

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(Tadmor, 1986) including natural processes involved in the coal's formation (Arbuzov et al., 2011) and isotopic partitioning in combustion processes (Karangelos et al., 2004). Anthropogenic isotopes, such as ^{137}Cs and ^{134}Cs, are often investigated in process of co-firing biomass with coal (Grammelis et al., 2006). The radioactive content of charcoal has been far less studied, and indeed one can find hardly any data in the literature (Rubio Montero et al., 2009).

The commonest technique used to determine the concentration of radioactive isotopes in coal and its derivates is gamma-ray spectrometry using NaI or HPGe detectors. This non-destructive technique requires minimal manipulation of the sample, and is therefore clean and obviates the tedious laboratory work needed for other techniques such as alpha-particle spectrometry. Another of its advantages is that it can be applied *in situ* using portable equipment. However, the determination of uranium isotope concentrations by gamma-ray spectrometry is only possible if secular equilibrium can be assumed. If this is not the case, alpha-particle spectrometry must be used (Salmon et al., 1984). In the present work, we shall describe procedures based on both gamma-ray and alpha-particle spectrometry, and analyze several coal and charcoal samples.

2. Experimental procedures

In this section, we shall describe the procedures used for the gamma-ray and alpha-particle spectrometric assays. All the samples were first pre-processed in a jaw crusher to a grain size of less than 1 mm, followed by crushing in an ultra-centrifugal mill which includes sieves of different mesh sizes to obtain a grain size of less than 0.50 mm for the gamma-ray spectrometry and 0.25 mm for the alpha-particle spectrometry. They were then homogenized, and finally dried in a forced convention oven at 105 °C.

2.1. Gamma-ray spectrometry

Gamma-ray spectrometry has the advantages of not requiring laborious sample preparation and that several nuclides can be evaluated from a single measurement. In particular, the use of high-resolution germanium detectors allows the precise determination of the activity concentrations of several nuclides in any type of sample. For these reasons, gamma-ray spectrometry was used in the present work to analyze the radioactive content of carbon samples. With this technique, one can investigate the uranium and thorium series together with the activity concentrations of other radionuclides, such as ^{40}K, ^{137}Cs, and ^{134}Cs.

An aliquot of each sample was put into a Marinelli beaker of 1200 cm^3 or 320 cm^3, depending on the amount of sample available. The beakers were then perfectly sealed to avoid the escape of radon, and left for 40 days before measurement, in order to ensure radioactive equilibrium. Spectra were measured for 72,000 s using a coaxial p-type HPGe detector with 20% relative efficiency for the 1.332 MeV ^{60}Co peak. Dead-time corrections were taken into consideration, while losses due to random pile-up were usually negligible because of the low activity concentrations of the samples.

The determination of the activity for each radionuclide requires prior knowledge of the peak efficiency at each photon energy for a given geometry. An efficiency calibration must then be performed using known standard sources of geometrical dimensions, density, and chemical composition very similar to those of the sample under study. It is not difficult to reproduce the sample geometry, but the photon attenuation in the samples of interest (carbon samples with very different densities) is usually not at all close to that in the calibration source (with a given fixed value of density) (Jurado Vargas et al., 2002). We have proposed an efficiency transfer method to surmount this problem (Jurado Vargas et al., 2003). In a first step, we carry out an experimental efficiency calibration by measuring a water sample spiked with a reference multi-gamma solution in both Marinelli beakers. In a second step, we use Monte Carlo simulation to evaluate, for any photon energy, the ratio of the efficiencies for the sample of interest and for the calibration sample. Finally, this ratio is multiplied by the experimental efficiency given by the measurement of the calibration source. This procedure saves both time and resources since no sample-specific experimental calibration is needed. Moreover, it has the advantage that many potential inaccuracies in the detector model cancel out to a large degree in the calculated ratio obtained by Monte Carlo simulation, making it possible to work directly with the non-optimized detector data supplied by the manufacturer (Vidmar et al., 2010). For this calculation, we used the well-known Monte Carlo simulation code DETEFF (Cornejo Díaz and Jurado Vargas, 2010) which has been widely used for the evaluation of coaxial gamma-ray detector efficiencies. A detailed description of the efficiency transfer method followed in the present work is given in Jurado Vargas et al. (2003). Corrections for coincidence-summing effects were applied for the gamma-ray lines exhibiting cascades, following the procedure described by Quintana & Fernández (1995).

In order to investigate the natural ^{232}Th series, the ^{228}Ra and ^{228}Th activity concentrations were determined. The emissions of ^{228}Ac (338.3 and 911.2 keV) were used to determine their ^{228}Ra progenitor, and the emissions of ^{212}Pb (238.6 keV) and ^{208}Tl (583.2 keV) were considered to determine their ^{228}Th progenitor. To study the ^{238}U series, the activity concentration of ^{226}Ra was determined from the emissions of its daughters ^{214}Pb (352 keV) and ^{214}Bi (609.3 keV and 1120.3 keV). The activity concentrations of the nuclides ^{137}Cs, ^{134}Cs, and ^{40}K were calculated from their emissions at 661.7, 795.9, and 1460.8 keV, respectively.

2.2. Alpha-particle spectrometry

Alpha-particle spectrometry must be applied to assay those radionuclides which are difficult to determine precisely by gamma-ray spectrometry. The technique requires prior chemical purification of the carbon sample in order to separate the corresponding radionuclides of interest from others that would interfere. The procedure followed to perform the extraction and subsequent analysis of the different isotopes of uranium and thorium had three well-defined stages.

The first stage (Fig. 1) consisted of an acid leaching process applied to 2 g of sample in concentrated nitric acid, stirring for over one hour for complete homogenization. Then the mixture was dried, and the residue calcined in a muffle furnace at 450 °C for 12 h. The ashes were dissolved in concentrated hydrochloric acid. Then ^{236}U and ^{229}Th yield tracers were added, and the solution was dried. This procedure is based on the work of Salmon et al. (1984).

The purification stage is illustrated in Fig. 2. Uranium and thorium isotopes were separated from the bulk of the matrix with $C_{12}H_{27}O_4P$ (tributyl phosphate, TBP). First, the actinides (uranium and thorium) were extracted in the organic phase (TBP) from the inorganic phase 8 M HNO_3 (40 mL) in which remain other elements that would interfere in the quality of the source. Then xylene was added, and the mixture of TBP and xylene shaken to break the links of the TBP with the actinides and allow their subsequent extraction in an inorganic phase. The thorium isotopes were extracted in 45 mL of HCL 1 M, and the uranium isotopes in 45 mL of DI H_2O. The thorium fraction has to be re-purified using two ion-exchange columns (Dowex 1 × 8 chloride form, 100–200 mesh) sequentially to eliminate trace amounts of uranium.

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