Chemical Extraction and Thermal Analysis Methods

Mercury Speciation in Various Coals Based on Sequential Chemical Extraction and Thermal Analysis Methods

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Abstract: Coal combustion is an anthropogenic source of mercury (Hg) emissions to the atmosphere. The strong toxicity and bioaccumulation potential have prompted attention to the control of mercury emissions. Pyrolysis has been regarded as an efficient Hg removal technology before coal combustion and other utilization processes. In this work, the Hg speciation in coal and its thermal stability were investigated by combined sequential chemical extraction and temperature programmed decomposition methods; the effect of coal rank on Hg speciation distribution and Hg release characteristics were clarified based on the weight loss of coal; the amount of Hg released; and the emission of sulfur-containing gases during coal pyrolysis. Five species of mercury were determined in this study: exchangeable Hg (F1), carbonate + sulfate + oxide bound Hg (F2), silicate + aluminosilicate bound Hg (F3), sulfide bound Hg (F4), and residual Hg (F5), which are quite distinct in different coal ranks. Generally, Hg enriched in carbonates, sulfates, and oxides might migrate to sulfides with the transformation of minerals during the coalification process. The order of thermal stability of different Hg speciation in coal is F1 < F5 < F2 < F4 < F3. Meanwhile, the release of Hg is accompanied with sulfur gases during coal pyrolysis, which is heavily dependent on the coal rank.

Keywords: distribution of Hg speciation; coal rank; thermal release

1. Introduction

Mercury (Hg) is regarded as a serious pollutant worldwide to public health due to its volatility, toxicity, persistence, and bioaccumulation in the human body and natural environment [1]. Although the average content of Hg in coal is only around 0.1 mg/kg [2,3], coal utilization through pyrolysis, gasification, and combustion is the main source of global anthropogenic mercury emissions because of the huge consumption in the coal processing industry with a limited Hg control technology [4]. Up to now, a variety of endpipe Hg capture technologies have been developed, but the costly sorbent materials, equipment corrosion, and contamination of fly ash have become unignorable factors [5]. Coal pyrolysis is a promising method for pre-removing Hg before combustion or gasification [5–8]. Several investigations [9,10] have confirmed that Hg release behavior is heavily dependent on the speciation in coal. Except for organic matter-bound Hg, the thermal stability for other Hg forms is similar in all samples from coal preparation plants [11]. Guo et al. [12] reported that Hg released at high temperature was mainly related to the material characteristics in eight Chinese bituminous coals. However, very limited information can be found for understanding mercury speciation in various coals.

In general, the Hg in coal can be represented by organic matrix-bound Hg, adsorbed and occluded elemental Hg, sulfide bound Hg, and silica mineral bound Hg, which is...
generated by geological transformation. These species of Hg are associated with the assessment of toxicity and bioaccumulation based on their special chemical properties in nature [13,14]. Furthermore, the speciation also affects Hg emissions during coal conversion processes such as pyrolysis, gasification, combustion, and liquefaction. Therefore, it is of importance to identify the Hg speciation in coal and the stability of Hg release from coal to understand Hg transformation during the clean coal utilization process.

Although different methods have been suggested to determine Hg speciation, it is disappointing that they are hardly in good agreement mainly due to the complicated chemical structure of coal, together with extremely low content and high volatility of Hg. These methods mainly include direct test analysis (DTA), the float-sink test (FST), statistical analysis (SA), sequential chemical extraction (SCE) procedure, and the thermal treatment method (TTM). DTA uses advanced equipment like x-ray absorption fine structure spectroscopy and x-ray absorption near-edge structure to identify Hg species directly [15–17], however, it was restricted to high Hg content samples [18,19], generally more than 100 mg (Hg)/kg (coal). FST could correlate the Hg content with the main components in different coal samples, divided by several organic solvents with different densities [20]. Finkelman [21] regarded Hg mainly existing in inorganic minerals based on the laboratory float-sink data and analysis of minerals separated from U.S. coals, whilst Wagner et al. [20] found Hg in both the float and sink fractions in FST, meaning organic- and inorganic-bound Hg coexisted in the coal samples. However, FST is mostly used for pre-combustion pollutant control research such as the coal washing process because organic matter cannot be effectively separated. SA was employed to investigate Hg speciation in coal [22–24], which was verified by Dzikol et al. [22] using the correlation between Hg and various forms of sulfur. They found Hg as both organic and inorganic fractions in Polish hard coals. However, the reliability of the SA method requires a huge database.

The SCE procedure was originally developed by Tessier et al. [25] to investigate the fractionation of Hg in sediments. Later, this protocol was improved [26–28] and regarded as a reliable method to determine different kinds of trace elements in coal [29,30]. This method is dependent on special chemical solvents to extract the fraction of Hg in coals step-by-step according to their difference in solubility [31]. Wang et al. [32] found that the Hg in Chinese Yima coal was mainly associated with pyrite and other minerals such as clays, silicates, and aluminum silicates. Even though the opportunity to quantify the speciation of Hg can be offered, the SCE procedure strongly depends on both the extractant selected and extraction method used. Furthermore, few reports have verified the occurrence regularity of Hg speciation in different ranks of coal by using the SCE method.

Currently, two methods of TTM have been suggested to identify the Hg species in coal. One is using synthetic standard reference materials [33–35], which hardly covers all Hg species due to the complicated chemical structure of coal. The other one is to infer the Hg speciation from the Hg release peak during coal pyrolysis by the temperature programmed decomposition (TPD) method, which needs to deal with the overlap of multiple well-resolved peaks, especially at high temperatures. Guo et al. [12] examined the Hg released during the pyrolysis of eight Chinese bituminous coals, and found that Hg species were dependent on the minerals in coal and Hg release at different peaks. However, traditional TTM is difficult to distinguish Hg speciation in the overlapping peaks of the thermal release curve. Meanwhile, thermogravimetry linked with mass spectrometry (TG-MS) has been recognized as a suitable common technique to investigate the pyrolysis behavior of solid fuels, which provides simultaneous and precise information on weight loss and gas products depending on the reaction temperature [36–39]. Once TG-MS is coupled with Hg thermal release performance, a great deal of additional information can be obtained for Hg thermal release with different species in coal, which indicates that the combination of several techniques such as SCE, TTM, and TG-MS is required to understand Hg speciation in coal and estimate the Hg stability of thermal release from coal.

The attention to the Hg of coal has led to requiring information concerning its mode of origin and correlation with the coal matrix in the coalification process. Several attempts
have been conducted on Hg speciation and its release behavior during coal pyrolysis. Goodarzi [40] reported that metallic Hg and organometallic Hg compounds were associated with Hg mineralization. Iwashita et al. [19] showed that Hg removal efficiency varied from 20% to 80% through the mild pyrolysis of different coals. Guo et al. [41] examined six Chinese coals with three coal ranks and found that Hg release from lignite generally began at a lower temperature than that from the other samples. The results from earlier studies demonstrated a strong and consistent association between coal rank and Hg speciation as well as the corresponding thermal release. However, previous studies have tried to use a signal type of coal or one area of coal to explain the Hg speciation for different coal ranks, resulting in an understandable disagreement among each other. Thus far, detailed information about Hg speciation and the influence of coal rank is still limited, especially the relationship between mercury release and its speciation in coals. Therefore, there needs to be further investigation into Hg migration in different species and the corresponding speciation and distribution in different coal ranks. Based on our preliminary results [42], the Hg speciation, its distribution, and thermal stability for 14 coals with different ranks were investigated by combining the SCE and TPD methods. The classification of Hg species was further verified by using TG-MS analysis of weight loss and gas products during coal pyrolysis. The aim of this study was to deeply understand the Hg speciation in coal and the Hg thermal release characteristics from coal, which could guide the control of Hg emissions during coal conversion and utilization such as pyrolysis, gasification, and combustion.

2. Materials and Methods

2.1. Coal Samples with Different Ranks

Fourteen samples with different coal ranks were selected in Shanxi, China, which belonged to peat (P1 and P2), lignite (L1, L2, and L3), sub-bituminous coal (SB1, SB2, and SB3), bituminous coal (B1, B2, and B3), and anthracite (A1, A2, and A3) based on the dry ash-free volatile content calculated from Table 1 in Section 3.1. Each sample was ground and sieved under 61 μm, divided into three portions, and processed, then dried at 105 °C under vacuum for 12 h. The main properties of coal samples such as proximate analysis and two elements of sulfur and mercury were measured in this study. Proximate analysis was performed by using a G20-FT automatic industrial analyzer (Fengtai Ltd., China) to obtain moisture, ash, and volatile matter. Sulfur content was determined by a KZDL-9W automatic sulfur analyzer (Fengtai Ltd., China). Hg content was analyzed using an RA-915M Zeeman cold atomic absorption Hg analyzer coupled with a PYRO-915+ pyrolysis attachment (Lumex Co., Ltd., Russia). The sampling method included triplicate sampling to determine the precision, the introduction of blanks to reduce memory effects, and standards to determine analytical accuracy.

Table 1. Proximate analysis and Hg content of samples (wt %).

| Sample          | Proximate Analysis, wt %, ad | S Content, Hg Content, wt % | ng/g, ad |
|-----------------|------------------------------|-----------------------------|----------|
| Peat            |                              |                             |          |
| P1              | 1.91                         | 51.80                       | 37.18    | 9.11    | 0.11 | 198.7 |
| P2              | 2.19                         | 56.04                       | 32.47    | 9.30    | 0.10 | 184.3 |
| L1              | 3.43                         | 26.88                       | 31.87    | 37.82   | 0.66 | 161.6 |
| Lignite         |                              |                             |          |
| L2              | 1.18                         | 35.67                       | 27.72    | 35.43   | 3.12 | 292.6 |
| L3              | 3.29                         | 28.23                       | 28.18    | 40.30   | 2.32 | 228.7 |
| Sub-bituminous  |                              |                             |          |
| SB1             | 1.09                         | 36.86                       | 24.16    | 37.89   | 0.85 | 181.9 |
| SB2             | 3.29                         | 34.35                       | 22.68    | 39.68   | 0.91 | 172.1 |
| SB3             | 2.70                         | 23.29                       | 26.02    | 47.99   | 0.64 | 164.0 |
| Bituminous coal |                              |                             |          |
| B1              | 2.94                         | 22.57                       | 21.23    | 53.26   | 2.24 | 175.3 |
| B2              | 1.33                         | 18.24                       | 11.52    | 68.91   | 1.16 | 138.5 |
2.2. Hg Speciation Determined by Sequential Chemical Extraction Method

In the sequential chemical extraction (SCE) procedure, magnesium chloride (MgCl₂) solution was used first to remove exchangeable Hg, followed by hydrochloric acid (HCl) to remove the Hg fraction associated with carbonates, sulfates, and oxides, then hydrofluoric acid (HF) to remove the fraction with silicates and aluminosilicates, and finally, nitric acid (HNO₃) to remove the fraction with sulfides, whilst the unextracted Hg in the residue was assumed to be present in the organic matrix. The above reagents were of analytical grade, and deionized water was used in all procedures. Experimental containers were made of glass or Teflon to avoid the loss of adhered Hg, which were previously soaked in 20% (v/v) HNO₃ and rinsed with deionized water. The leached solution was filtered and analyzed for Hg using the cold vapor atomic absorption spectrometry (CVAAS) technique by a Hydra IIAA Hg analyzer (Teledyne Leeman Labs Co., Ltd., USA), whilst the residue in the final stage was analyzed in the same manner for coal samples by an RA-915M coupled with PYRO-915+ pyrolysis attachment. All tests were performed in triplicate and their average values were regarded as the fraction of Hg extracted at each stage. As shown in Figure 1, a detailed explanation of the SCE procedure is follows:

Stage 1: 5.0 g ± 0.001 g coal sample was extracted by 50 mL ± 0.15 mL MgCl₂ to liberate exchangeable Hg (F1). The residue in this stage was free of F1.

Stage 2: The washed residue from Stage 1 was extracted with HCl solution (5 M) to dissolve the Hg associated with carbonates, sulfates, and oxides (F2). The residue was free of F1 and F2.

Stage 3: The obtained residue from Stage 2 was treated by HF (40%) to dissolve the Hg associated with silicates and aluminosilicates (F3). The residue was free of F1, F2, and F3.

Stage 4: 4 M HNO₃ was used to extract the Hg associated with sulfides (F4) from the previous extractions. The residue was free of F1, F2, F3, and F4, indicating the Hg associated with organic matter (F5) in this study.

The extraction at each stage was carried out in a sealed Teflon bottle, which was then placed in an ultrasonic bath for 10 min and rolled for 16 h at ambient temperature. The resulting suspension was centrifuged at 4000 rpm for 20 min. The supernatant was decanted in a vial whereas the residue was washed with deionized water, after centrifugation for 20 min, this second supernatant was added to the leachate. Then, the combined leachate was adjusted into a reasonable concentration range to measure the Hg concentration in the solution. It should be noted that the washed residue was obtained in twice parallel procedures, one of which was used for the extraction at the next stage and the other one was dried at 40 °C for the subsequent pyrolysis process.
In order to guarantee the analytical precision of Hg as a trace element that existed in coal, Hg mass balance was used to examine the reliability of the SCE procedure. As shown in Figure 2, the Hg recovery rate was between 80% and 115% in each coal sample, which was in the range of the 70% to 130% limitation suggested by the U.S. Environmental Protection Agency [43].

2.3. Hg Speciation Determined by Temperature Programmed Decomposition Method

The temperature programmed decomposition (TPD) method was employed to further determine Hg speciation in the coal samples and residues of the SCE procedure at each stage. This method was based on the continuous determination of Hg-compounds released from the solid sample at different temperatures during pyrolysis. As shown in Figure 3, a programmed-temperature-controller furnace was added before a set of a PYRO...
915 furnace and RA-915M Hg analyzer (Lumex Co. Ltd., Russia). Two furnaces were fitted closely to avoid mercury vapor condensing in the connecting quartz tube. Argon was used as the carrier gas for the PTC furnace to eliminate interference and undesired reactions during the thermal decomposition process of the solid, while oxygen was used for the PYRO 915 furnace to ensure all volatile Hg compounds oxidized into atomic form (Hg⁰) for determination by the RA-915 analyzer.

![TPD experimental system diagram](image)

**Figure 3.** Schematic diagram of the TPD experimental system.

In order to obtain a Hg content ranging from 50 ng/g to 372 ng/g in coal with different ranks, preliminary experiments were conducted to check the influence of sample mass, particle size, carrier gas flow rate, and heating rate on the dynamic behavior of Hg release from the sample. A reasonable operating procedure was obtained in this study. Before starting the heating program, the solid sample was ground to less than 61 μm to eliminate the effect of internal diffusion; 1.0 g ± 0.001 g of sample was put in the sample vessel and then introduced into the PTC furnace. The experimental system was purged with argon for 30 min to ensure an inert environment. During each test, the PTC furnace was heated from room temperature to 800 °C in which a heating rate of 10 °C/min was selected to reduce the overlap of mercury release peaks. Argon was maintained with a fixed flow rate of 100 mL/min. The PYRO 915 unit was kept at 800 °C with a flow of oxygen of 200 mL/min.

The replicability of the TPD method to determine the Hg release characteristics in the thermogram was checked by conducting three runs for all samples. Figure 4 is an example of B3 coal at different pyrolysis stages. As shown in Figure 4a, a dish line is obtained by taking the first derivative of the corresponding thermogram. Three regions of Hg release from the pyrolysis of the B3 sample can be categorized by the temperatures of 280 °C and 457 °C, which correspond to zero points of the first derivative during the rising stage. Both the intensity and position of Hg release peaks were similar for three parallel tests (Figure 4a). The average amounts of Hg release were 32.3 ng/g, 56.8 ng/g, and 73.3 ng/g in three pyrolysis regions, whilst the residual Hg in coke was less than 0.3 ng/g. The average Hg content at each pyrolysis stage was acceptable with a relative standard deviation (RSD) less than 3.5% (Figure 4b). Furthermore, Figure 5 shows that the Hg recovery rates of all coal samples were from 95% to 105% with a RSD between 0.9% and 4.6%, which is consistent with Tanamachi et al. [19].
2.4. Coal Pyrolysis in TG Coupled with MS

Pyrolysis characteristics of coal samples were determined by a thermogravimetric analyzer (STA 449F3, Netzsch Ltd., German) coupled with a mass spectrometer (HPR 20, Hiden Ltd., UK), abbreviated as TG-MS. Mass loss depending on the temperature generated from the TG tests reflects the thermal behavior by tracing the compositions of the initial sample, intermediate species, and final residue. In each experiment, 10 ± 0.1 mg of the sample was weighed and then loaded into an alumina crucible in an argon atmosphere with a flow rate of 80 mL/min. Before the heating program was operated, the experimental system was purged with argon for 30 min to maintain the desired environment. The above tests were carried out from an ambient temperature to 850 °C at a fixed heating rate of 10 °C/min.

For the sake of investigating the dependence of mercury on sulfur in the coal sample, the sulfur-containing gases from the pyrolysis process were measured by MS, which was connected with TG through the transfer tube, maintaining a constant temperature of 200 °C. MS was operated on 70 eV of the ionizing voltage of the electron impact ionization source, and the spectrum was scanned at the speed of 100 u/s over a mass range of 1 to 200 u in 0.01 u steps. H₂S, SO, COS, SO₂, and CS₂ were primarily identified based on the ratios of mass to charge (m/z) of 34, 48, 60, 64, and 76 u, respectively. Three parallel runs were carried out for each coal sample, and the result was acceptable for the relative deviation within ±3%.
3. Results and Discussion

3.1. Hg Content in Coal Samples

Table 1 summarizes the contents of mercury and sulfur together with proximate analyses of all coal samples collected in this study. It can be found that Hg content in the samples changed from 112.1 ng/g to 292.6 ng/g with an average of 181.1 ng/g, which is higher than the world’s average of 100.0 ng/g [2,44]. Among these samples were peat (P1, P2), lignite (L1, L2, L3), sub-bituminous coal (SB1, SB2, SB3), bituminous coal (B1, B2, B3), and anthracite (A1, A2, A3). Lignite L2 contained the highest amount of Hg and anthracite A3 contained the lowest. These specific Hg species that respond differently to individual reagents can be studied by the SCE procedure to judge the associations of Hg in coal. Furthermore, the relationship between Hg species with different binding energy and the coal matrix can be examined using the TPD method to evaluate the Hg released from coal.

3.2. Hg Speciation in Coal with Different Ranks

3.2.1. Hg Speciation in Coals

The content of each Hg fraction from the SCE procedure was first converted to Hg concentration distributions by each extraction stage. The content distribution was linked to the volume distribution of the leaching solution from each stage of extraction to transfer into the relative mass distribution of each Hg fraction. Then, the relative content of each Hg fraction in the samples was obtained as shown in Figure 5. Clearly, the major Hg species obviously varied with coal ranks. In all samples, F1 (exchangeable Hg) and F3 (Hg associated with silicates and aluminosilicates) were negligible, corresponding to ranges of 0% to 2.8% and 0% to 5.7% of total Hg, in which F3 is mainly affected by clay minerals in coal. Most Hg in coal exists in F2 (Hg associated with carbonates, sulfates, and oxides), F4 (Hg associated with sulfides), and F5 (Hg associated with organic matters). Generally, F4 accounts for 13.4% to 82.1% and is the dominant species of Hg in all samples, which is consistent with previous reports [8,45]. Each of these samples showed that F1 (exchangeable Hg) is generally not a major fraction of Hg even though it is readily extracted from coals. Virtually, the percentages of F1 in the selected coals were extremely low, which were lower than the detection limitation for most samples, except for 2.8% for B2. Previous studies have shown that F1 sharply varied with the coal samples. Bool et al. [8] thought that F1 leached by NH4OAC was 15% of total Hg in a bituminous Pittsburgh No. 8 coal and 28% in a sub-bituminous Powder River Basin coal. In contrast, Feng et al. [46] found a very small amount of F1 with an average of 0.3% existing in 32 coal samples obtained from Guizhou, China.

F2 (Hg associated with carbonates, sulfates, and oxides) ranged from 20.1% to 56% of total Hg in the sample of P1, P2, L1, L2, L3, SB1, SB2, or SB3, but less than the total Hg in coals of B1, B2, B3, A1, A2, and A3 with 17.2%, 18.1%, 17.0%, 14.7, 14.4% and 1.3%, respectively. Different methods have been employed to examine Hg release from carbonate minerals, which can be used to explore the contribution of carbonate-bound Hg in coal samples. Although some studies suggest that Hg in carbonate minerals can be neglected, this finding needs to be carefully considered. Bool et al. [8] utilized 1:3 HCl as the solution and found that carbonate-bound Hg was 26% of the total Hg in sub-bituminous coal and 22% in bituminous coal. Similarly, Zhang et al. [47] used 0.5% HCl as the solution and reported that carbonate-bound Hg ranged from 10% to 23% in four coal samples from Guizhou, China.

F3 (Hg associated with silicates and aluminosilicates) hosts in SB3, A2, and A3 accounted for 5.2%, 5.7%, and 5.3% of total Hg, respectively, but was less significant in the other samples contributing 0% to 2.9% of total Hg. Finkelman et al. [44] did not observe F3 from five bituminous coal samples, but some studies showed F3 ranging from 9% to 47% [45,47], which is possibly related to the clays in the samples.
F4 (Hg associated with sulfides) was the maximum Hg species in all samples except for P1, P2, and L1. This is consistent with the widely held notion that Hg is mainly combined with pyrite in coal, which was indirectly supported by Finkelman [21,48]. In this study, Hg was extracted from 40.5% (L2) to 82.1% (A3) by HNO$_3$, suggesting a strong pyrite association in these coals. Finkelman et al. [45] reported similar results for 11 bituminous coals.

F5 (Hg associated with organic matters) in fourteen coal samples accounted for 7.7% (A2) to 81.1% (P1), among which peat exhibited the highest content with an average of 77.0%, but anthracite had the lowest value with an average of 28.3%. Different results have been found in previous reports such as 38% F5 in Chinese lignite coal [41], and around 20% F5 in the Eastern Kentucky coal [49], which is largely contributed to organic sulfur [50], especially in peat samples.

3.2.2. Relationship between Hg Speciation and Coal Rank

Despite low Hg content in some samples resulting in some degree of analytical uncertainty, the SCE method can provide reliable quantitative information on Hg speciation in different ranked coals. The percentage of each Hg species in different ranked coals is shown in Figure 6. On average, more than 40% (40.7% on lignite, 51.4% on sub-bituminous coal, 66.2% on bituminous coal, and 74.5% on anthracite) of sulfur bound Hg was removed by HNO$_3$, but only 21.4% of Hg was removed from peat. It can be inferred that the bulk of Hg is bonded to sulfides, especially pyrite, which is the dominant sulfide in coal with a high rank. Hg was detected in sphalerite from Illinois Basin coals [51]. During coalification, sulfide mineralization likely adds Hg mainly due to a strong affinity between sulfur and mercury, which identified that the majority of Hg in coal is mainly related to pyrite [21]. Therefore, the biogeochemical behavior of sulfur in coal reflects the occurrence and origin of Hg to some extent. The formation of pyrite is a gradual process and the coexistence of various pyrite in coal is the product of different evolutionary stages. H$_2$S is produced by decomposing sulfur-containing organic matter such as protein in the process of coal formation dissolved in peat bogs, and then reacts with iron salt (FeCO$_3$) to form into pyrite [52]. Meanwhile, iron salt (ferric sulfate) in water is reduced to iron sulfide through long-term bacterial action. Hg enters pyrite by hydrothermal solution or is absorbed by pyrite from its surroundings. Hg can also exist in pyrite, thought to substitute for Fe$^{2+}$ as Hg$^{2+}$ [53].

Compared to the other-ranked coals, less F4 was found in two peat samples as the lowest rank of coal. However, Hg content in the two peats was similar to that in other high-ranked coal samples. The above fact cannot determine the relationship between sulfide bound Hg and Hg content in peat. The accumulation of Hg in peat usually originates from peat-forming plants, surface waters, and atmospheric Hg emissions [51,54]. As the main component of peat, humus has a strong binding ability with Hg, which identifies that the proportion of organic bound Hg in peat is higher than that in any ranked coals in this study. Peat samples contained 81.1% and 72.9% organic bound Hg, compared to only 10.6% of the average proportion in three anthracite coals. Yudovichet et al. [2] collected the samples from Russia, Ukraine, eastern Germany, China, and the United States, and found that the Hg content in high-rank coal ash was higher than that in low-ranked coal mainly because Hg accumulates gradually and enriches during coal formation.

F2 for Hg associated with carbonates, sulfates, and oxides to total Hg also varied substantially in different ranked coals. The average proportions of F2 in peat and lignite were 31.0% and 38.1%, respectively, and then decreased gradually with coalification, accounting for 25.4% of sub-bituminous coal, 17.4% of bituminous coal, and only 10.1% of anthracite. Similar results were obtained by Bool et al. [8]. Mercury enriched in carbonates, sulfates, and oxides may migrate to sulfides with the transformation of minerals during the process of coalification [40].

While the explanation of such a trend is equivocal, Hg originating from the coal-formation process (such as the humification of peat, early diagenesis, a series of complex
metamorphism) as well as from geologic change (including volcanism, cryogenic magmatic-hydrothermal action, and thermal fracture, sedimentation of rivers and lakes, climatic change) are certainly possible.

Figure 6. Distribution characteristics of five Hg species in coals. (a) Individual result of 14 coal samples. (b) Average value of coals with the same rank.

3.3. Hg Thermal Stability Based on Its Speciation

The thermal stability of each Hg species in coal was obtained by SCE coupled with the TPD experimental procedure. As shown in Figure 7, Hg release started from around 100 °C and completed before 800 °C during the coal pyrolysis process. For all coal samples, the Hg release with the same fraction displayed a similar temperature range and peak position, which demonstrates that the thermal stability is similar for various Hg species. However, one immediately obvious fact is that the extraction ability of Hg is not necessarily correlated with its volatility. For example, F5 is volatilized during the initial stage of pyrolysis and almost entirely driven off at 300 °C. However, F5 is virtually unaffected by any of the solvents.

Exchangeable Hg (F1) was the most unstable during coal pyrolysis, and its release peak was between 100 °C and 150 °C, which was released from coal earlier than all other species. The intensity of release peak by F1 was extremely weak, even below the detection limit of the instrument. Furthermore, it can be found in Figure 7 that not all coals had Hg release peaks below 150 °C, which is consistent with the F1 proportion in coal, as shown in Figure 6. F2 (Hg associated with carbonates, sulfates, and oxides) was detected in all coal samples and released from 150 °C to 250 °C with a peak at approximately 180 °C,
which is in a good agreement with other studies [3,41]. Compared with the distribution of different ranked coals in Figure 6, it can be seen that the area proportion of the release peak of F2 in total Hg was significantly lower in high-ranked coal than that in low-ranked coal, which is consistent with the results obtained by SCE in Figure 6. F3 (Hg associated with silicates and aluminosilicates) was released in all coals except for peat in Figure 7a and sub-bituminous in Figure 7j. The release temperature exceeded 600 °C, which means that F3 was the most stable of all Hg species, although its peak was relatively weak. Because silicate has a high melting point and stable chemical characteristics, it can be reasonably assumed that the combination of Hg and silicate is in a strong binding state. The release peak of Hg associated with sulfides (F4) appeared between 360 °C and 600 °C, which was only lower than that of F3. The overlapping of peaks indicates that there is more than one sulfur-bound sulfur compounds in coal. Windmoller et al. [34] found that Hg escape from pyrite required 450 °C, while Hg desorption in sphalerite had a peak at 600 °C. Therefore, it can be inferred that besides pyrite, Hg is also enriched in sulfides and selenides such as cinnabar, galena, and sphalerite. The release peak of Hg associated with organic matters (F5) appeared as a single peak ranging from 200 °C to 300 °C, which is synchronous with the decomposition of organic matter in coal.

Based on the Hg speciation thermogram during coal pyrolysis, the range of Hg release temperature and relative intensity of the release peaks were quite distinctive for different coals. It can be suggested that the thermal stability of Hg in coal depends on its speciation and coal rank.
3.4. Relationship between Hg Thermal Release and the Weight Loss of Coal

The thermal release characteristics of Hg in the sample from ambient temperature to 800 °C was identified by the TPD method in an argon atmosphere. Taking coal samples L2, SB3, A1 and A3 as examples, Figure 8 shows the Hg release distribution during coal pyrolysis. Clearly, Hg releases from 150 °C to 600 °C with one main peak between 210 °C to 400 °C and the other one between 400 °C to 600 °C. Guo et al. [12] found that the Hg began to release from eight bituminous coals at 150 °C or so and obtained two or three Hg peaks, which is similar to the results in this study. It should be noted that the blue curve in Figure 8 was obtained by taking the first derivative of the release curve of Hg. Every zero point during the rising temperature stage implies the beginning of the next Hg species to be released. Therefore, these points can serve to decide the temperature range of the Hg species interval and to explore the Hg species at each stage. It can be found that the temperature points of approximately 300 °C, 450 °C, and 600 °C for all samples, but a small difference exists between each other. As a whole, the Hg thermal release during the coal pyrolysis process can be separated into four stages.
Figure 8. The thermogram of Hg release in coals: (a) L2, (b) SB3, (c) A1, (d) A3.

Figure 9 displays the release characteristics of mercury depending on the weight loss of coal by using the TPD and TG technique. Taking five samples with different ranked coals as samples, four temperature stages were divided as Stage I (40 to 300 °C), Stage II (300 to 450 °C), Stage III (450 to 600 °C), and Stage IV (600 to 800 °C), which revealed the release of Hg speciation in the coal pyrolysis process. The weight loss amount of these samples was in the order of P1 > L3 > SB2 > B1 > A1, which consists of the characteristics from a low-ranked coal to a high-ranked one.

In Stage I, the weight loss P1 was 10.42% and the corresponding Hg release was 78.44%, which were the highest among all of the samples, whilst the Hg release was from 20.08% to 34.65% for the samples of L3, SB2, B1, or A1 with the weight loss from only 0.80% to 1.53%. The weight loss of each sample mainly includes a loss of moisture and absorbed gases phase as well as the weak bond depolymerization into molecular chains and a part of decomposition from the organic functional groups. The release of Hg speciation contained F1 (exchangeable Hg) and F5 (Hg associated with organic matters), which is consistent with the result in Figures 6 and 7. For F5, the organic bound Hg released belonged to the decomposition of organic matter, indicating that these species of Hg are unstable. Stage II of pyrolysis ranged from 300 to 450 °C, although the weight loss was very low, Hg release was from 19.75% to 35.00%, which demonstrates the majority of Hg, mainly F2 (Hg associated with carbonates, sulfates and oxides) at a thermally unstable state, turns into gas largely due to the decomposition of volatile matters and inorganic minerals. Compared to L3, SB2, B1, and A1, the P1 sample released Hg mainly due to the organic bound Hg enriched in coal. In Stage III, the Hg release from L3, SB2, B1, and A1 accounted for 43.38%, 39.50%, 48.72%, and 37.34% with weight losses of 11.35%, 10.54%, 2.48%, and 2.49%, respectively. The released Hg was determined as F4 (Hg associated with sulfides) based on the results of the SCE and TPD data. The Hg release losses of the five samples in Stage IV only accounted for 1.09% to 2.71%, despite the high weight loss of coal from 3.88% to 5.84%. The released Hg can be ignored, which suggests that there was little F3 (Hg associated with silicates and aluminosilicates) in the coal samples.
Figure 9. The relation of weight loss and the released loss of Hg in different samples. (a) P1 (peat); (b) L3 (lignite); (c) SB2 (sub-bituminous coal); (d) B1 (bituminous coal); (e) A1 (anthracite).

3.5. Relationship between Hg and Sulfur-Containing Gases from Coal Pyrolysis

The affinity between Hg and sulfur makes sulfur-containing substances a major host of Hg in coal. Sulfur in coal is distributed in organic matter including thiols, sulfides, disulfides, and thiophenes, and their derivatives, and in inorganic matter such as sulfate sulfur and pyrite. During the coal pyrolysis process, the majority of sulfur is released into sulfur-containing gases, which can be used to determine the Hg speciation in coal. Figure 10 shows the release characteristics of Hg and sulfur-containing gases from five coal samples during pyrolysis. Herein, m/z = 34 stands for H$_2$S, m/z = 48 for SO, m/z = 60 for COS, m/z = 64 for SO$_2$, and m/z = 76 for CS$_2$. It was found that two obvious release peaks of sulfur-containing gases were located in the temperatures from 100 °C to 400 °C and 450
°C to 600 °C. Meanwhile, obvious release peaks of Hg appeared in similar temperature ranges.

During coal pyrolysis, pyrite is decomposed into sulfur-containing gases together with Hg release in the temperature range between 450 °C and 600 °C, which can be explained because Hg vaporizes during the decomposition of pyrite to pyrrhotite [55,56]. Moreover, the majority of aliphatic and partial aromatic sulfurs in coal can be decomposed when the temperature is lower than 600 °C. The peaks of sulfur-containing gases detected below 450 °C indicate that the release of sulfur-containing gases is largely from the decomposition of organic matter and sulfate sulfur. The previous study showed that distributions of H2S, COS, SO2, and CS2 below 500 °C were directly related to the decomposition of aliphatic and unstable aromatic sulfur such as thiols, disulfide [57]. As the pyrolysis temperature was higher than 600 °C, sulfur-containing gases were still released from the samples selected in this study. These are mainly caused by stable sulfur-containing bridge bonds such as cyclic and aromatic sulfurs and thiophenes. Nevertheless, most Hg was released below 600 °C, but only 1.09% to 2.71% of Hg was released from 600 °C to 800 °C. In general, Hg is primarily released below 600 °C, sulfur-containing gases and Hg was still released from the samples selected in this study. These are mainly caused by stable sulfur-containing bridge bonds such as cyclic and aromatic sulfurs and thiophenes. Nevertheless, most Hg was released below 600 °C, but only 1.09% to 2.71% of Hg was released from 600 °C to 800 °C. In general, Hg is primarily released with pyrite, but with a small amount in organic matter in coal, which is consistent with the Hg species and its thermal stability in the SCE and TPD experiments of the 14 coal samples.

The release of sulfur-containing gases and Hg is heavily dependent on the type of coal during the pyrolysis process, which is mainly concentrated in the low-temperature section for low-ranked coal and transfers to a high-temperature for high-ranked coal. This phenomenon indicates that the Hg speciation in coal is directly related to the coal rank. Figure 10 compares the release of sulfur-containing gases and Hg distributions for five coal samples with different ranks, and shows strong evidence of Hg speciation depending on the coal rank. Significantly, the largest amount of weight loss of pyrolysis occurred below 300 °C from low-ranked coal P1. Furthermore, both sulfur-containing gases and Hg in low-ranked coal were also released in a large quantity below 300 °C compared with other kinds of coals. Therefore, there was a higher content of organic bound Hg in low-ranked coal samples, which is consistent with the thermal stability of F5 from the SCE and TPD experiments.
Figure 10. Evolution characteristics of pyrolysis products. (a) P1 (peat); (b) L3 (lignite); (c) SB2 (sub-bituminous coal); (d) B1 (bituminous coal); (e) A1 (anthracite).

4. Conclusions

The Hg speciation and its thermal stability in different ranked coals were investigated by combining the SCE and TPD methods, and the species was verified by coupling with TG-MS analysis. The main conclusions were obtained as below:

The Hg speciation in coal can be divided into five fractions: exchangeable Hg (F1); Hg associated with carbonates, sulfates, and oxides (F2); Hg associated with silicates and aluminosilicates (F3); Hg associated with sulfides (F4); and Hg associated with organic matters (F5). Among them, F1 and F3 accounted for a small part, whilst F2, F4, and F5 were the main Hg species enriched in coal.

The difference in the proportion of different Hg species in coals is directly related to the coal rank. Hg enriched in carbonates, sulfates, and oxides may migrate to sulfides with the transformation of minerals during the coalification process. The largest proportions of F5 and F4 were respectively in the peat and anthracite samples. When the coalification degree was deepened, F2 and F5 decreased, but F4 increased.

The release behavior of five Hg species was similar in different rank coals. F1, F2, and F5 was released below 450 °C, F3 started to be released above 600 °C, and F4 was released in the temperature range of 450 to 600 °C. Compared to L3, SB2, B1, and A1, the P1 sample released Hg mainly due to the organic bound Hg enriched in coal during the pyrolysis process.

During coal pyrolysis, the simultaneous release of Hg and sulfur-containing gases is closely related to the coal rank, which is mainly concentrated in the low-temperature section for low-ranked coal and transfers to a high-temperature for high-ranked coal.

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