

REMOVAL OF ORGANIC HALOGENS FROM INORGANIC CHLORIDES BY ACTIVATED CHARCOAL IN AIR SAMPLES

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ABSTRACT

Determination of inorganic chloride from stationary sources in the presence of organic chloride compounds is of great importance during the analysis. The amount of released inorganic chloride into atmosphere was determined with burned refuse-derived fuel (RDF) originated plastic wastes according to the rule of Hazardous Waste Regulations. Organic chlorides absorbed in scrubber solution during the sampling time interfere for analysis of inorganic chloride by ion chromatography. Organic chlorides are removed by using two different activated charcoal tubes so that inorganic chloride analysis is provided more reliably. Recovery of inorganic chloride levels in the scrubber solution was obtained approximately 50% by using granular activated charcoal where these levels increased by approximately 95% when it is passed from the powdered activated charcoal. The amounts of chlorides were obtained 0.13, 0.50, 0.91 mg Cl/Nm³ using 0%, 8%, 12% and 15% RDF ratio after Di.Elle activated charcoal and 0.13, 0.63, 0.93, 1.13 mg Cl/Nm³ using 0%, 8%, 12% and 15% RDF ratio after Merck activated charcoal. Results show that powdered activated charcoal is more effective than granular activated charcoal.

KEYWORDS:

air sample, chloride, activated charcoal, analysis

1. INTRODUCTION

Discharge of industrial wastes from chemical industry activities, components of the urban solid waste and the leaching from agricultural and forest land are the main sources of organic pollution in water streams. These compounds are used on a large scale even in everyday and may be industrial effluent contaminants. Some of them are toxic and slow to biodegrade, they accumulate in the environment [1-3].

There are a variety of methods available for removal of organic pollutants from wastewater and the most important of them are reverse osmosis, electrochemical oxidation, incineration, ion exchange, precipitation, and adsorption. Of those adsorption is by far the most versatile and widely used method for the removal of toxic pollutants as it is inexpensive and eases to use operation. Different materials are used as adsorbents for the removal of different pollutants. Activated charcoal (AC) is frequently used for the removal of organic pollutants from wastewater for more than three decades [4-12].

AC are known as very effective adsorbents due to their high porosity, large surface area (that can reach 3000 m² g⁻¹), and high adsorption capacity. This is a very versatile material show that the unique properties of AC, which has not been used only as adsorbents, but also used as catalysts and catalyst supports for different purposes such as the removal of pollutants from gaseous or liquid phases and the purification or recovery of chemicals. Despite the satisfactory results obtained using some of these low-cost adsorbents, AC are known to be more effective adsorbent for removal of greater amount of pollutants than other adsorbents [3, 13].

The most important characteristics of AC in the adsorption of organic compounds are pore size distribution, surface chemistry (functionality) and mineral matter content. Adsorption capacity is defined as the accumulation of the solute molecules at the surface of a solid. This capacity is directly proportional to the area of the surface exposed and is dependent on the solute partial pressure and the temperature. Coal-based activated carbons are typically used to remove both low-molecular weight hydrocarbons, such as chlorinated organics, and high-molecular weight materials, like pesticides [14-16].

RDF technology can be applied in large municipal solid waste (MSW) facilities. RDF is a fuel produced from flammable components of the urban solid waste. RDF production consists of grinding, classification and disposal operations in order to remove metal components from the solid waste. The last step of RDF production is to bring the samples to a uniform size by shredding. RDF pellets compared to clean coal are environmentally friendly, en-

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ergy efficient and provide advantages in removing dust [16-21].

The aim of this study is to analyze the released inorganic chloride into the atmosphere during incineration of plastic originated RDF. However, other organic halogens may pass into the scrubber solution and interfere with the detection of inorganic chloride by ion chromatography. So this study has been done to resolve the problems using two different activated charcoals.

2. MATERIALS AND METHODS

All chemicals were of analytical reagent grade and used without further purification. Deionized water of 18.2 M Ω cm resistivity obtained from a Milli Q-water purification system (Millipore) used for the preparation of all solutions. Sampling and analysis of studies were carried out in TUBITAK MRC laboratory which accredited by German DAR/DAP according to DIN EN ISO / IEC 17025:2005 and Zambelli 6000 equipment was used for sampling with isokinetic conditions.

2.1. Sampling

In this study, the plastic wastes originated RDF 0%, 8%, 12% and 15% has been disposed of by burning under Hazardous Waste Control Regulation. Limit values have been determined according to the regulation in case of waste disposal by burning for release of pollution parameters into the atmosphere and one of these parameters are

also inorganic halogens. The samples which containing different proportions RDF waste disposal by burning in high temperature rotary kiln were obtained by using USEPA method 26.

USEPA method 26 is applicable for determining emissions of hydrogen halides (HX) [HCl, HBr, and HF] and halogens (X₂) [Cl₂ and Br₂] from stationary sources when specified by the applicable subpart. By this method emission sample is collected isokinetically and is therefore particularly suited for sampling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (e.g., hydrogen halides dissolved in water droplets).

An integrated sample is extracted from the source and passed through a prepurged heated probe and filter into dilute sulfuric acid and dilute sodium hydroxide solutions which collect the gaseous hydrogen halides and halogens, respectively. The filter collects particulate matter including halide salts but is not routinely recovered and analyzed. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl⁻), bromide (Br⁻), and fluoride (F⁻) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H⁺), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added in excess to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC) [22].

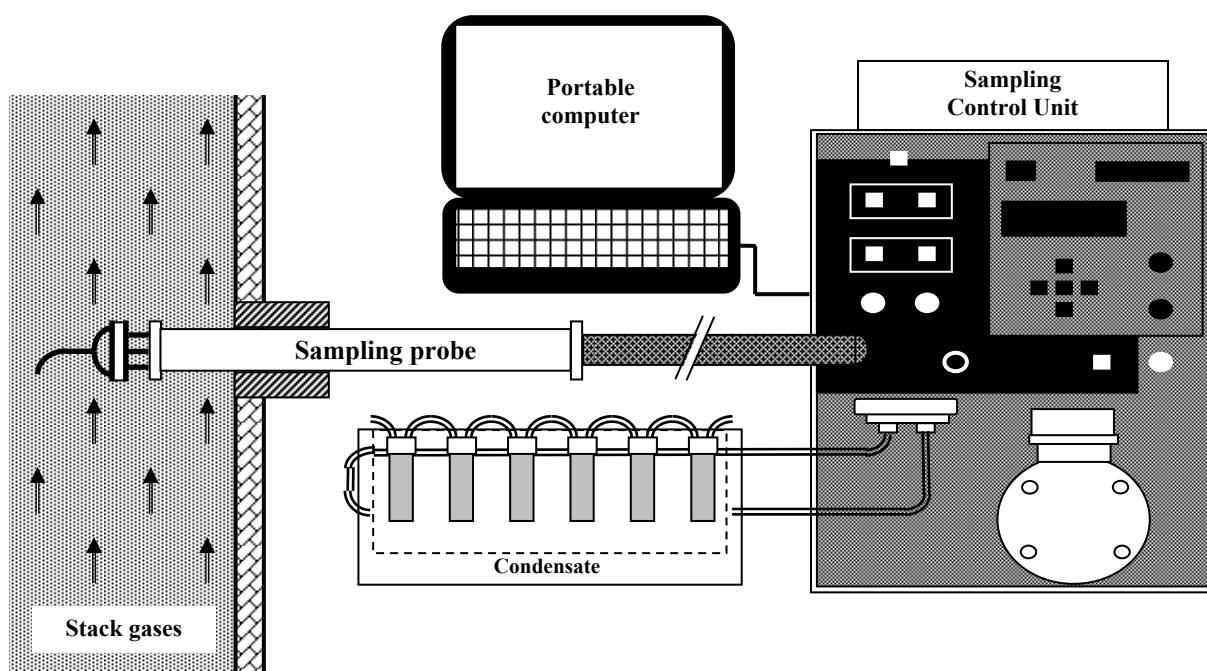


FIGURE 1 - Sampling train for halogens according to USEPA method 26.

According to USEPA method 26 the sampling train for halogens is given in Figure 1. The sampling train was prepared as follows: pour 15 ml of the 0.1 N H₂SO₄ scrubber solution into first and second of impingers, 15 ml of the 0.1 N NaOH scrubber solution into third and fourth of impingers and place 200 g fresh charge of silicagel at the end of the impinger train. The air was drawn through a teflon-glass filter (TGF) to collect particles and then through scrubber solution to collect the gaseous hydrogen halides and halogens, respectively. Approximately after 1 hour sampling period scrubber solution was added in 100 mL calibrated flask. The flask was diluted to the mark with prepared scrubber solution. Sampling volume was recorded to notebook for calculate mg chloride per standardized sampling volume. Samples were transported to laboratory for analysis.

2.2. Removal of organic chloride with activated charcoal

In this study, two different activated charcoal produced by Merck and Di.Elle were used for removal of organic chloride from scrubber solutions. The physical properties of used activated charcoals are given in Table 1. Glass adsorbent tubes (6mm O.D., 178mm length) were prepared in the laboratory consisting of two separate sections filled with activated charcoal of 400 and 100 mg. A 0.5 µm pore size prefilter was fixed in the sampling train in order to eliminate entrance of particles into the tube.

TABLE 1 - Physical properties of activated charcoals.

Properties	Particle size	Type	Specific surface area (BET)
Merck activated charcoal	50-100 µm ≥ 80 %	Powder	about 800 m ² /g
Di.Elle activated charcoal	0.42-0.84 mm ≥ 85 %	Granule	about 300 m ² /g

5 mL portions from diluted to 100 mL of samples has been passed through sampling tubes using Eppendorf pipets. Then be passed through activated charcoal tube samples were analyzed by Dionex ICS-1000 Ion Chromatograph. Each value reported in this study is an average of at least five separate measurements.

2.3. Analysis

The following system is used for sample analysis: DIONEX ICS-1000 Model Ion Chromatography System AS9 HC column, 9 mM Na₂CO₃ buffer solution, flow rate 1.0 CCPM, conductivity dedector, 200 µL loop system, cell temperature 35 °C, column temperature 30 °C. A teflon filter (0.25 µm pore size) was used for removing particles before analysis.

To a serie of chloride aliquots containing 0.01–0.2 mg chloride (Cl⁻) (10.00–200.00 µL with calibrated Eppendorf automatic pipet) prepared from Ultra Scientific (ICC-003) standard chloride solution is added in 100 mL calibrated flasks. The flask is diluted to the mark with prepared 0.1 N H₂SO₄ - 0.1 N NaOH solution. The peak

areas are measured in conductivity dedector against reagent blank which is prepared in the same manner but in the absence of chloride. A calibration graph is plotted for chloride. A straight line passing through the origin has been obtained. Ultra Scientific CRM (ICC-210) IC Anions Mixture is used for quality control of analysis system.

3. RESULTS AND DISCUSSION

The mass of inorganic chloride per standardized sampling volume (mg Cl⁻/Nm³) was calculated by using the following expression:

$$\text{mg Cl}^{-}/\text{Nm}^3 = [C \times V_T / V_S]$$

where C (ppm) is the analysis result of 5 mL portions from diluted to 100 mL of samples, V_T is total diluted volume of sampling periyod (100 mL), V_S is standardized sampling volume (0.1 Nm³).

Results of analysis are given in Table 2 and 3 as ppm chloride and mg/Nm³ concentration of chloride in dry gas volume measured by the dry gas meter (DGM), corrected to standard conditions. A serious difference of chloride results are seen between before and after using activated charcoal. The lowest amount of inorganic chloride was obtained by burning 0% RDF ratio value compared to others, the highest chloride value was clearly seen in the sample by burning 15% RDF. The amount of chloride increases depending on the RDF ratio [23].

TABLE 2 - Analysis result of chloride using DL(Di.Elle) activated charcoal.

RDF %	before activated carbon		after activated carbon		% Recovery
	analysis result, ppm Cl ⁻	^{a,b} mg/Nm ³ , Cl ⁻	analysis result, ppm Cl ⁻	^{a,b} mg/Nm ³ , Cl ⁻	
0 %	0.12±0.002	0.12±0.004	0.13±0.002	0.13±0.004	8.3
8%	0.32±0.005	0.32±0.011	0.50±0.008	0.50±0.018	56.3
12%	0.48±0.007	0.48±0.020	0.74±0.011	0.74±0.026	54.2
15%	0.59±0.009	0.59±0.021	0.91±0.014	0.91±0.032	54.2

a: Calculated by the 0.1 Nm³ dry gas volume

b: N=5; t = t-distribution for confidence level of 95% with N-1 degrees of freedom

TABLE 3 - Analysis result of chloride using Merck activated charcoal.

RDF %	before activated carbon		after activated carbon		% Recovery
	analysis result, ppm Cl ⁻	^{a,b} mg/Nm ³ , Cl ⁻	analysis result, ppm Cl ⁻	^{a,b} mg/Nm ³ , Cl ⁻	
0 %	0.12±0.002	0.12±0.004	0.13±0.002	0.13±0.004	8.3
8%	0.32±0.005	0.32±0.011	0.63±0.009	0.63±0.022	96.9
12%	0.48±0.007	0.48±0.020	0.93±0.014	0.93±0.033	93.8
15%	0.59±0.009	0.59±0.021	1.13±0.017	1.13±0.040	91.5

a: Calculated by the 0.1 Nm³ dry gas volume

b: N=5; t = t-distribution for confidence level of 95% with N-1 degrees of freedom

Comparing the effectiveness of Merck and DL (Di-Elle) activated charcoal, the important difference between them is clearly seen in Table 2 and 3.

Recovery values of inorganic chloride are calculated as 56.3%, 54.2% and 54.2% after scrubber solution passed

through by using DL(Di.Elle) activated charcoal for 8%, 12% and 15% RDF ratio. However, when Merck activated charcoal was used in the same RDF ratio, recovery values are calculated as 96.9%, 93.8 and 91.5%. It can be ex-

plained that type of Merck activated charcoal is powder so particle size is less than DL(Di.Elle) granular activated charcoal and different large surface area (Table 1) [24].

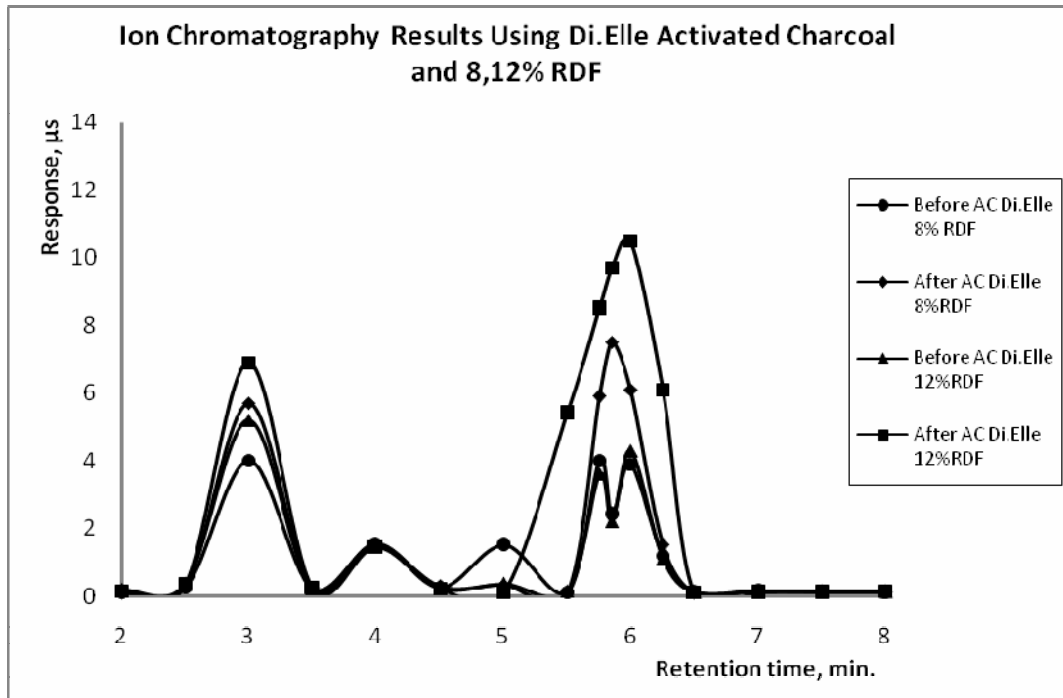


FIGURE 2 - Ion Chromatography Results Using Di.Elle Activated Charcoal and 8,12%RDF

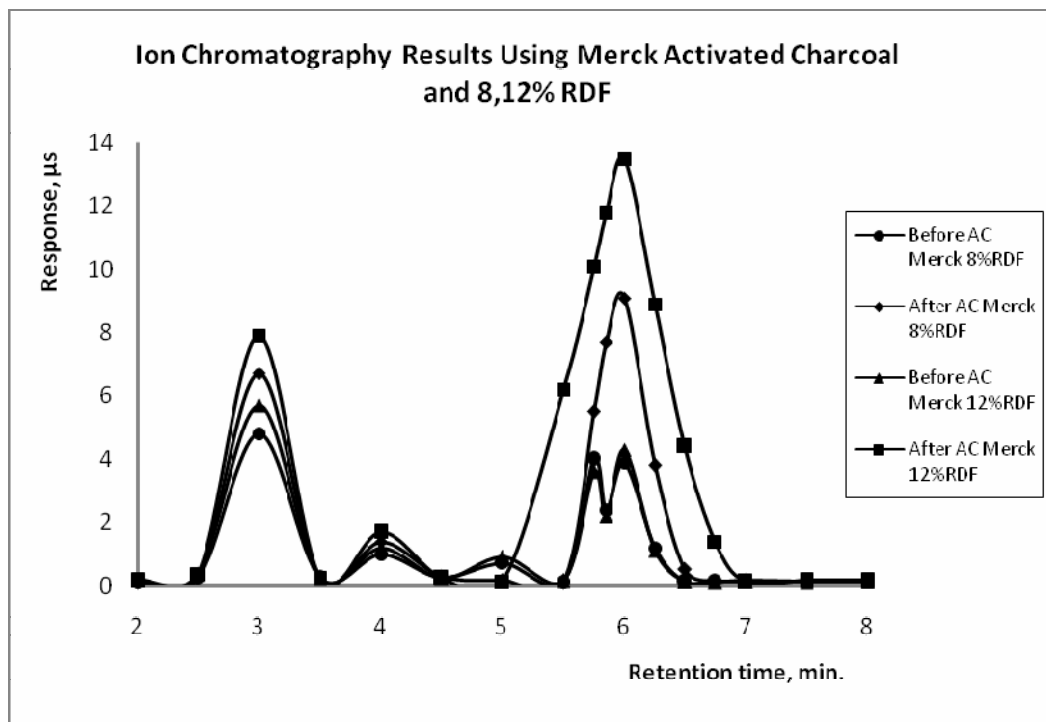


FIGURE 3 - Ion Chromatography Results Using Merck Activated Charcoal and 8,12%RDF

There is also a significant influence on the results to analyze the samples after using activated charcoal. In Figure 2 and 3 it can be seen that very different response values were obtained between before no passed and after passed activated charcoal by using rates of all RDF material.

The chloride peak values were shown almost same retention times for all samples, better resolved peaks and response values were obtained after activated charcoal compared to other.

The organic compounds that absorbed in scrubber solution and negative impacts during analysis were removed by using activated charcoal in this study. The placement of guard column before the main column can be faster and more practical during the chromatographic analysis of water and soil samples in order to remove of organic compounds. However, limited number of air samples were collected during incineration of plastic originated RDF wherefore not obtained same process conditions. Therefore, use of activated charcoal instead of guard column for removal of organic compounds in air samples that are more practical and feasible.

ACKNOWLEDGEMENTS

The author would like to thank TUBITAK Marmara Research Center Water and Wastewater Laboratory for analyses.

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Received: August 19, 2011
Revised: October 20, 2011
Accepted: November 07, 2011

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