

Distribution of Metallic Elements in Four Group Components of High-Temperature Coal Tar Pitch

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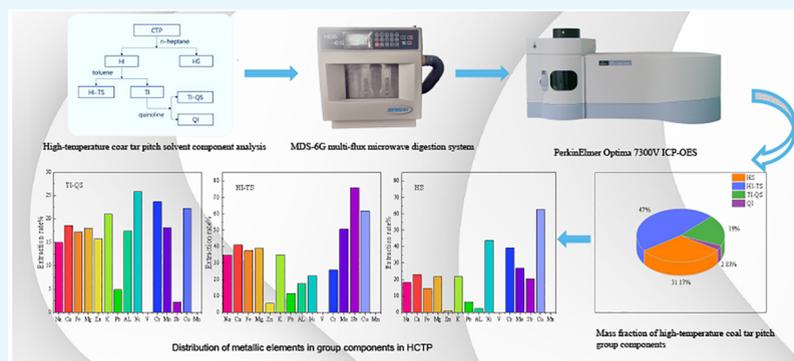
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ABSTRACT: The metallic elements in high-temperature coal tar pitch (HCTP) will affect the properties of carbon materials produced from the HCTP. The study on the metallic elements in HCTP is essential for the quality improvement of its derived carbon materials. In this paper, the content of 15 metallic elements in HCTP and its four group components, including *n*-heptane-soluble substance (HS), *n*-heptane-insoluble–toluene-soluble substance (HI-TS), toluene-insoluble–quinoline-soluble substance (TI-QS), and quinoline-insoluble substance (QI), was determined. The results show that the content of Na, Ca, Fe, Mg, Zn, K, Pb, and Al is more than 100 ppm and is much higher than that of other metallic elements. The content of Ni, V, Cr, Mo, Sb, Cu, and Mn ranges from 0 to 50 ppm. By mass calculation of the contents of four group components in HCTP, it can be concluded that Na and Fe are randomly distributed in the group components. Al, Zn, Pb, V, and Mn are mainly distributed in the inorganic form in the QI component. Ca, Mg, K, Ni, Cr, Mo, Sb, and Cu are mainly distributed in the small molecular group components such as HS and HI-TS.

1. INTRODUCTION

HCTP is the residue of coal tar distillation, which is a byproduct of metallurgical coke production, accounting for about 50–60% of the total coal tar.¹ The chemical composition and structure of HCTP are very complex. It is mainly composed of more than 5000 kinds of polycyclic aromatic compounds with more than three rings and a small amount of high-molecular-weight substances.² HCTP is often used in aluminum and steel industries as an adhesive and impregnant for the production of carbon anode and graphite electrodes due to its high carbon content and easy graphitization. In recent years, it has been widely used as a feedstock for carbon materials such as needle coke, carbon microspheres, porous carbon, and carbon fiber for use in machinery, electronics, aerospace, and military industries.^{3–6}

HCTP contains a small number of impurities, including inorganic salts, organic salts, QI, O, N, S, metal atoms, and other impurities. The presence of impurities leads to the reduction of HCTP reaction activation energy and the increase of reaction rate constant, which is not conducive to the growth

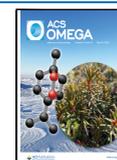
and fusion of mesophase spheres during carbonization of HCTP, reducing the anisotropic region of carbonization products and increasing the thermal expansion coefficient of products, thus affecting the quality of the carbon materials.⁷

Therefore, many researchers have devoted efforts into the research of impurities in HCTP. Also, several commonly used methods to remove impurities such as QI in HCTP are as follows: solvent sedimentation method, solvent extraction method, hot solution filtration method, centrifugation method, supercritical extraction method, etc.⁸ However, more attention has been paid to the removal of QI, sulfur, and nitrogen in HCTP, and there are few studies on metallic elements in

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HCTP because of their low content in HCTP. Although the content of metallic elements is not high, their combination with substances in HCTP can form metallic compounds, which can affect the fluidity, plasticity, adhesion, coking values, and other properties of HCTP,⁹ thus adversely affecting the performance of products manufactured by HCTP. Therefore, the removal of metallic elements in HCTP is highly desired, and consequently, information about the metallic element in HCTP is also required in order to remove the metallic element in HCTP. Thus, an in-depth analysis of the metallic elements in HCTP is necessary for the development of metallic element removal techniques. As a result, the content of metallic elements in HCTP and its four group components was analyzed, and the distribution of metallic elements in HCTP was explored, which is conducive to the deep analysis of metallic elements in HCTP and the development of metallic element removal technologies.

In this experiment, the commonly used group component separation method for HCTP is adopted. Four group components with similar properties and composition are separated by using the different solubility of HCTP in different solvents.¹⁰ HCTP and the four group components have been studied respectively to obtain the content of metallic elements in HCTP and each component, so as to explore the mass distribution of metallic elements among each component, which provides a certain theoretical basis for removing metal in HCTP.

2. EXPERIMENTAL SECTION

2.1. Materials. The HCTP used in the experiment is a kind of high-temperature coal tar pitch, which is from the coke plant in Ningxia province, and its properties are presented in Table 1. All reagents used in this study, such as *n*-heptane, toluene, quinoline, and nitric acid were purchased from Tianjin Comio Chemical Reagent Co. and were of analytical grade.

Table 1. Basic Properties of HCTP^a

AP	SP (°C)	QI (wt %)	A (wt %)	CV (wt %)	S (wt %)
HCTP	74	2.87	0.16	46.74	1.133

^aAP: analyzed project, SP: softening points, QI: quinoline-insoluble substance content, A: ash content, CV: coking value, S: sulfur content.

2.2. Instrument and Analysis. The samples were digested using the MDS-6G multiflux microwave digestion system produced by Shanghai Xinyi Microwave Chemical Technology Company, China. The element of the samples was determined using a PerkinElmer Optima 7300V ICP-OES.

2.3. Method. **2.3.1. Soxhlet Extractor Method for Separation of HCTP.** In this experiment, the four group components of HCTP were separated by *n*-heptane, toluene, and quinoline solvents in a Soxhlet extraction device. The separation process is shown in Figure 1. The specific steps are as follows:¹¹

10 g of HCTP was weighed and put into the extraction pipe of the extractor. Then, 120 mL of *n*-heptane was added into the extraction tube and heated to about 100 °C. In the extraction pipe, the HCTP was continuously extracted by *n*-heptane until the liquid entering the siphon was nearly colorless, and the heating was stopped. The filter paper cylinder in the extraction pipe together with the HCTP was taken out, put into the oven for drying, and then cooled and weighed. Then, *n*-heptane-insoluble substance (HI) was

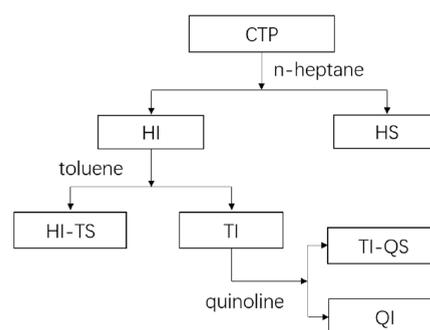


Figure 1. Component separation process of HCTP.

obtained. The solid obtained by solvent recovery of the solution in the flask is *n*-heptane-soluble substance (HS).

The above HI was taken out and put into the extraction tube, and 120 mL of toluene solution was added into the extraction tube to maintain the temperature at about 120 °C. HI was extracted with the same extraction method as above until it was nearly colorless. The filter paper cylinder in the extraction pipe together with the HCTP was taken out, put into the oven for drying, and then cooled and weighed. Then, toluene-insoluble substance (TI) was obtained. The solid recovered by liquid distillation in a round bottom flask is *n*-heptane-insoluble–toluene-soluble substance (HI-TS).

The above TI was taken out and put into the extraction tube, 120 mL of quinoline was added into the extraction tube to maintain the temperature at about 250 °C, and extracted until it was nearly colorless by the same extraction method as above. The solid in the extraction tube was dried and cooled to obtain a quinoline-insoluble substance (QI). Due to the high boiling point of quinoline, the liquid in the round bottom flask is recovered by vacuum distillation, and the obtained solid is a toluene-insoluble–quinoline-soluble substance (TI-QS).

2.3.2. Determination of Metallic Elements. About 0.1 g of HCTP, HS, HI-TS, TI-QS, and QI as well as 10 mL of 70% nitric acid was put into the microwave digestion tank separately for microwave digestion. After digestion, the microwave digestion tank was taken out, left to stand for half an hour, and transferred into a 25 mL volumetric flask for constant volume and prepared for inductively coupled plasma–optical emission spectrometry (ICP-OES). And the elements of Na, Ca, Fe, Mg, Zn, K, Pb, Al, Ni, V, Cr, Mo, Sb, Cu, and Mn in HCTP and in the four group components were determined.

The metal extraction rate (ER) of HCTP is calculated as follows

$$\text{ER} = \frac{M_i \times \eta_i}{M_c} \times 100\%$$

where M_i represents the metal content in each group component, η_i represents the yield in each group component, and M_c represents the content of metal elements in HCTP.

3. RESULTS AND DISCUSSION

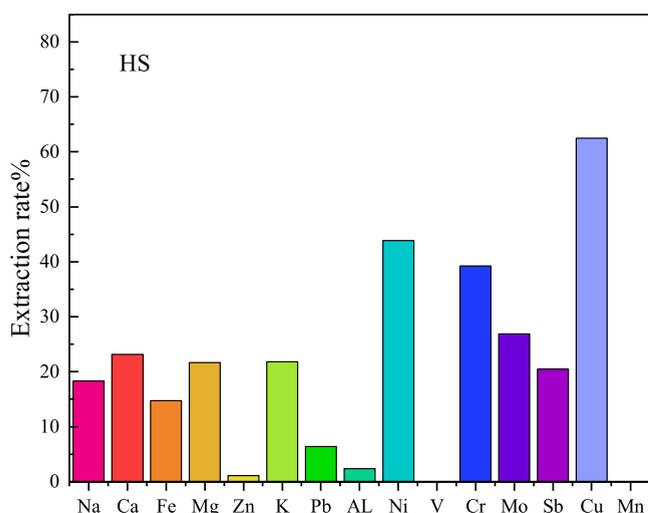
3.1. Content of Metallic Elements in HCTP. The analysis results of the metallic elements in HCTP are presented in Table 2. The content of the metallic elements in HCTP is in the order Na, Ca, Fe, Mg, Zn, K, Pb, Al, Ni, V, Cr, Mo, Sb, Cu, and Mn. The contents of Na, Ca, Fe, Mg, Zn, K, Pb, and Al in HCTP are more than 100 ppm. The content of Ni is 46.1 ppm.

Table 2. Content of Metallic Elements in HCTP (ppm)

samples	HCTP	HS	HI-TS	TI-QS	QI
Na	731.5	429.1	545.4	575.5	8164.7
Ca	402.9	296.9	350.5	391.2	2417.6
Fe	345.3	162.5	276.7	311.6	1928.6
Mg	258.2	179.3	214.5	243.5	627.2
Zn	219.4	7.5	25.5	180.5	2510.3
K	216.5	151.2	162	238.9	859.8
Pb	182.8	37.5	45.2	46.5	2689.3
Al	148.1	11.4	56	136.5	3279.3
Ni	46.1	64.8	22	62.5	128.3
V	8.5	0	0	0	61.9
Cr	7.6	9.6	4.2	9.5	23
Mo	6.5	5.6	7.1	6.2	9.19
Sb	5.2	3.4	8.4	0.6	10.6
Cu	2.4	4.8	3.16	2.8	7.8
Mn	1.5	0	0	0	27.5

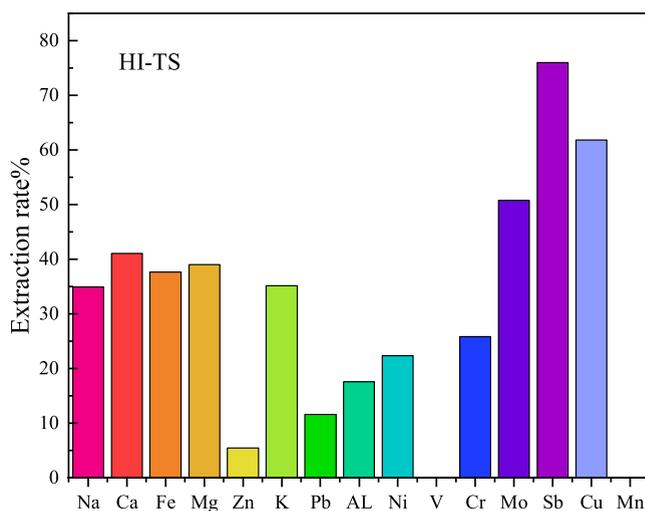
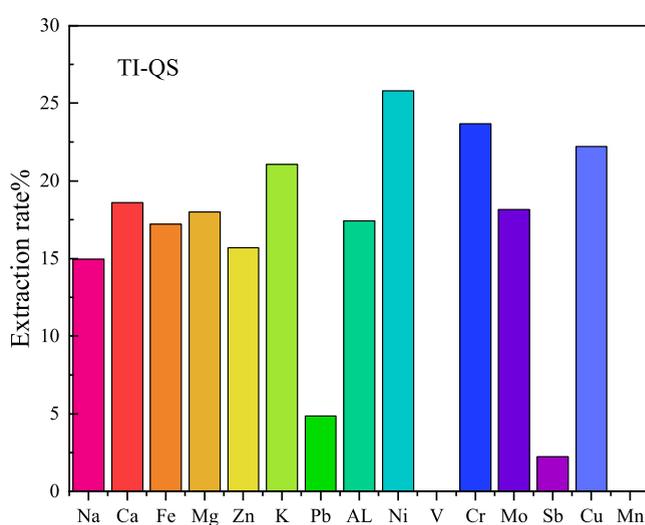
Table 3. Mass and Yield of the Four Group Components

sample	HCTP	HS	HI-TS	TI-QS	QI
mass (g)	6	1.87	2.82	1.14	0.17
yield (%)		31.17	47.00	19.00	2.83

**Figure 2.** Extraction rate of metallic elements in HCTP with the extraction of *n*-heptane.

The contents of V, Cr, Mo, Sb, Cu, and Mn in HCTP are below 10 ppm. Because HCTP is the product of coal tar distillation, the metallic elements in HCTP mainly originate from coal tar. A large number of studies have shown that there are three main forms of metallic elements in coal tar: metal exists in the form of solid particles, metal exists in the form of water-soluble inorganic salts in the emulsified water of coal tar, and metal exists in the form of organic salts in coal tar.¹² Although the proportion of metallic elements in different coal types and coking processes varies greatly, it is not difficult to find that the overall content of metallic elements in coal tar is lower than that in HCTP, indicating that metallic elements are enriched in coal tar pitch during coal tar distillation.^{13,14}

The metallic elements in HCTP mainly come from the following sources. First, the metallic elements present in raw coal itself. Second, coal pyrolysis occurs during coke processing, releasing large amounts of volatilized organic

**Figure 3.** Extraction rate of metallic elements in HCTP with the extraction of toluene.**Figure 4.** Extraction rate of metallic elements in HCTP with the extraction of quinoline.**Table 4. Mass of Metallic Elements in the Four Group Components ($\mu\text{g/g}$ HCTP)**

sample	HCTP	HS	HI-TS	TI-QS	QI
Na	4397.8	804.3	1536.8	658.7	1398
Ca	2405.9	556.5	987.6	447.7	414
Al	896.9	21.4	157.8	156.2	561.5
Fe	2071.8	304.6	779.7	356.6	330.2
Mg	1549.2	335.5	604.4	278.7	107.4
Zn	1316.4	14.1	71.9	206.6	429.8
K	1299	283.4	456.5	273.4	147.2
Pb	1096.8	70.3	127.4	53.2	1043.5

matter into the air, including organically bound metal compounds such as Na, Fe, Mg, Ca, and K.¹⁵ In addition, the electrochemical corrosion from ammonium chloride or ammonia produced in the coal tar process accelerates the corrosion of equipment and pipelines, resulting in the formation of inorganic soluble metal complexes.¹⁶ Na is the most abundant metallic element in HCTP, mainly because sodium carbonate (Na_2CO_3) or sodium hydroxide (NaOH) is

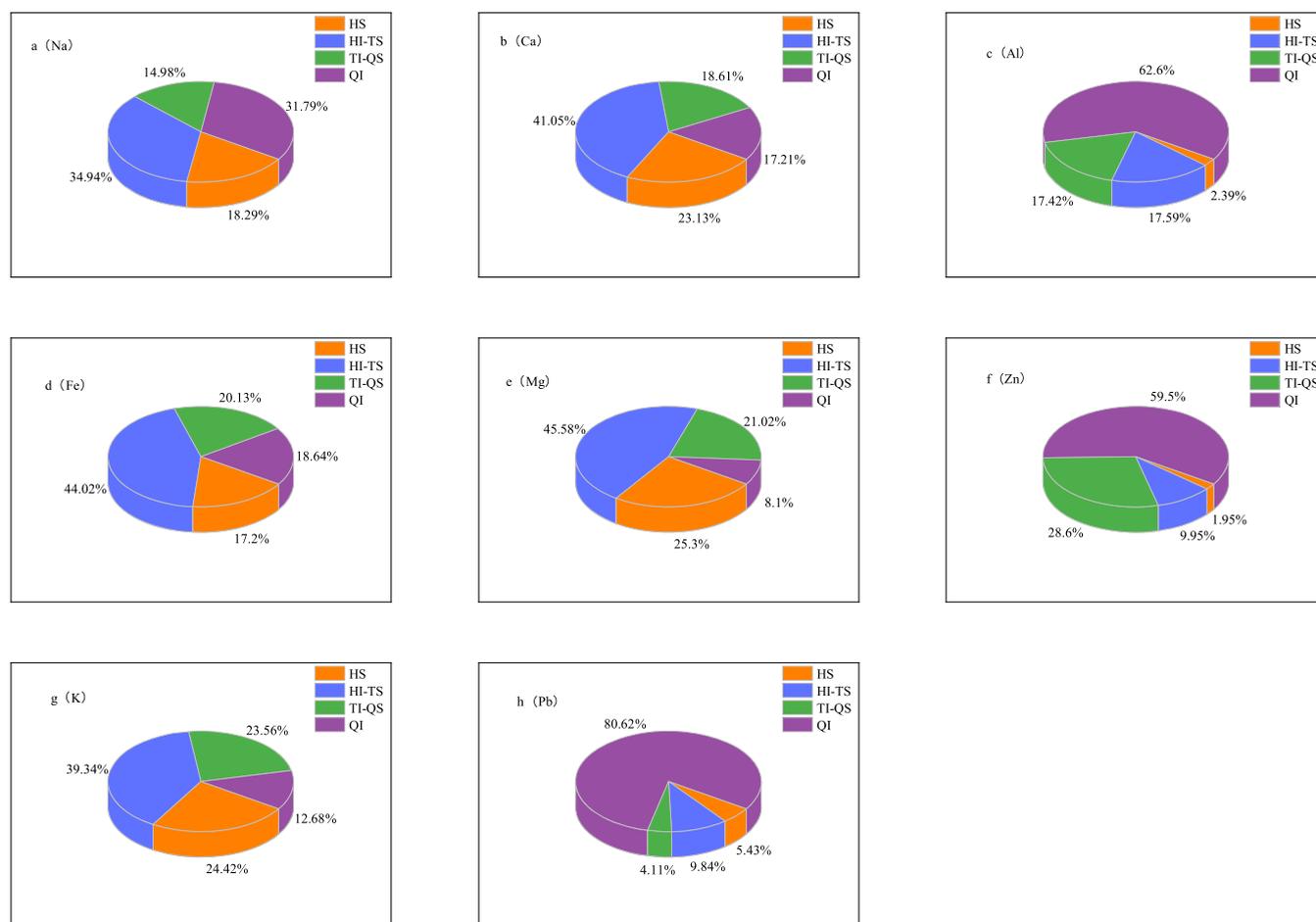


Figure 5. Mass distribution of Na, Ca, Al, Fe, Mg, Zn, K, and Pb.

Table 5. Mass of Trace Metallic Elements in HCTP ($\mu\text{g/g}$ HCTP)

sample	HCTP	HS	HI-TS	TI-QS	QI
Ni	277	121.5	62	71.5	21.9
Cr	45.6	17.9	11.8	10.8	3.9
Mo	39.4	10.6	20	7.2	1.6
Sb	31.2	6.4	23.7	0.7	1.8
Cu	14.4	9	8.9	3.2	1.3
V	21	0	0	0	10.6
Mn	9	0	0	0	4.7

added in the process of HCTP production to neutralize amine chloride (NH_4Cl) and ammonia produced in coal tar distillation.^{17,18}

3.2. Analysis of HCTP Group Components. The four group components, namely, HS, HI-TS, TI-QS, and QI, were obtained with the Soxhlet extractor method mentioned above. The relative molecular weight of HS is mostly less than 100 and contains more alkyl chain structures. The HI-TS component, i.e., γ resin, with a relative molecular weight of 200–1000, is a light component in HCTP and can inhibit the carbonization of HCTP. The TI-QS component, i.e., β resin, is mainly composed of medium- and high-molecular-weight polycyclic aromatic hydrocarbons with high carbon content.¹⁹ The QI component, i.e., α resin, is a heavy component of HCTP, with an average molecular weight of 1800–2600.²⁰

The mass and yield of the four group components are presented in Table 3. It can be seen that the yield of the four group components after extraction with three organic solvents is in the order HI-TS > HS > TI-QS > QI. HI-TS accounts for 47% and HS accounts for 31.17%, followed by TI-QS and QI, accounting for 19 and 2.83%, respectively. In all, HI-TS is the most abundant component in HCTP.²¹

The four group components play different roles in the production of carbon materials due to their different molecular weights and properties. The light group components, i.e., HS and HI-TS, have good wettability and molecular fluidity, which help to reduce the viscosity during the preparation of carbon fiber and make the spinning process more controllable.²² The higher the HS and HI-TS component content, the more conducive to the formation of the streamlined structure of carbon material. However, an excessive light component will result in highly volatile content, reducing HCTP carbon residue rate and affecting the density and mechanical strength of carbon materials. Removing the appropriate number of light group components from HCTP is beneficial for increasing the tensile strength of carbon fiber.²³ TI-QS are conducive to HCTP bondability and play the role of an active center in carbonization. They will contact each other and undergo polycondensation and aromatization, which favors the formation of regional structures during carbonization. The QI component particle is unfavorable for the production of needle coke, as it adheres to the surface of mesophase pellets, hindering the fusion of mesophase pellets and allowing HCTP

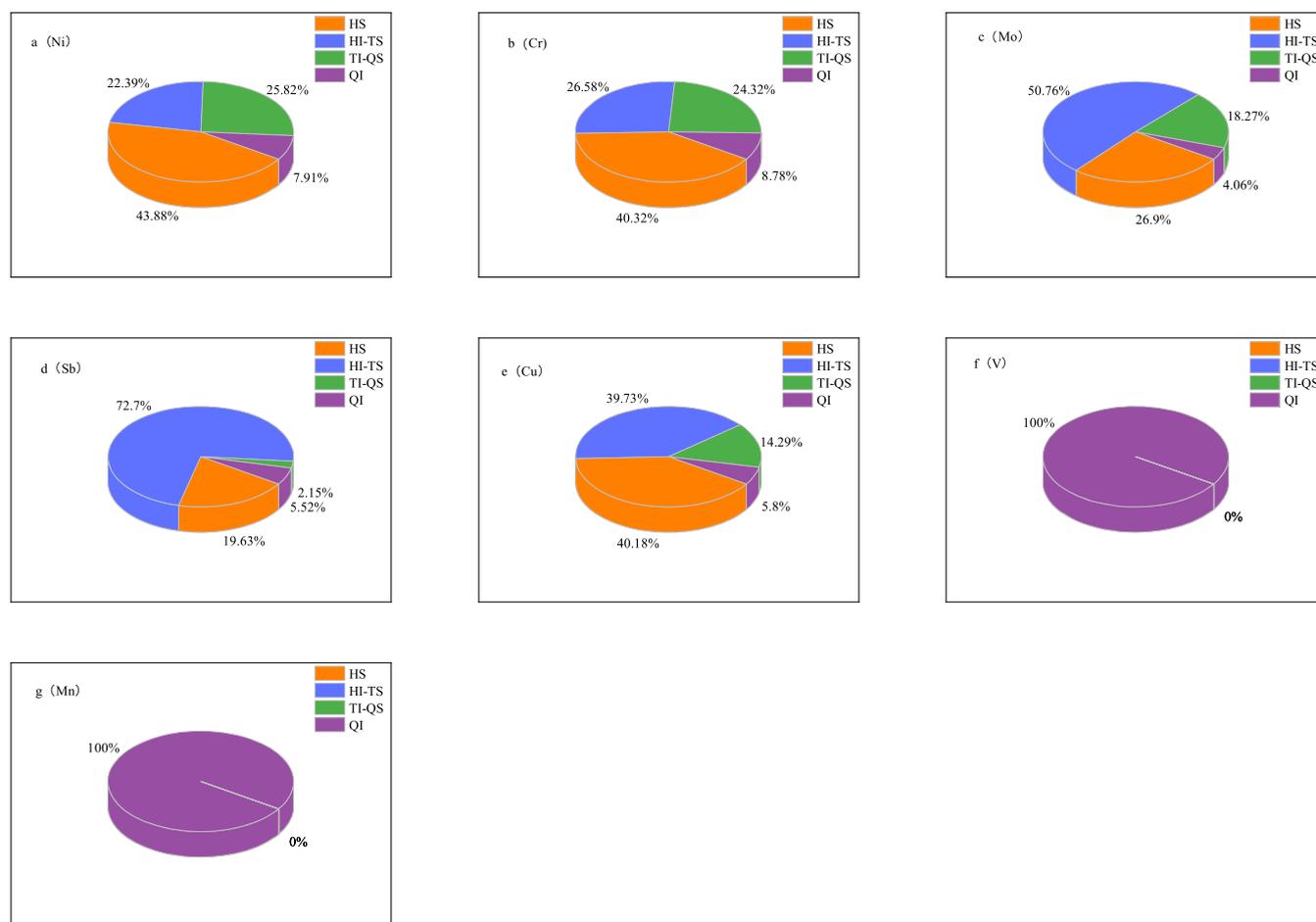


Figure 6. Mass distribution of Ni, Cr, Mo, Sb, Cu, V, and Mn.

to form coke with a mosaic structure. However, an appropriate amount of QI can improve the carbon residue rate of HCTP and increase the density and mechanical strength of carbon materials.²⁴

In conclusion, each group component plays its own role in HCTP. In order to explore the content of metallic elements in each group component, the distribution of metallic elements in the four group components has been investigated.

3.3. Distribution of Metallic Elements in Four Group Components in HCTP.

3.3.1. Distribution of Metallic Elements in HS. From Table 2, it can be seen that the content of metallic elements in HS is in the order Na > Ca > Mg > Fe > K > Ni > Pb > Al > Cr > Zn > Mo > Cu > Sb > V > Mn. The metallic elements' content of Ni, Cr, and Cu in HS is higher than that in HCTP. It indicates that these three elements are highly enriched in HS and exhibit high affinity with small organic molecules. Meanwhile, the content of Na, Ca, Fe, Mg, Zn, K, Pb, Al, V, Mo, Sb, and Mn in HS is lower than that in HCTP, especially the V and Mn content in HS is much lower than that in HCTP and below the detection limit of ICP-OES instrument, suggesting that the V and Mn compounds in HCTP are almost insoluble in *n*-heptane reagent.

Figure 2 describes the extraction rate of metallic elements in HCTP with the extraction of *n*-heptane. It can be seen from Figure 2 that the extraction rate of Ni, Cr, and Cu can reach 40–60%, and the extraction rate of Na, Ca, Fe, Mg, K, Mo, and Sb can reach 15–30%. The extraction rate of Zn, Pb, Al, V, and

Mn is below 10%; especially, the extraction rate of V and Mn is almost zero. The results obtained from Figure 2 are basically consistent with those from Table 2. Figure 2 can more intuitively show that HS has a better extraction effect on Ni, Cr, and Cu, while a poor extraction effect on Zn, Pb, Al, V, and Mn.

3.3.2. Distribution of Metallic Elements in HI-TS. From Table 2, it can be seen that the content of metallic elements in HI-TS is in the order Na > Ca > Fe > Mg > K > Al > Pb > Zn > Ni > Sb > Mo > Cr > Cu > V > Mn. The content of Mo, Sb, and Cu in HI-TS is much higher than that in HCTP. The above results indicate that Mo, Sb, and Cu are highly enriched in HI-TS and show high affinity for organic small molecules. Meanwhile, the content of Na, Ca, Fe, Mg, Zn, K, Pb, Al, Ni, V, Cr, and Mn in HS is lower than that in HCTP; especially, the content of V and Mn in HI-TS is below the detection limit of ICP-OES instrument, suggesting that V and Mn compounds in HCTP are almost insoluble in toluene reagent.

Figure 3 depicts the extraction rate of metallic elements in HCTP with the extraction of toluene. The extraction rates of Mo, Sb, and Cu can reach 50–80%, the extraction rates of Na, Ca, Fe, Mg, and K can reach 30–40%, the extraction rates of Pb, Al, Ni, and Cr can reach 10–30%, and the extraction rate of Zn, V, and Mn is below 10%; especially, the extraction rate of V and Mn is almost zero. The results show that toluene solvent has a better extraction effect than *n*-heptane solvent. Also, it has a better extraction effect on most metals, especially Mo, Sb, and Cu, but a poor extraction effect on Zn, V, and Mn.

3.3.3. Distribution of Metallic Elements in TI-QS. The content of metallic elements in TI-QS shown in Table 2 is in the order Na > Ca > Fe > Mg > K > Zn > Al > Ni > Pb > Cr > Mo > Cu > Sb > V > Mn. The content of K, Ni, Cr, and Cu in TI-QS is higher than that in HCTP. It indicated that these elements are highly enriched in TI-QS and exhibit high affinity for organic macromolecules. Meanwhile, the content of Na, Ca, Fe, Mg, Zn, Pb, Al, V, Mo, Sb, and Mn in TI-QS is lower than that in HCTP; especially, the content of V and Mn is below the detection limit of ICP-OES instrument in HI-TS, suggesting that V and Mn compounds in HCTP are almost insoluble in quinoline reagent.

Figure 4 shows the extraction rate of metallic elements with quinoline. The extraction rates of K, Ni, Cr, and Cu can reach 20–30%, the extraction rates of Na, Ca, Fe, Mg, Zn, Al, and Mo can reach 10–20%, and the extraction rates of Pb, V, Sb, and Mn are lower than 10%. The results show that the quinoline reagent is not as effective as the toluene solvent and *n*-heptane solvent for the extraction of most metals, especially for Pb, V, Sb, and Mn.

3.3.4. Distribution of Metallic Elements in QI. From Table 2, it can be seen that the content of metallic elements in QI is in the order Na > Al > Pb > Zn > Ca > Fe > K > Mg > Ni > V > Mn > Cr > Sb > Mo > Cu. The content of all metallic elements in QI is higher than that in HCTP, indicating that these elements are highly enriched in QI and exhibit high affinity for inorganic molecules. In particular, the contents of V and Mn in the three soluble group components of HCTP are below the detection limit of the ICP-OES instrument, while the contents in QI were 61.9 and 27.5 ppm, respectively, indicating that V and Mn in HCTP are mainly related to QI substances.

3.4. Distribution of Metallic Elements of Na, Ca, Al, Fe, Mg, Zn, K, and Pb in the Four Group Components. Table 4 shows the mass of Na, Ca, Al, Fe, Mg, Zn, K, and Pb in the four group components, and Figure 5 shows the mass distribution ratio of Na, Ca, Al, Fe, Mg, Zn, K, and Pb in the four group components in HCTP.

3.4.1. Distribution of Na Element. Na in HCTP is divided into inorganic Na and organic Na.²⁵ Generally, inorganic Na mostly exists in the form of Na₂SO₄, NaHCO₃, NaCl, and hydrated ion, while a small amount of insoluble Na exists in the form of silicate aluminate. Organic Na is mostly sodium in the form of carboxylate and sodium in the form of coordination on the nitrogen- or oxygen-containing functional groups of the HCTP structure.²⁶ The mass distribution of Na element in HCTP can be clearly observed in Figure 5a. 18.29% of Na in HCTP migrated to *n*-heptane-soluble group components with the extraction of *n*-heptane, while 34.94% of Na migrated from *n*-heptane-insoluble group components to toluene-soluble group components with toluene extraction. After the quinoline extraction, about 14.98% of Na element migrated to the soluble component of quinoline and 31.79% of Na remains in the insoluble component of quinoline.

A higher proportion of Na partitioning in HI-TS and QI verifies that Na is present in HCTP in both inorganic and organic forms. The inorganic form of Na is relatively high mainly because the sodium carbonate (Na₂CO₃) or sodium hydroxide (NaOH) was added to neutralize the amine chloride (NH₄Cl) and ammonia produced during coal tar processing. Overall, the proportion of Na in HS was the lowest. The HS component should be given priority in the preparation of low Na carbon materials.

3.4.2. Distribution of Ca Element. Figure 5b shows that the Ca content in HS, HI-TS, and QS is 23.13, 41.05, and 18.61%, respectively. After the extraction of quinoline, 17.21% of Ca remained in the QI group in the form of inorganic state. Owing to the lowest content of Ca for HS among the four group components (see Table 2), HS should be preferable in order to obtain carbon material with lower Ca content.

3.4.3. Distribution of Al Element. The mass distribution of Al element in HCTP can be observed in Figure 5c. 2.39% of Al in HCTP migrated to HS with the dissolution of *n*-heptane, and 17.59% of Al migrated to HI-TS with toluene dissolution. After the dissolution of quinoline, about 17.42% of Al element migrated to the TI-QS, and about 62.6% of Al is in the insoluble component of quinoline, which further indicates that Al exists mainly in the inorganic form in HCTP. Overall, the HS component is the best choice for the preparation of low-Al carbon material precursors.

3.4.4. Distribution of Fe Element. In Figure 5d, it can be seen that Fe in HS accounts for about 20.13%, and about 44.02% of Fe is extracted into the HI-TS group. After adding quinoline, 20.13% of Fe was extracted into the quinoline-soluble group, and 18.64% of Fe was stored in the QI group in the form of inorganic state. Since the content of Fe in the HS composition is the lowest, the HS component can be used to prepare carbon materials with lower Fe content.

3.4.5. Distribution of Mg Element. Figure 5e shows that about 25.3% of Mg is extracted into the HS group by *n*-heptane, 45.58% of Mg is extracted into the HI-TS group by toluene, and 21.02% of Mg is extracted into the TI-QS group by quinoline. However, the mass fraction of Mg in the most Mg-rich QI group is only 8.1%. Since the content of Mg in HS is the lowest, the HS component can be used as a raw material for lower Mg carbon material.

3.4.6. Distribution of Zn Element. Figure 5f shows that about 1.95% of Zn in HCTP is extracted into HS by *n*-heptane, 9.95% of Zn is extracted into the HI-TS group by toluene, and 28.6% of Zn is extracted into the TI-QS group by quinoline. 59.5% of Zn was stored in the QI group, which further indicates that Zn has a strong inorganic affinity in HCTP and that Zn in HCTP exists mainly in inorganic form. It is best to use the HS component as a precursor for low Zn-carbon materials because of the lowest Zn content in HS.

3.4.7. Distribution of K Element. The distribution of K element in HCTP can be observed in Figure 5g. Figure 5g shows that 24.42% of K element in HCTP migrated to HS with the dissolution of *n*-heptane, while 39.34% of K element migrated to HI-TS after toluene dissolution. After the dissolution of quinoline, about 23.56% of the K element migrated to the soluble fraction of quinoline, and the K element remaining in the insoluble fraction of quinoline accounted for only 12.68%. The distribution of K element in HCTP is essentially similar to that in coal. The K in coal is mainly inorganic K in the form of K chloride and K sulfate, and organic K in the form of carboxylate and coordination on nitrogen or oxygen functional groups in coal structure.²⁷ Since the K content in HS and TI-QS is lower than that in HI-TS and QI, it is the best choice to use the HS and TI-QS component as a precursor for low K-carbon materials.

3.4.8. Distribution of Pb Elements. As can be seen from Figure 5h, Pb in HS and HI-TS accounts for 5.43 and 9.84%, respectively. After quinoline extraction, QS accounts for only 4.11%, and the remaining 80.62% was enriched in the QI component. The uniform distribution of Pb in HS, HI-TS, and

TI-QS and the small distribution of Pb in all three soluble fractions indicated that Pb in HCTP has a weak organic affinity. Pb in QI accounted for more than half of the overall HCTP. It can be inferred that Pb in HCTP has a strong affinity for inorganic molecules. It can be further speculated that the Pb in HCTP is predominantly inorganic Pb and that only a small fraction of Pb is organically bound, which is in agreement with the occurrence state of Pb in coal. Inorganic Pb is reported to be the great majority in coal, and only a small proportion of Pb is found in the combined state of organic matter.²⁸ Therefore, HS, HI-TS, and TI-QS can be used as raw materials for the preparation of low Pb carbon materials.

3.5. Distribution of Trace Metallic Elements of Ni, Cr, Mo, Sb, Cu, V, and Mn in Four Group Components.

Table 5 shows the mass of Ni, Cr, Mo, Sb, Cu, V, and Mn in the four group components, and Figure 6 shows their mass distribution ratio in the four group components.

Figure 6 shows that the mass proportion of Ni in HS, HI-TS, TI-QS, and QI is 43.88, 22.39, 25.82, and 7.91%, respectively. Similar to Ni, the mass proportion of Cr in HS, HI-TS, TI-QS, and QI is 40.32, 26.58, 24.32, and 8.78%, respectively. However, the mass proportion of Mo and Sb in HI-TS is the highest among the four groups. In addition, the mass proportion of Cu in both HS and HI-TS is about 40%. Note that the mass of V and Mn in HS, HI-TS, and TI-QS is 0 and accounts for 20.87 and 52.22%, respectively, in QI.

In summary, the Ni mass distribution in the HI-TS fraction is low and can be used as a raw material to produce low Ni carbon materials. Cr, Mo, Sb, and Cu have a low mass distribution in the TI-QS fraction, so the TI-QS fraction is suitable as a raw material to produce high-quality carbon materials. All V and Mn exist in the inorganic form in QI, so extraction with quinoline is a feasible method to remove V and Mn from HCTP.

4. CONCLUSIONS

Four group components of HCTP with similar composition and structure were obtained by fractional extraction with three solvents: *n*-heptane, toluene, and quinoline. The contents of metallic elements in the four group components of HS, HI-TS, TI-QS, and QI were determined, and the mass distribution of metallic elements in each component was explored. The following conclusions can be drawn:

- (1) The content of metallic elements in HCTP is in the order Na, Ca, Fe, Mg, Zn, K, Pb, Al, Ni, V, Cr, Mo, Sb, Cu, and Mn. The content of Na, Ca, Fe, Mg, Zn, K, Pb, and Al in HCTP is much higher than that of other metallic elements, exceeding 100 ppm. The content of Ni, V, Cr, Mo, Sb, Cu, and Mn ranges from 0 to 50 ppm.
- (2) Na and Fe are randomly distributed in the four group components. Al, Zn, Pb, V, and Mn are mainly distributed in the QI component in the inorganic form, and Ca, Mg, K, Ni, Cr, Mo, Sb, and Cu are mainly distributed in the small molecule group components such as HS and HI-TS.

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Notes

The authors declare no competing financial interest.

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