Determination of Total Chlorine Content in Sewage Sludge

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Abstract. Cl in sewage sludge may form HCl when burning, and caused acid rain or damaged the chemosphere; meanwhile, it could also enhanced the volatilization of heavy metals. It was important to know the Cl content in sewage sludge. The water extraction method, the Eschka method, the alkali absorption method, the oxygen bomb method, XRF, as well as their combined method were compared and the most suitable method to measure the Cl content in sludge was found. The water extraction- Eschka- alkali absorption method was the best method to measure the Cl content in sewage sludge, and had a good repeatability and veracity.

1. Instruction
With the development of the society, the output of sewage was increasing, and so did the sewage sludge. It was reported that China had an annual sewage sludge output of over 50 billion tons [1]. Sewage sludge was often incinerated for the purpose of reduction and utilization[2]. Sludge combustion may cause chlorine in the sludge to form HCl and enter the atmosphere. HCl in the atmosphere may result in acid rain and damaged the chemosphere. Meanwhile, the migration characteristics of heavy metals was the research focuses because sludge was rich in heavy metals[3]. Many reports had pointed out that chlorine enhanced the volatilization of heavy metals [4-6]. The carcinogenic heavy metals entering the atmosphere will be more difficult to dispose of than that in slag. Controlling the Cl content in the fuel was one of the effective ways to reduce the volatilization of heavy metals. Therefore, it was important to know the chlorine content in sludge accurately. However, there had been no definite measurement method to measure the chlorine content in sewage sludge so far.

At present, there were several methods for the determination of chlorine in solid samples, including the oxygen bomb method, the Eschka method and XRF. Europe had established a method for the determination of chlorine content in solid fuels by oxygen bombs[7]. China had formulated the Eschka method for the measurement of chlorine content in coal in accordance with international standards[8]. XRF was also usually used in chlorine measurements [9, 10].

However, the characteristics of sewage sludge were different from those of biomass or coal. The volatile matter of sewage sludge was much lower than biomass or coal, and the ash was higher[11, 12]. These would result in the worse ignition and burning condition. Meanwhile, the Cl species in sewage sludge was complex. Therefore, whether the above measurement method was applicable or not and
which method was most suitable for the measurement of chlorine content in sludge needed to be further explored. In this work, five methods were carried solely, and their combined methods were also performed.

2. Materials and methods

Sewage sludge was collected from a sewage plant in Guangzhou. It was dried for 72 h immediately and then pulverized to a mesh size of 178 μm. The elemental and proximate analysis (dry basis) of sewage sludge were shown in Table 1. Oxygen content was obtained by subtraction method. However, the Cl content was still unknown. Therefore, the oxygen content was also not given in Table 1.

| Element | C     | H     | N     | S | Ash | Volatile matter | Fixed carbon |
|---------|-------|-------|-------|---|-----|-----------------|--------------|
|         | 13.28 | 2.04  | 2.13  | 0.08 | 68.09 | 28.10           | 3.82         |

The treatment included water extraction method (WEM), the Eschka method (EM), alkali absorption method (AAM), the oxygen bomb method (OBM), and XRF. The Cl content of the solutions that obtained from the different treatments (except for XRF) was determined by chromatography (ICS-900, Dionex) with an AS23 column. All the pretreatment was carried at least twice.

2.1. Water extraction method

Sewage sludge (0.2 g) was added into 40 ml deionized water, and then was oscillated in an ultrasonic wave for 1 hour. The solution was centrifuged at 3500 RPM for 20 min and the upper settling liquid was dumped into a 150 ml volumetric flask. Deionized water (40 ml) was added to the centrifugal tube and the solution was oscillated for 1 h again. The upper settling liquid was dumped into volumetric flask after centrifuge and then was diluted with deionized water to volume. The solution was used for the subsequent Cl content measurement.

2.2. The Eschka method

The Eschka reagent was a mixture of MgO and Na₂CO₃ with a mass fraction of 2:1. Sewage sludge (0.2 g) was mixed with Eschka reagent (0.2 g). The blend was putted into a 15 ml crucible and covered by 1 g Eschka reagent. After burning in a muffle furnace at 680°C for 3 hours, the cooled residue was treated in the manner of water extraction method according to chapter 2.1. The solution was used for the subsequent Cl content measurement.

2.3. Alkali absorption method

Sewage sludge (0.2 g) was burned in a tube furnace at 680°C for 1 h. The gas was absorbed by the NaOH solution in two absorption bottles that was attached to the tail of the tube furnace. The NaOH solution was 0.5 mol/mL and 50 ml to each absorption bottle. After combustion, the NaOH solution was transferred to a 150 ml volumetric flask. The absorption bottles was washed three times with deionized water and the water was also transferred into the volumetric flask. After being diluted with deionized water to volume, the solution was used for the subsequent Cl content measurement.

2.4. The Oxygen bomb method

Absorption solution (25 ml, 2.52 g/L Na₂CO₃, 2.54 g/L NaHCO₃, 0.75% H₂O₂) was added into the oxygen bomb. Sewage sludge (0.1 g) and the ignition wire were placed in the sample tank. The oxygen bomb was filled with oxygen and the pressure was 3 MPa. Then ignite the ignition wire. After combustion, shake the oxygen bomb every five minutes and the whole process was contained for 30 minutes to make sure the gas was absorbed completely. The solution was used for the subsequent Cl content measurement.
2.5. **XRF**  
Sewage sludge (0.2 g) was pressured into tablet. The Cl content was determined by X Ray Fluorescence (XRF, Axios Pw4400, Panaco, Netherlands).

3. **Result and discussion**

3.1. **Comparison of fives single methods**  
The content of Cl in the raw material according to the five kinds of measurements was shown in figure 1. It could be seen that the Cl content varied a lot form different measurements, it was also one of the reasons why the Cl content of sludge had not been accurately measured so far. The Cl content according to the Eschka reagent method was the highest one among the five measurements (0.1570%); what’s more, the error of this measurement was also small enough (±0.00075%). It was believed that the Eschka reagent method was the most plausible measurement among these five.

![Figure 1. Cl content of raw material according to different measurements.](image)

Water extraction method showed 0.0144% Cl content with the smallest error of ±0.00025%. The small error bar showed that it was the most repeatable one; however, the mean value was far away from the Eschka reagent method, showing that a certain proportion of chlorine in the sludge is insoluble. Another method with a small error bar (±0.00060%) was the alkali absorption method. Its principle was the same as the Eschka method. The gaseous chlorine that released during incineration was absorbed by absorber, and the chlorine content in absorber was measured. While the smaller mean Cl content (0.0398%) showed that the NaOH solution was less absorbent than the Eschka reagent. The principle of the oxygen bomb method was similar to that. However, the pressure was higher than the former and the incineration time was much shorter. It could be seen that the error bar in bomb method was the highest one (±0.04721%), which was 91.22% of its mean value (0.0518%), showing that it was the method with the worst repeatability. It was because that the volatile matter of sewage sludge was much lower when compared to biomass[13], as shown in table 1; while the incineration time of oxygen bomb method was much shorter than the Eschka method or the alkali absorption method, resulting in the poor ignition and burning condition. Another method with large error bar was XRF. XRF was mostly used for principal component analysis[14]; however, from all the method, it could be seen that the Cl content in sewage sludge was low. This was one of the reason why XRF could not measure Cl content well. Meanwhile, XRF performed better in the measurement of simple components. However, except for inorganic chlorine, there were still lots of organic chlorine in sewage sludge. Organic chlorine included polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) [15], and the latter came from the sewage that was washed through the rain from the farm into the sewer. Octa- and heptachlorodibenzo-p-dioxins (OCDD and HpCDD) could be also formed during semi anaerobic digestion of sewage sludge at low temperature[16]. Complex components also made XRF a poor measurement of chlorine in sewage sludge.
3.2. Combined and improved methods
The measurement method was further improved and different methods were combined. As big error was found in the oxygen bomb method and XRF, it was believed that the two methods were not suitable for the measurement. The Eschka method was considered as the most reliable measurement; therefore, it was combined with the water extraction method and the alkali absorption method, respectively. The Cl content in raw material according to different combined methods was compared to the single Eschka method, as shown in figure 2.

![Figure 2. Cl content of raw material according to combined methods.](image)

It could be seen that Cl content in the water extraction- Eschka method (WE-EM) was higher than the single Eschka method. If the chlorine in the tail gas was in the form of HCl, the Eschka reagent could capture all the Cl. However, if the chlorine was in the form of CH₃Cl(g), which may be released at 150~350°C, the Eschka reagent was incapable[17]. Although the gaseous Cl was mainly in the form of HCl, it was believed that there was a small part of Cl was in the form of CH₃Cl (g), resulting in the underestimation of Cl by the Eschka method. It was speculated that the pre-treatment of water extraction may reduce the generation of CH₃Cl (g), leading to the more accurate measurements. Cl content in the Eschka method- alkali absorption method (E-AAM) was also higher than the single Eschka method. Although the effect of alkali absorption on Eschka method was less than that of water extraction, it still proved that a part of Cl was not captured by Eschka reagent and escaped. Therefore, neither WE-EM nor E-AAM could measure the Cl content exactly. Hence, water extraction- Eschka- alkali absorption method (WE-E-AAM) was further carried. The water extraction could be seen as the pre-treatment of the Eschka method, and the alkali absorption could be seen as the after treatment. After adding the pre-treatment and the after treatment, the Cl content rose from 0.1570% to 0.1758%. Compared with all the measurement methods carried out, the water extraction- Eschka- alkali absorption method was considered to be the closest to the real value.

The relative standard deviation (RSD) and relative error (RE) were calculated to know the repeatability and veracity of the water extraction- Eschka- alkali absorption method. In this method, the RSD was 0.2980% and the RE was 0.4215%, proving that this method had a good repeatability and veracity.

4. Conclusion
The water extraction- Eschka- alkali absorption method was the best method to measure the Cl content in sewage sludge. It had a good repeatability and veracity with a RSD value of 0.2980% and a RE of 0.4215%. According to this method, the total Cl content in sewage sludge was 0.1758% and the soluble Cl content was 0.0144%.
Acknowledgements
This work was supported by Guangzhou Science Research Program Key Project (201804020082), Guangdong Province Key Laboratory of Efficient and Clean Energy Utilization (2013A061401005, South China University of technology); General Administration of Quality Supervision, Inspection and Quarantine of the PRC Projects (2017QK152).

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