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A Method for the Quantification of Chlorine in Low-Rank Solid Fuels

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ABSTRACT: This study reports a method for quantifying total chlorine (Cl) in low-rank solid fuels such as biomass and brown coal. It is a two-step method that separates fuel Cl into Cl released in volatiles and that retained in char via slow pyrolysis at 500 °C. The Cl in volatiles is converted to gaseous chloride (e.g., HCl) via in situ volatiles combustion at 950 °C, followed by subsequent collection and quantification. The Cl in char is quantified via conventional Eschka method. The total Cl content in fuel is then calculated as the sum of the Cl in volatiles and that in char. The method is validated using five standard samples (i.e., a high-purity polyvinyl chloride sample, an inorganic-free cellulose char, and three NaCl-loaded cellulose chars of different chlorine-loading levels). The two-step method was then used to quantify the Cl contents in three typical low-rank solid fuels (i.e., a mallee bark, a brown coal, and a water-washed brown coal), benchmarking against those analyzed using the conventional water-washing and Eschka methods. The results suggest that the water-washing method gives similar Cl content in the bark compared to that from the two-step method because all Cl in the bark is water-soluble. However, the water-washing method substantially underestimates Cl content in the brown coal due to the presence of water-insoluble Cl. The conventional Eschka method is capable of quantifying Cl in the brown coal. However, it substantially underestimates Cl content in the bark due to the loss of Cl during Eschka combustion. It is therefore noted that in using the two-step method, the choice of 500 °C as the pyrolysis temperature is essential. This temperature is sufficiently high to avoid Cl loss in char during Eschka combustion and sufficiently low to avoid Cl loss during in situ volatiles combustion.

1. INTRODUCTION

Chlorine (Cl) is commonly present in low-rank solid fuels such as brown coal (or lignite)[1,2] and biomass.[3] During combustion or gasification, Cl is responsible for various operating problems such as ash deposition,[4,5] corrosion,[6,7] particulate matter emission,[8−10] and other ash-related issues.[11,12] Understanding its transformation behavior is important and requires accurate quantification of Cl contents in these fuels.

A number of methods are available for determining Cl contents in solid fuels.[3,13−25] These methods can be briefly classified into three categories, i.e., combustion-based, hydrolysis-based, and extraction-based methods, as summarized in Table 1. The combustion-based methods, including bomb combustion,[26−28] direct combustion,[29,30] and Eschka method,[14,31,32] were extensively employed in some previous publications. Principally, all these combustion-based methods convert fuel Cl into chlorides that are either released as gaseous HCl or retained in ash as chloride salts, followed by subsequent capture and quantification of the converted chlorides. Thus, the complete conversion of fuel Cl, the exhaustive capture/recovery of the converted chlorides, and their accurate quantification are equally important, in order to obtain credible Cl content in solid fuels.

However, it was reported previously that the combustion-based methods may not be able to meet such essential requirements. For instance, the bomb combustion method might encounter incomplete combustion and thereby fail to convert all fuel Cl into chlorides.[33] The direct combustion method faces the challenge of the presence of alkali chlorides (e.g., NaCl and/or KCl) vapors in flue gas because these vapors may condense on and/or react with reactor surface and thereby cause Cl loss.[13] The Eschka method relies on the capture of released Cl, in form of HCl (g) using Eschka flux (sodium carbonate and magnesium oxide) during combustion.[32] However, if Cl is released in forms other than HCl (g) during the early stage of combustion (i.e., pyrolysis), it is questionable whether the Eschka mixture can still effectively trap the released Cl.[34]

The quantification of Cl in low-rank solid fuels such as biomass and brown coal using combustion-based methods (e.g., the direct combustion method and the Eschka method) would be more challenging because of their unique fuel properties. On one hand, these low-rank fuels are generally rich in alkali metals (Na and/or K) that are easily volatilized into gas phase during combustion.[35] On the other hand, Cl in these fuels can be released into volatiles, in forms other than HCl (g), during pyrolysis at relatively low temperatures (e.g., 400 °C). Indeed, our previous study[36] has clearly demonstrated that, during the slow-heating-rate pyrolysis of mallee bark at 400 °C, the majority (∼77%) of Cl released is in forms other than HCl (g).

This study aims to develop a method for the quantification of total Cl in low-rank solid fuels. The method has two steps, taking advantage of slow-heating-rate pyrolysis as a mean to separate total Cl into Cl released in volatiles and that retained in char. The Cl in the volatiles produced from pyrolysis was quantified via in situ combustion and subsequent capture in 0.1 M sodium hydroxide (NaOH) solution. The Cl retained in the char was then determined using the Eschka method. The total Cl in a fuel was then quantified as a sum of the Cl in volatiles and that in char. Various low pyrolysis temperatures (200−500 °C) and several low-rank solid fuels (i.e., a mallee bark, a brown coal, and a water-washed brown coal) were considered. The

Table 1. Methods of Cl Quantification in Solid Fuels

no.	method	Cl species	instrument	temperature	absorption	Cl detection technique
combustion-based methods						
1	Eschka method (AS 1038.8.1−1999,[32] ISO−587[14])	total Cl	muffle furnace	675 °C[14]	diluted nitric acid	modified Volhard method,[32] Mohr titration or potentiometric titration[14]
2	direct combustion (AS 1038.8.2[15])	total Cl	tube furnace	1350 °C,[15] 900 °C[13]	hydrogen peroxide solution	titration,[15] ion chromatography (IC)[13]
3	oxygen bomb combustion (I.S. EN 15289:2011,[16] I.S. EN 15408,[17] D4208−13,[18] D E776−87 reapproved 2009)	total Cl	oxygen bomb		water/alkaline solution, carbonate or bicarbonate solutions or H_2O_2,[16] water or 0.2 M KOH,[17] and 2% Na_2CO_3.[18]	IC/inductively coupled plasma (ICP),[16] IC,[17] ion−selective electrode[18]
4	microwave-induced combustion technique[24]	total Cl	microwave sample preparation system	1400 °C	water or $(NH_4)_2CO_3$ solution	IC
5	elemental analyzer[45]	total Cl	Analytik Jena multi EA 2000	700, 850, or 1000 °C		coulometric detector for gas chlorine, IC for Cl in ash
6	Schöniger flask combustion[45] (EN14582: 2007)	total Cl	Schöniger flask		mixed solution of Na_2CO_3, $NaHCO_3$, and H_2O_2	ion chromatography
7	sintering with ICP−sector field mass spectrometry (ICP−SFMS)[23]	total Cl	Heraeus KM 170 furnace	560 °C (sintering temperature)	water leaching with cation−exchange clean−up, microwave−assisted digestion	ICP−SFMS
hydrolysis-based methods						
8	oxidative hydrolysis microcoulometry[19] (ASTM D6721−01 Reapproved 2006)	total Cl	hydrolysis furnace	900 °C	titration cell	microcoulometry
extraction-based methods						
9	modified Kjeldahl method[46]	total Cl				gravimetric determination
10	extraction with solution of 0.1 M KNO_3 in dimethyl sulphoxide[22]	inorganic Cl			dimethyl sulphoxide	IC and titrimetry
11	water washing[47]	inorganic Cl				Volhard method

two-step method has two key innovations. One is that the volatiles produced from pyrolysis at low temperatures (≤500 °C) at a slow heating rate is free of alkali and alkaline earth metallic species (AAEM species, mainly Na, K, Mg, and Ca),[36] minimizing Cl loss during in situ volatiles combustion. The other is that, after pyrolysis, the Cl in char is stabilized and unlikely to be released during the early stage of the Eschka combustion. The Cl in char can thus be effectively captured using the Eschka method.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. A total of eight solid samples were used in this study. Five samples are standard samples with known Cl contents for method validation. The first standard sample is a high-purity polyvinyl chloride (PVC) sample purchased from Sigma-Aldrich (Product No. 81388). The PVC sample was sieved to 75−150 μm for experiments. It has a standard Cl content of 567.3 mg per g PVC (db) and all Cl is organically bound. The second standard sample is a char prepared from the slow-pyrolysis of inorganic-free microcrystalline cellulose (Avicel PH−101, particle size of 30−50 μm) at 310 °C. The char, referred as "cellulose char" hereafter, is Cl-free. The last three standard samples were prepared via loading a known amount of NaCl into the cellulose char via wet impregnation. Briefly, a known amount of cellulose char was mixed with a solution of water and a known

amount of NaCl in a beaker to prepare char-water slurry. The slurry was then stirred and dried at 35 °C to obtain a NaCl-loaded cellulose char sample. The Cl contents in the three NaCl-loaded cellulose chars are 1.8, 4.6, and 6.6 mg per g of char (db), respectively.

The other three fuel samples were typical low-rank solid fuels (including a bark sample, a brown coal sample and its water-washed coal) for comparing the analysis results from the two-step method with those from the conventional water-washing method and the Eschka method. The Cl in the bark sample is present mainly as inorganic chloride[36] while the brown coal contains both inorganic chloride and water-insoluble Cl.[37] The bark and brown coal samples were air-dried, ground, and sieved to a size fraction of 75−150 μm. The brown coal was also washed using Milli-Q water for 24 h (at a solid to liquid ratio of ∼4 g/L), yielding a water-washed brown coal sample that contains water-insoluble chlorine only. The washed coal was sieved again to 75−150 μm after air drying at 35 °C.

2.2. Production of Volatiles and Quantification of Chlorine in Volatiles via in Situ Combustion. A two-stage pyrolysis/combustion quartz reactor (see Figure 1) was employed for the production of Cl-containing volatiles and its in situ combustion. The reactor consists of two zones, i.e., a fixed-bed pyrolysis zone and a tubular combustion zone. Temperatures of the two zones were controlled individually by two independent electrically heated furnaces that were stacked. There are four steps for an experiment. First, the bottom furnace used for heating the combustion zone was preheated to 950 °C. Second, ∼1 g of sample was loaded into the pyrolysis zone
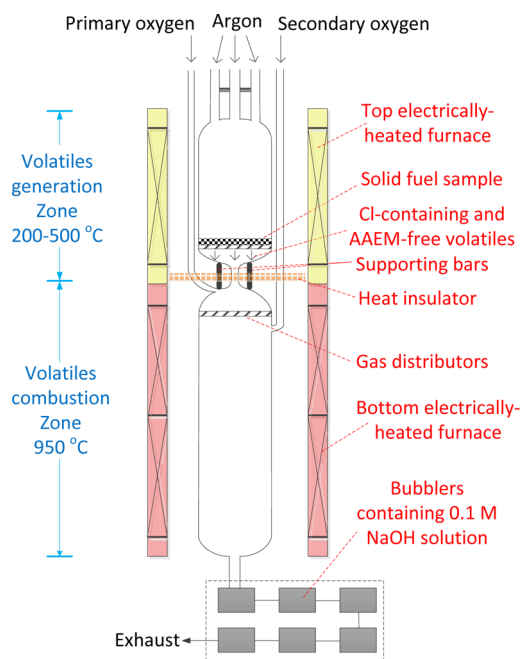
Figure 1. Schematic diagram of a two-stage pyrolysis/combustion reactor system.

of the two-stage reactor. Ultra High Purity (UHP) argon (flow rate: 2 L/min) was introduced into the pyrolysis zone. Two streams of oxygen including 0.4 L/min of primary oxygen and 0.4 L/min of secondary oxygen were introduced into the combustion zone from ports above and below a gas distributor (see Figure 1), respectively. Third, once the combustion furnace reached 950 °C, the two-stage reactor was inserted into the two stacked furnaces from the top furnace. A heat insulator was installed between the pyrolysis zone and the combustion zone of the two-stage reactor to minimize thermal radiation from the bottom furnace (see Figure 1). The outlet of the two-stage reactor was then connected to bubblers that were loaded with 0.1 M NaOH solution. Fourth and last, the top furnace (hence the pyrolysis zone of the two-stage reactor) was then heated from room temperature to a desired pyrolysis temperature (200−500 °C) at a slow heating rate of 10 °C/min, with a further holding time of 10 min at the pyrolysis temperature. Therefore, during the process of fuel pyrolysis in the pyrolysis zone, once produced, the Cl-containing volatiles were immediately burnt in situ in the combustion zone. The in situ combustion converted Cl in volatiles to ionic chloride (most likely as HCl) in flue gas, which was then captured by the NaOH solution. The chloride recovered in the solution was analyzed by ion chromatography (IC, Dionex ICS-1100) with an IonPac AS22 fast analytical column (4 × 150 mm) and 2.25 mM Na_2CO_3/0.7 mM $NaHCO_3$ solution as an eluent.

2.3. Quantification of Chlorine in Chars and Their Parent Fuels. The solid char samples produced from the pyrolysis zone were collected for Cl quantification. Hereafter, solid products from the pyrolysis of the bark, brown coal, and water-washed brown coal samples are denoted as "bark−char−XXX", "brown coal−char−XXX" and "water-washed brown coal−char−XXX", respectively, where XXX represents the pyrolysis temperature (°C). Cl contents in chars were quantified by the conventional Eschka method according to Australian Standard AS1038.8.1−1999.[32] For the purpose of comparison, the Cl contents in the parent fuels were also analyzed using the Eschka method and the water washing method. The water-washing of the bark and brown coal samples was carried out using a semi-continuous leaching procedure detailed in our previous studies.[36,38] For comparison purpose, some char samples were also washed by Milli-Q water under batch leaching conditions for 24 h at a solid to liquid ratio of ∼4 g/L.

2.4. Characterization of Fuel Properties of Chars and Their Parent Fuels. Proximate analysis, ultimate analysis, and analysis of AAEM contents in chars and their parent fuels were conducted using methods detailed elsewhere.[36] Briefly, the proximate analysis of the three fuels studied was conducted using a Mettler thermogravimetric analyzer (TGA) according to ASTM E870-82.[39] Total contents of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) were determined using a Perkin-Elmer 2400 series II CHNS/O elemental analyzer, following Australian Standard AS1038.6.4.[40] Oxygen (O) content was calculated by difference on a dry and ash-free (daf) basis. AAEM species were quantified via ashing, acid digestion, and quantification by IC (model: Dionex ICS 3000) with a CS12A column and 20 mM methanesulfonic acid (MSA) as an eluent.[10] The results are summarized in Table 2. Ignition temperature of selected

Table 2. Properties of Low-Rank Solid Fuels Studied

samples	Mallee bark	Victorian brown coal	water−washed Victorian brown coal
proximate analysis			
moisture, wt % ad[a]	5.7	5.0	4.6
VM[b], wt % db[c]	77.3	51.1	53.1
FC[d], wt % db[c]	18.0	47.9	46.2
Ash, wt % db[c]	4.7	1.0	0.7
ultimate analysis (wt %, daf[e])			
C	48.92	67.71	67.37
H	4.97	4.94	5.14
N	0.23	0.71	0.65
S	0.03	0.26	0.27
Cl[f]	0.42	0.11	0.06
O[g]	45.43	26.27	26.51
contents of AAEM species (wt %, db[c])			
Na	0.1364	0.0901	0.0189
K	0.2589	0.0019	0.0013
Mg	0.2062	0.0632	0.0624
Ca	1.3677	0.0850	0.0837

[a]Air-dried basis. [b]Volatile matter. [c]Dry basis. [d]Fixed carbon. [e]Dry and ash-free basis. [f]Quantified using the two-step method at a pyrolysis temperature of 500 °C. [g]By difference.

chars and their parent fuels was determined using the same TGA, according to a method described elsewhere.[41] Briefly, ∼10 mg sample was heated to 105 °C in argon and held for 20 min to remove moisture. The sample was then combusted in air with increasing TGA temperature to 800 °C at a heating rate of 5 °C/min.

3. RESULTS AND DISCUSSION

3.1. Design and Validation of a Two-Step Method for Quantifying Cl in Low-Rank Fuels. Figure 2 depicts an overview of the two-step method for quantifying Cl in low-rank fuels. Using the two-stage reactor (see Figure 1), total Cl in a fuel sample is separated into Cl released in volatiles and that retained in char via slow pyrolysis at pyrolysis temperatures between 200 and 500 °C. The Cl in volatiles is then in situ combusted, captured in 0.1 M NaOH solution, and quantified by IC (see Section 2.2). In the second step, the Cl retained in char is determined by the Eschka method.[32] The total Cl (Cl_{total}, mg/g fuel, db) can thus be calculated as follows:

$$Cl_{total} = Cl_{volatiles} + Cl_{char} \times \frac{Y_{char}}{100} \qquad (1)$$

where $Cl_{volatiles}$ (mg/g fuel, db) is the Cl recovered in volatiles. Cl_{char} (mg/g char, db) is the Cl content in char and Y_{char} (wt %, db) is the char yield from slow pyrolysis.
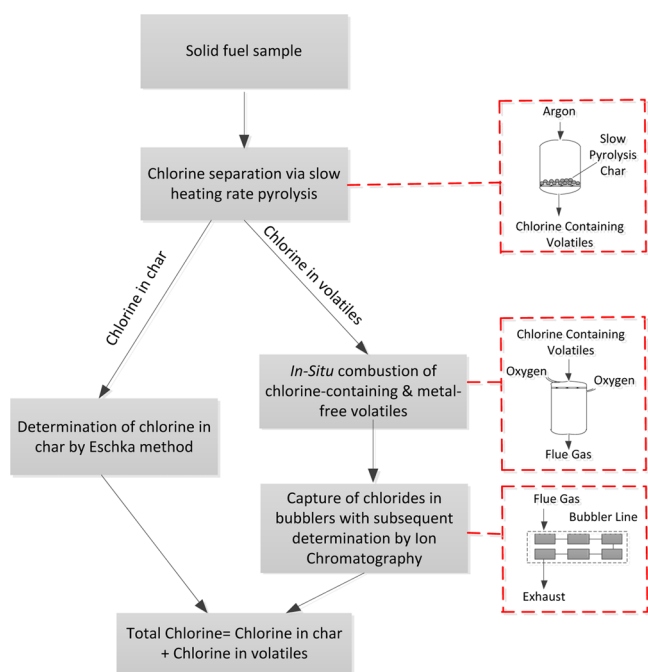
Figure 2. Design of the proposed two-step method for quantifying Cl in low-rank fuels.

Figure 3. Yields of (a) char and (b) volatiles from the slow pyrolysis of the bark, brown coal, and water-washed brown coal samples.

Slow pyrolysis was chosen to separate fuel Cl for three reasons. First, during slow pyrolysis, volatiles are released slowly and progressively. This nature lowers the concentration of combustible matter in volatiles and in turn eases its complete combustion. Second, during slow pyrolysis, volatiles produced can be swept away immediately, minimizing recombination of Cl into char.[36] Third, slow pyrolysis produces volatiles free of AAEM species.[36] At 200−500 °C, the yields of char and volatiles from the slow pyrolysis of the bark, brown coal, and water-washed brown coal samples are shown in Figure 3. Under such slow heating conditions, 100% of AAEM species are retained in char during the pyrolysis of the bark, brown coal and water-washed brown coal samples, as shown in Figure 4. The production of volatiles free of AAEM species is particularly important because AAEM species (especially alkali metals) in volatiles would react with Cl during combustion and the alkali chlorides formed may deposit on and/or react with quartz reactor. In fact, during direct combustion of the bark and the brown coal in a drop-tube quartz reactor at 950 °C, only 1.1 and 0.2 mg of Cl per gram of fuel (db) were recovered from flue gas. Such recovery rates are significantly lower than those (∼4.0 and ∼1.1, respectively) from the in situ combustion of AAEM-free volatiles generated from the slow pyrolysis of these fuels at 500 °C (see subsequent discussion in Section 3.2).

The use of the two-step method at a pyrolysis temperature of 500 °C for quantifying Cl in low-rank solid fuels was then validated using the five standard samples (i.e., PVC, cellulose char, and three NaCl-loaded cellulose chars). Figure 5 depicts the results of method calibration using these standard samples. Close agreement between Cl contents quantified by the two-step method and their actual values clearly suggests that the method is indeed capable of quantifying Cl contents in low-rank solid fuels over a wide range (up to ∼567.3 mg/g fuel, db). The precision of the method was assessed by repeating at least 3 times for each standard sample. The relative standard errors are within 5%, indicating the high precision of the two-step method. Furthermore, Figure 5 also indicates that the two-step
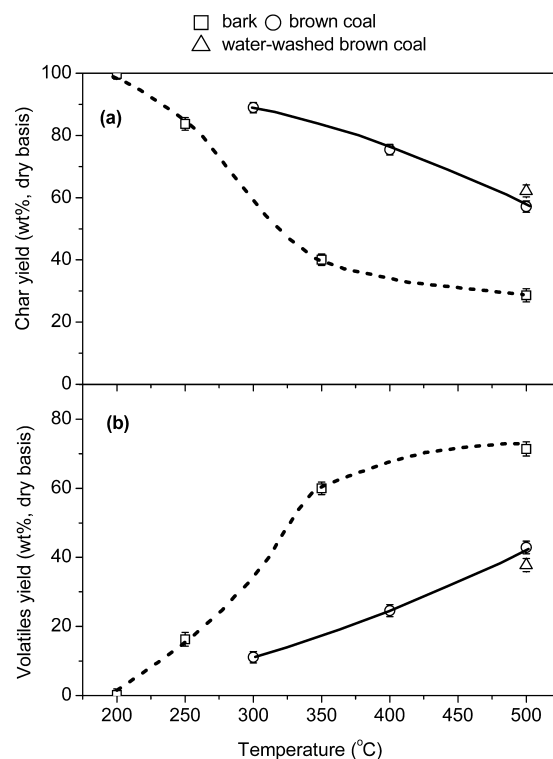
method is widely applicable for quantifying both inorganic and organic Cl in solid fuels, even in the presence of abundant AAEM species.

3.2. Application of the Two-Step Method for Quantifying Total Cl in Low-Rank Fuels. Figure 6 illustrates the total Cl contents of the bark, brown coal, and water-washed brown coal samples, quantified by the two-step method. To investigate the effect of pyrolysis temperature, analysis using the two-step method was also carried out at lower pyrolysis temperatures (200−400 °C). There are three important findings from Figure 6. First, the Cl released into the volatiles during the bark pyrolysis increases rapidly from ∼1.2 to ∼4.0 mg/g fuel db with increasing temperature from 200 to 350 °C and levels off with further increasing temperature to 500 °C. Increasing pyrolysis temperature also intensifies Cl release during the brown coal pyrolysis, but to a lesser extent compared to that of the bark pyrolysis. For both the bark and the brown coal, the increase in the quantified Cl in the volatiles via the in situ combustion method is clearly accompanied with the reduction in the quantified Cl in the corresponding char via the Eschka method.

Second, the total Cl in the bark quantified by the two-step method is also sensitive to pyrolysis temperature. It increases from ∼2.7 mg/g fuel db at 200 °C to ∼4.0 mg/g fuel db at 250 °C and then levels off with further increasing temperature to 500 °C. The validation using the five standard samples demonstrates that as long as released into volatiles, Cl can be completely captured and quantified via the in situ combustion (see Section 3.1). Therefore, the underestimation of the total Cl in the bark at a pyrolysis temperature of 200 °C must be due to Cl loss during the Eschka combustion. This is confirmed by comparing Cl content in bark−char−200 quantified by the Eschka method and that by the water-washing method, as shown in Figure 7. The sum of Cl in the bark−char−200
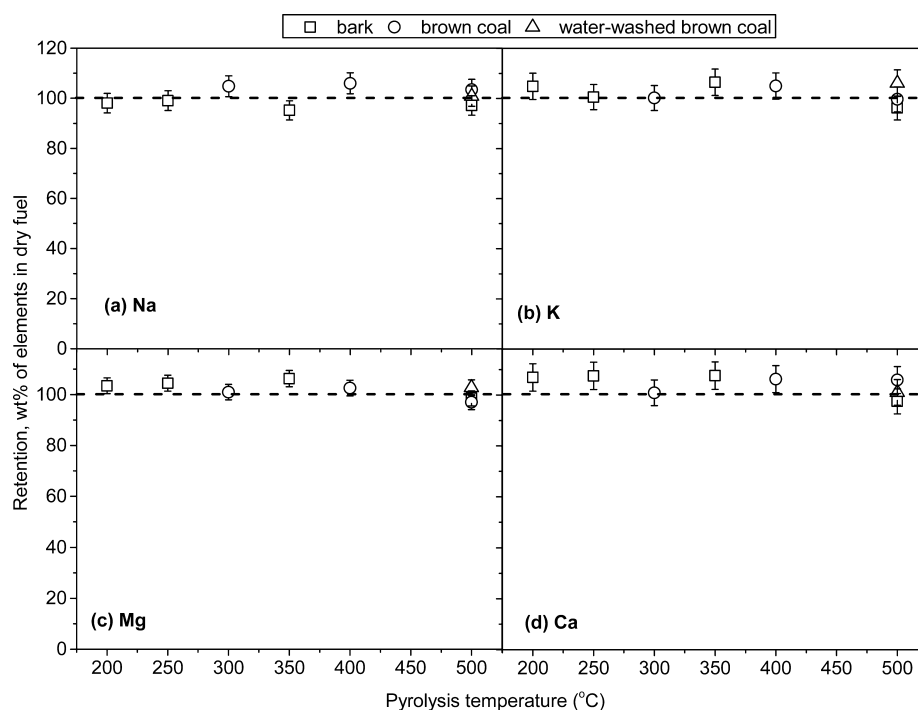
Figure 4. Retentions of (a) Na, (b) K, (c) Mg, and (d) Ca in the chars produced from the slow pyrolysis of the bark, brown coal, and water-washed brown coal samples, as a function of pyrolysis temperature.
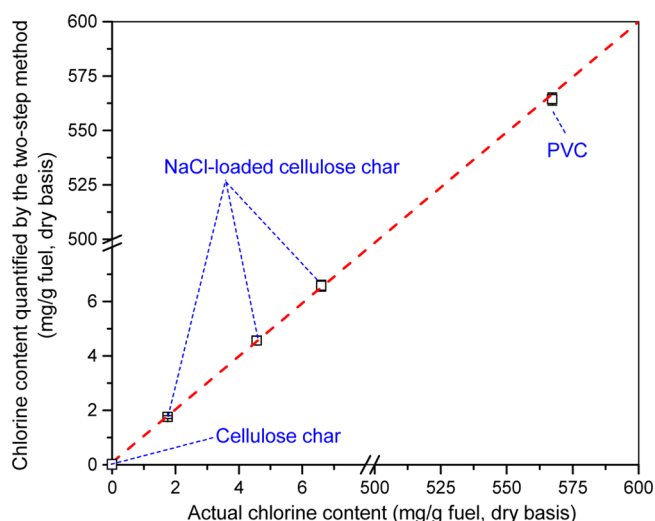

Figure 5. Comparison between the actual chlorine contents in the standard samples and those quantified by the two-step method (at a pyrolysis temperature of 500 °C).

quantified by the water-washing method and Cl in volatiles produced at 200 °C gives a total Cl content of ~4.0 mg/g fuel db. This is similar to the Cl content analyzed using the two-step method at other pyrolysis temperatures, indicating that after the pyrolysis of the bark at 200 °C, the Cl retained in char remains as water-soluble chlorides.

It is known that during the combustion of fuel and Eschka flux mixture, fuel Cl is retained in solid ash in form of chloride salts and/or possibly released into gas phase.[32] The Eschka flux would be only capable of trapping released HCl (g) while Cl released in other forms might escape from the Eschka flux bed.[32] Therefore, Cl loss during the Eschka combustion process is most likely due to the release of Cl into gas phase in forms

other than HCl (g). It was also previously reported that the forms of Cl released are dependent on the stages of combustion process.[36,42] For example, during the early stages where the temperature is low and pyrolysis dominates, a significant amount of Cl can be released in forms other than HCl (g).[36] Once char particles are ignited, during the char combustion stage, Cl is mainly released as HCl (g)[42] and/or retained in ash as solid chlorides under Eschka combustion conditions. Therefore, the Cl loss during the Eschka combustion might be explained by the ignition temperature of the chars and their parent fuels.

Further efforts were thus made to determine the ignition temperatures of the bark, brown coal, and their derived chars sample using the TGA, following a method detailed elsewhere.[41] The ignition temperatures of the chars and their parent fuels are determined and plotted versus char preparation (pyrolysis) temperature (see Figure 8) to assess the stability of Cl in the chars before ignition. If the ignition temperature of a char is lower than its preparation (pyrolysis) temperature, then Cl in the char would be stable before ignition as the char has experienced a higher temperature during pyrolysis. Otherwise, Cl in the char would be released and likely in forms other than HCl (g) before ignition.

Indeed, for the bark−char−200, of which Cl content is significantly underestimated by the Eschka method, its ignition temperature (~263 °C) is considerably higher than its preparation temperature (200 °C). This means that, before the ignition of the char particles, further secondary pyrolysis would take place, during which Cl may be released in forms other than HCl (g). On the contrary, ignition temperatures of bark chars prepared at 250 and 350 °C are either close or lower than their preparation temperatures. The Cl in these chars is thus stable before ignition. Therefore, once these chars are ignited, the Cl would be either released as HCl (g) or retained
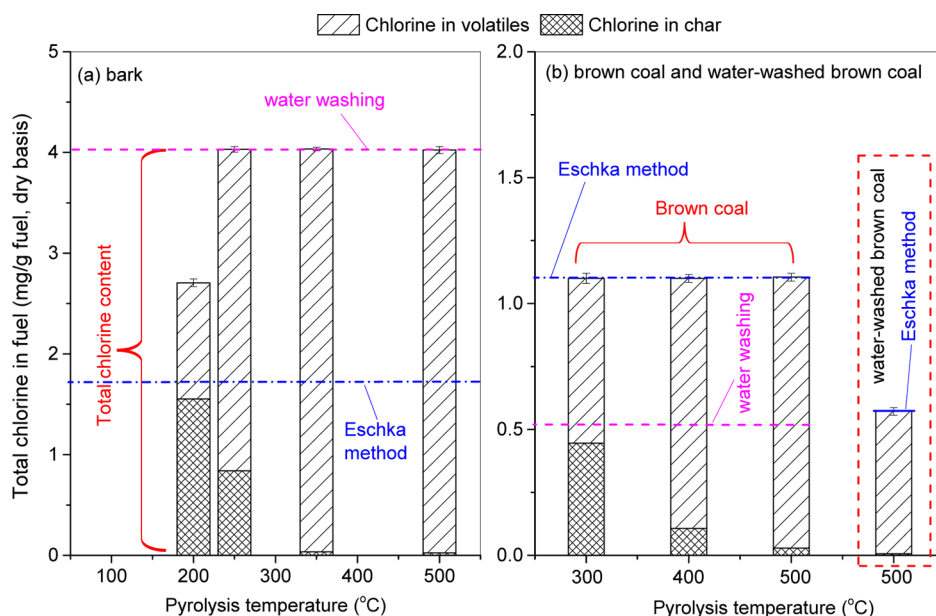
Figure 6. Total chlorine contents in the bark, brown coal and water-washed brown coal samples quantified by the two-step method, benchmarking with those quantified by the water washing method and the Eschka method.
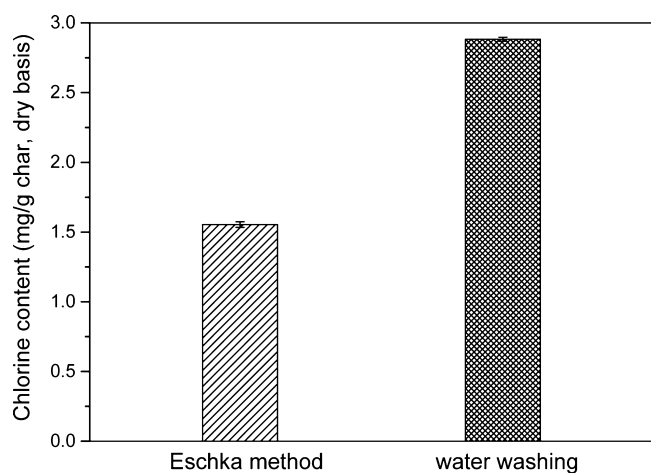

Figure 7. Comparison between chlorine contents in bark char prepared from slow pyrolysis at 200 °C, quantified by the Eschka method and the water-washing method.
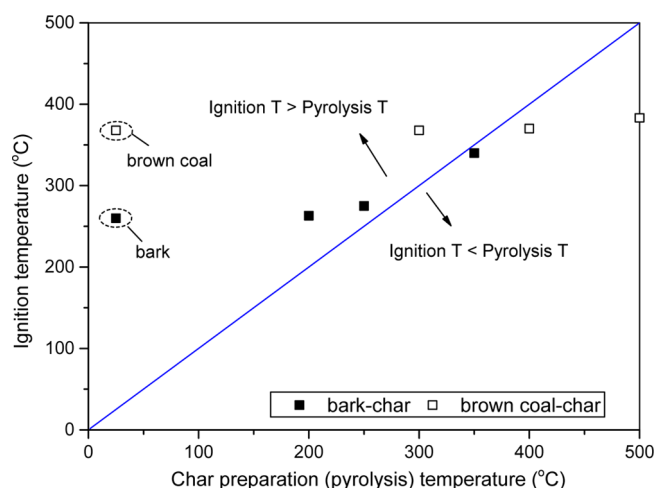

Figure 8. Comparison of ignition temperature of the char samples and their preparation (pyrolysis) temperature.

in residue ash as chloride. Therefore, the Cl in these chars can be efficiently recovered by the Eschka method.

Third, the total Cl in the brown coal quantified by the two-step method is insensitive to pyrolysis temperature. Although the ignition temperature of the brown coal−char−300 is considerably higher than its preparation temperature, the Eschka method does not underestimate its chlorine content. This can be explained by Cl release form during the brown coal pyrolysis. As shown in Figure 9, for the slow pyrolysis of the brown coal at 300 °C, the amount of Cl recovered in the volatiles without volatiles in situ combustion is similar to that obtained via volatiles in situ combustion. This clearly indicates that during the pyrolysis of the brown coal Cl is mainly released as HCl (g) that can be effectively captured and subsequently quantified by the Eschka method. The release of HCl (g) during the pyrolysis of coals of various ranks was also reported in previous studies.[43,44]
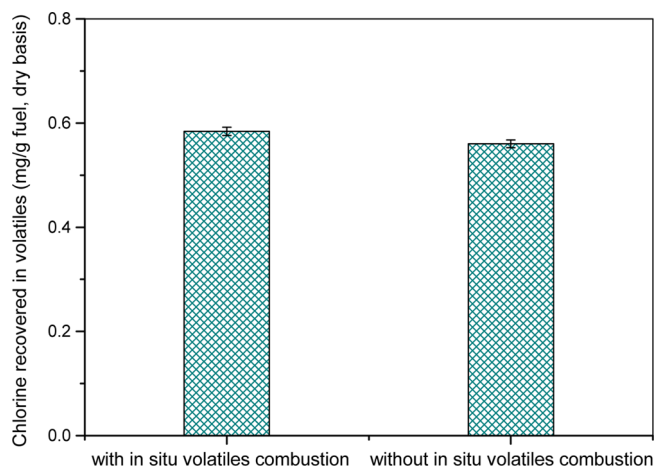

Figure 9. Chlorine recovered from volatiles during the pyrolysis of the brown coal at 300 °C with and without in situ combustion of volatiles.

Overall, the results in Figure 6 highlight that the choice of 500 °C as the pyrolysis temperature is essential to Cl quantification using the proposed two-step method. On one hand, such a pyrolysis temperature is sufficiently high (higher than 250 °C in this study for bark) to ensure that the Cl retained in char is stable enough to be quantified by the Eschka method. On the other hand, such a pyrolysis temperature ensures that 100% of AAEM species in the sample are retained in the char (see Figure 4). Thus, the Cl contents of the bark, brown coal, and water-washed brown coal samples quantified by the two-step method at 500 °C are reported as total Cl contents in these fuels, i.e. ~4.0, ~1.1, and ~0.6 mg/g fuel db, respectively.

3.3. Benchmarking of Two-Step Method against the Water-Washing and Eschka Methods. The Cl contents of the bark, brown coal, and water-washed brown coal samples quantified by the two-step method were then compared with those by the water-washing method and the Eschka method, respectively, as shown in Figure 6. For the bark, water washing gives similar Cl content to that determined by the two-step method. This further confirms that that Cl in the bark is present mainly as inorganic chlorides. However, the applicability of the water washing method is largely dependent on the occurrences of Cl in fuel samples, i.e., only water-soluble chlorides in the fuels can be quantified. This is clearly demonstrated by the fact that the water washing of the brown coal significantly underestimates its total Cl content, because that part of Cl in the brown coal is present in water-insoluble forms.

The data in Figure 6 clearly show that compared to the two-step method, the Eschka method significantly underestimates the Cl content of the bark but gives similar Cl content of the brown coal. As discussed, the Cl loss during the Eschka combustion process of bark is most likely to be associated with the devolatilization (or pyrolysis) process that releases Cl in the forms other than HCl (g). Indeed, as shown in Figure 8, the ignition temperature of bark is ~260 °C, which means that a considerable amount of Cl would be released before sample ignition (see Figure 6). With respect to brown coal, Figure 9 clearly indicates that during the brown coal pyrolysis Cl is released as HCl (g) that can be captured by the Eschka method.

4. CONCLUSIONS

This work has developed a two-step method for the quantification of total Cl in low-rank solid fuels. The method has been validated by five standard samples and employed to quantify the total Cl in a bark, a brown coal, and a water-washed brown coal. Compared to the two-step method, the water-washing method yields similar result on the Cl content of the bark, in which Cl is present in water-soluble forms, but underestimates the Cl content of the brown coal samples due to the presence of water-insoluble Cl. While the conventional Eschka method can quantify the Cl content of the brown coal, it substantially underestimates the Cl content of the bark due to the Cl loss during Eschka combustion. Further investigation shows that in employing the two-step method, a pyrolysis temperature of 500 °C is suggested, at which the Cl loss during volatiles in situ combustion and char Eschka combustion can be avoided.

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Notes
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