



## Molecular characteristics of a Chinese coal analyzed using mass spectrometry with various ionization modes



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### HIGHLIGHTS

- Fragments and molecular association may induce more molecules >500 *u* detected by ESI.
- The mechanisms of assisted-ionization for dopant affect the ionization efficiency.
- Direct APPI mode realized ionization of molecules not detected by APPI with dopants.

### ARTICLE INFO

#### Article history:

Received 26 November 2014  
Received in revised form 11 March 2015  
Accepted 4 April 2015  
Available online 9 April 2015

#### Keywords:

Atmospheric pressure photoionization  
Electrospray ionization  
Heteroatom  
Dopant

### ABSTRACT

A Xinjiang subbituminous coal was directly oxidized in aqueous sodium hypochlorite and sequentially extracted with diethyl ether and ethyl acetate. The extracts were esterified with diazomethane and the esterified products were analyzed using a high performance liquid chromatograph/mass spectrometer (HPLC/MS) equipped with atmospheric pressure photoionization (APPI) or electrospray ionization (ESI) ion source. Toluene and a toluene/anisole mixture (vol/vol = 95:5) were used as dopant for APPI-MS. The relative of organic species with molecular mass over 500 *u* detected by ESI-MS is much higher than that identified by APPI-MS with and without dopant. The addition of dopant greatly enhanced the ionization efficiency and toluene induced better ionization effects compared to the mixture in both ion signal intensity and number of detected species. However, according to the ionization mechanism of APPI, a small portion of analytes could be well ionized under direct APPI mode rather than dopant-assisted mode.

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## 1. Introduction

It is important to understand the structure and composition of molecules in coals for effective utilization of coals as feedstock for chemicals [1]. Oxidation has been used as a pretreatment process for the investigation of coal structure [2] and a degradation method to acquire organic acids from coals [3,4]. Lots of analytical efforts, especially mass spectrometry (MS), have been contributed to the understanding of organic species in the derivatives from coal

*Abbreviations:* APPI, atmospheric pressure photoionization; APPI-M, atmospheric pressure photoionization-mixture; APPI-T, atmospheric pressure photoionization-toluene; ESI, electrospray ionization; GC, gas chromatography; HPLC, high performance liquid chromatography; MS, mass spectrometry; TOF, time-of-flight.

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oxidation [4–6]. Artok et al. indicated that aliphatic bridges connecting more than two aromatic rings existed in Taiheiyao coal, because abundant aliphatic polycarboxylic acids formed through oxidation were identified with gas chromatograph/mass spectrometer (GC/MS) [5]. Using a high performance liquid chromatography/MS (HPLC/MS), Kailuan bituminous coal was oxidized by alkali-oxygen at 300 °C to obtain benzenepolycarboxylic acids mainly derived from bridged-bond breaking and aromatic ring opening [4]. Direct analysis in real time MS was applied in the analysis of oxidation derivatives to obtain molecular mass distributions in Shengli lignite [6].

Chromatograph coupled with MS has been proven a powerful tool for identifying unknown species, and developed for separating and characterizing components in coals and coal derivatives [7]. GC/MS is suitable for analyzing relatively volatile, thermally stable, and low polar molecules [8,9]. For the separation and analysis of organic species with higher molecular mass over 500 *u*, and/or

lower thermal stability, HPLC/MS is a better choice [10]. Electrospray ionization (ESI) is suitable for analyzing polar molecules such as polar lipids [11], while atmospheric pressure photoionization (APPI) is available for the analysis of less polar compounds which are poorly ionized by ESI [11,12]. Dopants such as toluene and anisole are always needed for APPI to increase the ionization efficiency [13]. Dopant-assisted APPI has been applied in the analysis of paraquat and diquat in human serum [14], flavonoids [15], and anabolic steroids in urine samples [16], etc. But the application of dopant-assisted APPI-MS for the identification of organic compounds in coals and the corresponding mechanism have not been well studied.

Although various mass spectrometers and other analytical techniques have been successfully applied in the characterization of coal derivatives, the limitations of analytical methods still hamper the identification of organic matter in coals [17], which induces a low efficiency in coal utilization [10]. The ion source of MS serves to convert gaseous, liquid, and solid samples into gaseous ions that can be analyzed while at the same time preserving the properties of interest [18]. For complex mixture like coal derivatives, it is hard to ionize all the organic molecules inside under only one ionization mode because of the limitations in identification of organic species with different polarities [19]. To obtain the complete chemical composition of coals, various ionization methods for MS are required. With regards to the range of analyzed compounds, APPI and ESI are relatively orthogonal ionization sources [20] and can be complementary relying on the analytes and the separation conditions. In the analysis of olive oil, APPI is more sensitive for mono- and diacylglycerol fragment ions, and ESI is suitable for triacylglycerols [21]. APPI is more sensitive than ESI to the analysis of trifluorobenzoic acid [22] and more effective for identifying unconjugated hormones in river water, while ESI is suitable for identifying conjugated hormones [23].

In this work, two ion sources were applied in a HPLC/MS system to obtain more molecular information of oxidation derivatives from a Chinese coal. Effects of toluene and toluene/anisole as the dopant for APPI source were compared and the related ionization mechanisms were discussed. The combination of various ionization modes will explore the understanding of coal structures and facilitate the development of directional coal conversion.

## 2. Material and methods

### 2.1. Samples and reagents

The subbituminous coal sample was acquired from Dzungaria mine in Xinjiang, China. The pulverized coal was passed through a 150-mesh screen and dried at 80 °C for 10 h in vacuum. The proximate and ultimate analyses for the coal sample are shown in Table 1.

Aqueous HCl (36%), aqueous sodium hypochlorite (NaOCl, active chlorine content  $\geq 6\%$ , alkali content 7–8%), diethyl ether, ethyl acetate, NaOH, anhydrous  $MgSO_4$ , and anhydrous  $Na_2SO_3$ , are commercially purchased analytical reagents. All the solvents

for extraction are of analytical grade and were purified by distillation using a Büchi R-210 rotary evaporator (Büchi Labortechnik AG, Flawil, Switzerland) prior to use. All the solvents were filtered with a polytetrafluoroethylene membrane (average pore size 0.22  $\mu m$ ) before HPLC/MS analysis. Toluene and anisole with chemically pure were used as the dopant reagents for APPI.

### 2.2. Extraction procedure

As Fig. 1 shows, the sample was oxidized with aqueous sodium hypochlorite and anhydrous  $Na_2SO_3$  was added to the mixture to decompose excess NaOCl followed by filtration through a 0.45  $\mu m$  organic membrane to obtain filtrate 1 and filter cake 1. Filtrate 1 was acidified with aqueous HCl to pH < 2 to convert  $-COONa$  into  $-COOH$ , then filtrated to acquire filter cake 2 and filtrate 2. Filtrate 2 was extracted with diethyl ether to obtain extract solution 1 and inextractable solution 1, which was repeatedly extracted with ethyl acetate to acquire extract solution 2 and inextractable solution 2. Extract solutions 1 and 2 were dried over anhydrous  $MgSO_4$  and filtrated to remove  $MgSO_4 \cdot nH_2O$ . Organic solvents in extract solutions 1 and 2, and inextractable solution 2 were removed using the Büchi R-210 rotary evaporator to acquire extracts 1 and 2, and inextractable portion, respectively, which were esterified and the esterified samples were analyzed using an Agilent 1200/6210 HPLC/time-of-flight (TOF)-MS coupled with ESI and APPI ion sources. The effects of toluene and toluene/anisole as dopants in APPI ionization were compared and the related ionization mechanisms were discussed.

### 2.3. Instrumentation

The operating parameters (calibrated) for APPI- and ESI-TOF-MS in positive ion mode are listed in Table S1. Dopant for APPI was

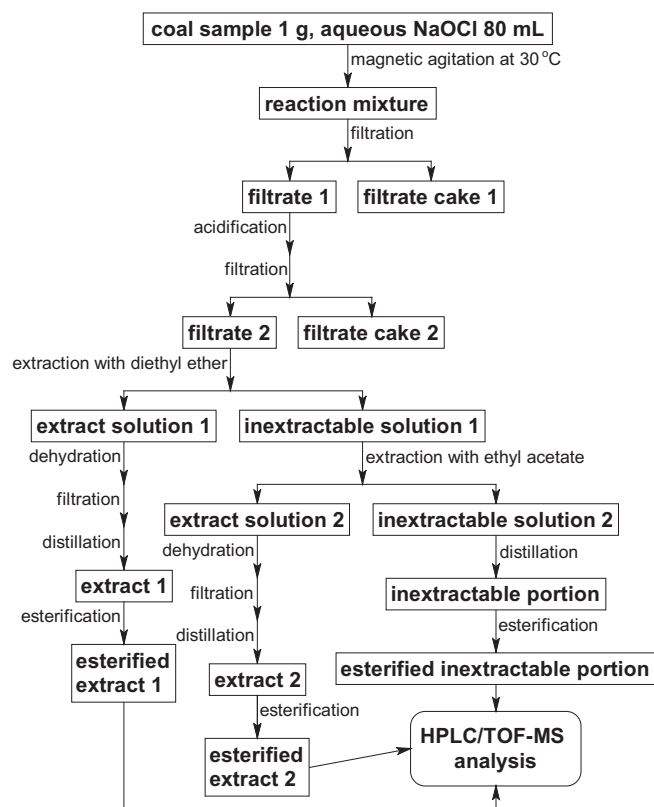


Fig. 1. The experimental procedure.

Table 1  
Proximate and ultimate analyses (wt%) of the coal sample.

Proximate analysis			Ultimate analysis				
$M_{ad}$	$A_d$	$VM_{daf}$	$C_{daf}$	$H_{daf}$	$N_{daf}$	$S_{t,d}$	$O_{diff}^a$
8.68	5.47	35.24	74.54	3.17	0.71	0.56	> 21.02

$M_{ad}$  = moisture (air dried base);  $A_d$  = ash (dried base, i.e., moisture-free base);  $VM_{daf}$  = volatile matter (dried and ash-free base);  $S_{t,d}$  = total sulfur (dry base);  $daf$  = dry and ash-free base.

<sup>a</sup> by difference (dried and ash-free base).

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