

Identification of organic fluorides and distribution of organic species in an anthracite with high content of fluorine



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Fluorine emission from coal combustion not only causes air pollution but also limits the value-added utilization of coal [1–2]. The environmental problems induced by fluorine volatilized during coal utilization have been reported at various countries [3–5]. Fluorosis mainly occurs in developing countries and is induced by drinking water sources [6–8] or indoor coal combustion [9]. Especially, raw coal is directly burned in inverted stoves in the remote area, which exposes residents to the emission of toxic metals and organic compounds with high levels [10].

The modes of occurrence and concentration of fluorine in coals have been studied to understand the chemical behavior during utilization and control the hazardous elements [11–12]. Although the modes of occurrence of fluorine in coals are unknown [10] or under debating [13], most of reports treat fluorine being associated with inorganic constituents (minerals) such as carbonates, fluorite, oxides, phosphates, silicates, and sulfates [12,14–16]. Organic association of fluorine in coals was revealed by float-sink experiments [17]. However, direct proofs for

the modes of occurrence such as molecular formula and structure are needed to verify the organic association of fluorine. The molecular information of organic fluorides in coal may offer useful knowledge to geologists, biologists and chemists to understand the mechanism of biological C–F bond formation during the evolutionary process [18]. At the meantime, attention needs to be paid to the other organic species in coals with high content of fluorine, because the textural relations between hazardous elements and organic components may help predict the potential impacts on environment during coal cleaning, weathering, leaching, combustion and conversion.

The heterogeneous distribution of constituents in solid fossil fuel increases the difficulty in the characterization of organic compounds at molecular level [19–20]. Extraction is a nondestructive method to obtain soluble organic species from coals. The solvent properties, extraction conditions and coal types determine the constituents of extract and residue. Wei et al. used fractional extraction and mass spectrometry (MS) to achieve the molecular level determination for organochlorines and organobromines in coals [21]. Distribution and geochemistry of iodine in coals with different ranks were also investigated [22–23]. Most of the iodine in peat is organically bound, but generally inorganically bound for other ranks.

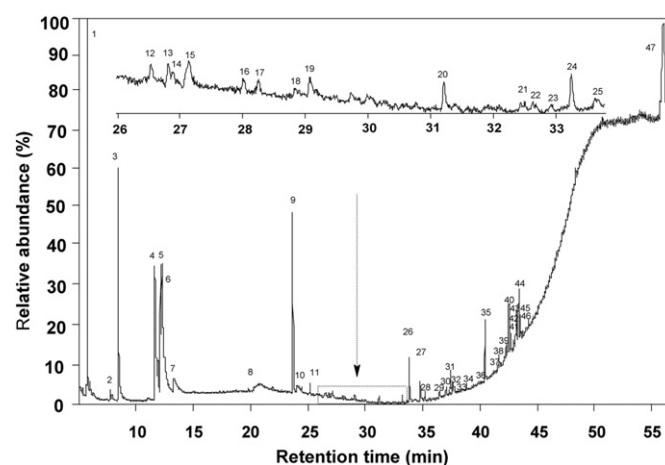


Fig. 1. Total ion chromatograms of SP_M.

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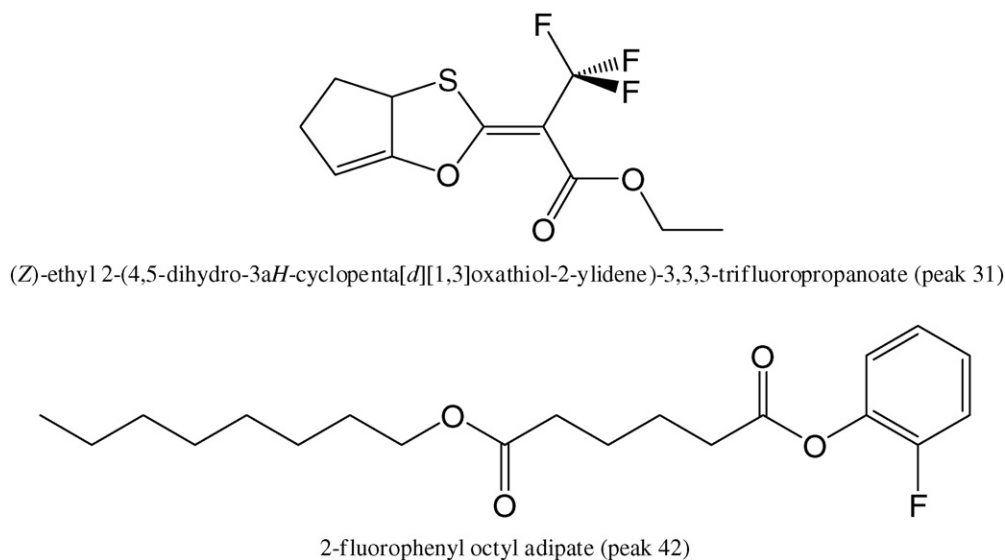


Fig. 2. Chemical structures of two organic fluorides in the methanol fraction (corresponding to peaks 31 and 42 in Fig. 1).

The prevailing view of the organic structure of coals is a three-dimensional macromolecular network and species with low molecular weight scattered inside the network [24–25]. Organic species can be extracted with organic solvents to examine the composition and acquire chemicals [26–27]. However, the extractable species only account for a small portion of organic matter in coal due to the operating conditions under room temperature [26]. Thus extraction may not be a suitable method to separate organic components with low content such as organofluorines from coals. Thermal dissolution of coals can obtain up to 80% of organic matter in the coals, because of decomposition by solvents under supercritical state [28]. Lots of efforts relating to thermal dissolution have been contributed to examine the coal structure through detailed analyses of the extract and the residue, and explore the possibility of preparing clean fuels and/or raw materials for the subsequent conversion [29–31]. But little attention has been paid to utilize thermal dissolution to acquire organic components with low content in coals.

Anthracite coal with high content of fluorine was collected from Zhijin, one of the most severe endemic fluorosis-stricken areas in western Guizhou, China [9]. Methanol and acetone were chosen as the solvents for thermal dissolution, and experimental details are presented in Supplementary information. An Agilent 7890/5975 gas chromatograph/mass spectrometer (GC/MS) and an LTQ-Orbitrap XL ultra-high resolution MS (Thermo Fisher, USA) were applied in the work.

Anthracite with high content of fluorine was collected from Zhijin coal mine located in Guizhou, the southwest province in China, and sealed in a

wide-mouth glass bottle with a corning screw cap to avoid contamination from aerosols. The coal sample was pulverized to pass through a 200-mesh screen followed by drying in vacuum at 80 °C for 24 h. Proximate and ultimate analyses of Zhijin coal are shown in Table S1. Total fluorine content measured according to ASTM D5987-96(2007) (pyrohydrolytic extraction and ion selective electrode methods) is 211 ppm.

Methanol, acetone, carbon disulfide, and n-hexane are analytical reagents and were distilled prior to use with a rotary evaporator. 2.5 g of coal powder and 30 mL of methanol or acetone were put into a 100 mL stainless-steel, magnetically stirred autoclave. The air inside was exhausted by a vacuum pump and nitrogen (99.5%) was flushed into the autoclave as protective gas with a 0.1 MPa pressure. The sealed autoclave was heated to 300 °C and maintained for 1 h. Then it was cooled to room temperature in a water bath, and the reaction mixture was filtrated into filtrate and filter cake. The filter cake was exhaustively extracted with acetone/CS₂ (1:1 in vol.) mixed solvent under ultrasonic irradiation at room temperature to obtain extract and residue. The extract was incorporated with the filtrate followed by elution with 50 mL acetone/hexane (2:98 in vol.) mixed solvent through a silica gel-packed column to obtain eluted fractions. The following analyses and corresponding instrumental parameters are in the Supplementary information.

In the experimental process, the solvents were under supercritical state at 300 °C because the critical temperatures of methanol and acetone are 239 and 235 °C, respectively. The solubility for solid mixture is increased by supercritical method [32]. Shown in Fig. 1 is

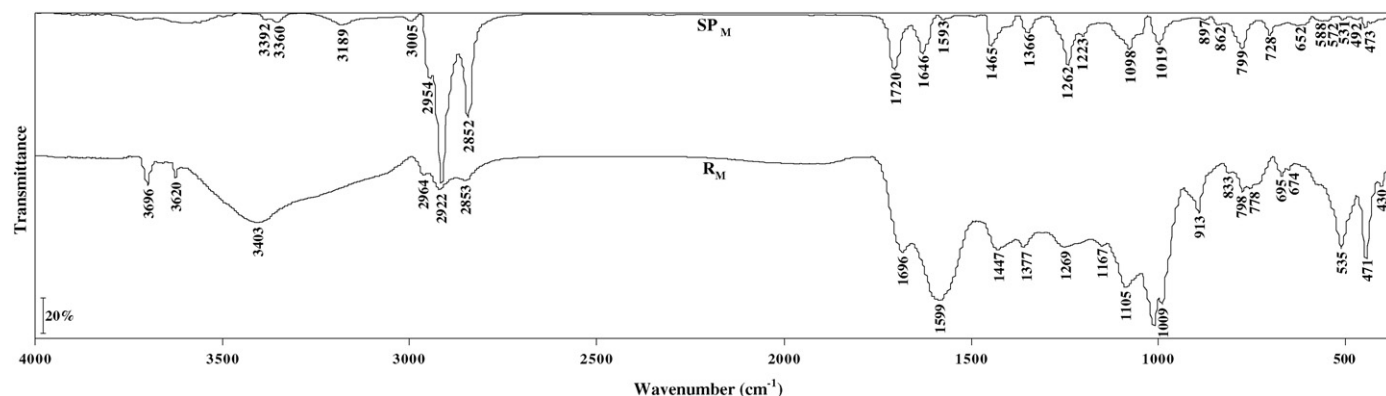


Fig. 3. Infrared spectra of methanol fraction and residue.

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