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Influence of Hg occurrence in coal on accuracy of Hg direct measurement based on thermal decomposition

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To better monitor and control Hg emissions from coal-fired power plants, quantification of Hg contents in coal is essential. Thermal decomposition is widely used to pretreat solid samples. The complete thermal release of Hg in coal samples is a premise for obtaining accurate results of measured Hg contents. The recommended heating temperature is 800 °C for coal samples. The research work in this paper has verified the existence of an abnormal phenomenon, where some Hg occurrences in typical coal at 800 °C could not fully decompose. The temperature-programmed pyrolysis was designed to validate the assumption and determine the optimum decomposition temperature. The results demonstrate that Hg combined with montmorillonite mineral fully decomposes at temperatures above 800 °C. The obtained results help to clarify the relationship between the decomposition temperature and Hg occurrence. The study offers good guidance to improve the accuracy of measured Hg contents by thermal decomposition, thus expanding the laboratory and industrial application.

1. Introduction

Coal-fired power plants are the main sources of Hg emissions to the environment (Pacyna et al., 2006). The UNEP report (UNEP, 2013) states, Hg emissions in China accounted for 1/3 of the global value. In order to better monitor and control Hg emissions from coal-fired power plants, quantifying the Hg content in coal is essential. Hg is one of the hazardous trace elements in coal (Fu et al., 2013), ranging from 0.01 to 1 μg/g (Yudovich and Ketris, 2005), which poses a considerable challenge with respect to obtaining accurate Hg contents. In addition, the measurements are influenced by the occurrence of Hg with other minerals and Hg compounds in individual coal particles (Jongwana and Crouch, 2012; López-Antón et al., 2006; Lusilao-Makiese et al., 2012; Rumayor et al., 2015a; Saikia et al., 2015; Vejahati et al., 2010). The structure and chemical composition of coal is complex (Dai et al., 2012; Mathews and Chaffee, 2012; Speight, 2012), which furthermore makes accurate and precise Hg analysis difficult.

A number of methods for Hg analysis of coal samples have been developed (Clevenger et al., 1997; Kelly et al., 2012; Krishna et al., 2015; López-Antón et al., 2012; Park et al., 2013; Sager, 1993). Among most techniques employed today, inductively coupled plasma-mass spectrometry (ICP-MS) has been used in laboratories for Hg analysis, due to its good sensitivity (theoretically between 1 and 10 pg/ml) (Allibone et al., 1999; Bettinelli et al., 1987; Wilbur, 1999; Wu et al., 1996). However, several problems may appear because of the volatility of Hg compounds and the memory effects, which restrict its use to some extent. For this reason, the conventional methods of measuring total Hg, i.e., cold vapor atomic absorption spectrometry (CVAAS) and cold vapor atomic fluorescence spectroscopy (CVAFS), are more favorable. Before conducting analyses using CVAAS and CVAFS, the pretreatment of coal samples should be carried out. This mainly includes two kinds of techniques: one is chemical digestion (Knechtel and Fraser, 1979; Rahman et al., 2000), and the other is thermal decomposition (Chen et al., 2015). With a long history and high recognition, the former analytical method is widely adopted. However, this method consists of many steps and requires the Hg to be dissolved in solution. It also requires the experimental personnel to be well trained. Hence, there would be higher possibility of sample contamination and errors introduced during the digestive process. With respect to the thermal decomposition method, Hg evaporates from coal samples by heating treatment based on the principle of US Environmental Protection Agency (2007). This technology is favored by industry and laboratories for its advantages of quickness, convenience and high efficiency.

There are several types of commercially available Hg analyzers (DMA) on the market (Ochoa-González et al., 2011; Fuente-Cuesta et al., 2012). They include the DMA-80 Direct Hg Analyzer (MILESTONE), the AMA 254 Hg Analyzer (LECO), the Hydra-C Hg Analyzer (Teledyne Leeman Labs), and the RA-915 + Hg Analyzer equipped with the pyrolyzer PYRO-915. Many researchers have demonstrated 800 °C is sufficient for complete Hg release from their studied coal samples (Biester and Scholz, 1996; Lopez-Anton et al., 2010; Rumayor et al.,

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