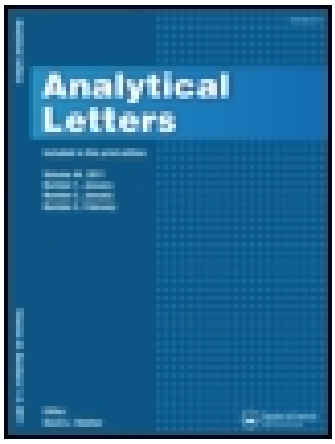
This article was downloaded by: [University of Otago]
On: 05 July 2015, At: 10:25
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: 5 Howick Place, London, SW1P 1WG



CrossMark
Click for updates

Analytical Letters
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lanl20

Experimental Design Optimization of the Determination of Total Halogens in Coal by Combustion - Ion Chromatography

Ivana D. Sredović Ignjatović[a], Antonije E. Onjia[bc], Ljubiša M. Ignjatović[d], Žaklina N. Todorović[bc] & Ljubinka V. Rajakovic[e]

[a] Faculty of Agriculture, University of Belgrade, Belgrade, Serbia

[b] Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

[c] Anahem Laboratory, Belgrade, Serbia

[d] Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia

[e] Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia

Accepted author version posted online: 22 Jun 2015.

To cite this article: Ivana D. Sredović Ignjatović, Antonije E. Onjia, Ljubiša M. Ignjatović, Žaklina N. Todorović & Ljubinka V. Rajakovic (2015): Experimental Design Optimization of the Determination of Total Halogens in Coal by Combustion - Ion Chromatography, Analytical Letters, DOI: 10.1080/00032719.2015.1041029

To link to this article: http://dx.doi.org/10.1080/00032719.2015.1041029

Disclaimer: This is a version of an unedited manuscript that has been accepted for publication. As a service to authors and researchers we are providing this version of the accepted manuscript (AM). Copyediting, typesetting, and review of the resulting proof will be undertaken on this manuscript before final publication of the Version of Record (VoR). During production and pre-press, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal relate to this version also.

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [University of Otago] at 10:25 05 July 2015

Supertitle: Chemometrics

Experimental Design Optimization of the Determination of Total Halogens in Coal by Combustion – Ion Chromatography

Ivana D. Sredović Ignjatović[1,*], Antonije E. Onjia[2,3], Ljubiša M. Ignjatović[4], Žaklina N. Todorović[2,3], and Ljubinka V. Rajakovic[5]

[1]Faculty of Agriculture, University of Belgrade, Belgrade, Serbia

[2]Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

[3]Anahem Laboratory, Belgrade, Serbia

[4]Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia

[5]Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia

[*]Address correspondence to Ivana D. Sredović Ignjatović. Faculty of Agriculture, University of Belgrade, Nemanjina 6, 11080 Belgrade, Serbia. E-mail: isredovic@agrif.bg.ac.rs

Received 08 November 2014; accepted 09 April 2015.

Accepted Manuscript

Abstract

Determination of total halogens in coal was investigated with oxygen bomb combustion followed by ion chromatography. Experimental parameters were optimized by fractional factorial design

and response surface methodology. Fractional factorial design was employed in screening experiments to evaluate the influence of the oxygen pressure, catalyst, absorption solution, reduction reagent, bomb cooling time, and a combustion aid on the combustion of coal in an oxygen bomb. Response surface methodology was conducted to further refine the results obtained by fractional factorial design and to define parameters for the procedure. The accuracy and precision of combustion with ion chromatography were evaluated by the use of two certified reference materials and by fortified in-house coal standards. The limits of detection and quantification for total halogens were 0.84 and 2.80 milligrams per kilogram, respectively, for 500 milligrams samples. Ion chromatography provided relative standard deviations less than 4 percent, recoveries exceeding 95 percent, and was convenient. This method is recommended for routine determination of total halogens in coal because of its reliability.

Keywords

combustion, fractional factorial design, ion chromatography, response surface methodology, total coal halogens

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Introduction

Halogens are minor or trace elements in coal, but great attention has been paid to their environmental and health impacts during coal processes (Finkelman 2004; Chen et al. 2013). During coal combustion, fluorine generally is released as HF, SiF_4, and CF_4. Chlorine in coal is emitted mainly as HCl. In addition to environmental concerns, HCl gives rise to equipment corrosion problems in power plants (Domazetis et al. 2006; Guo, Yang, and Liu 2006). During coal combustion, bromine is volatilized and enters the atmosphere as HBr, a toxic pollutant (Ratafia-Brown 1994; Xu et al. 2003). Determination of halogens in coal is particularly important

to evaluate the environmental impact of coal-fired power plants (Wang et al. 2010). The halogen concentration in coal is important for environmental and health issues and for coal utilization. In order to estimate the efficiency of coal desulfurization systems, it is important to know halogen concentrations in coal (Warych and Szymanowski 2001).

The determination of halogens in solid samples usually involves sample preparation to place the analytes into solution followed by analysis. Classical procedures for sample pretreatment involve the digestion of solid samples by dry ashing (Nadkarni 1980) or fusion (Wood, Dale, and Riley 2003). Microwave-assisted wet digestion in closed vessels with acid(s) and hydrogen peroxide, and in presence of persulfate as oxidizing reagent, have been used for bromine and iodine (Gao et al. 2007; Sun et al. 2010). Coal combustion in the presence of oxygen, using microwave-induced combustion with a reflux step for digestion, was reported for the simultaneous determination of halogens in coal (Flores et al. 2008). Pyrohydrolytic decomposition of solid samples may be performed using an in-house made apparatus consisting of a quartz tube in a stream of air/water vapor (Dressler et al. 2002) or oxygen/water vapor (Sredović and Rajaković 2010). Pyrohydrolytic decomposition of coal in a tube furnace, using an oxygen/water steam and quartz for sample ventilation during combustion was used for the catalytic spectrophotometric determination of iodine in coal (Wu et al. 2007). Simultaneous determination of halogens in coal may be performed with pyrohydrolytic sample decomposition and carbonate buffer (pH = 10.3) as the absorption solution (Peng et al. 2012).

Sulfur, N, F, and Cl in coal and oil shale were determined by oxygen bomb combustion, using water and dilute sodium carbonate as the absorbing media with hydrazine as the reducing reagent (Nadkarni and Pond 1983). For oil shale combustion, white oil was added as a combustion aid. An oxygen combustion bomb method has been reported for elemental analysis of heteroatoms in

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

organic compounds, fuel, and waste (Fung and Dao 1995, 1996). Problems involving combustion followed by chromatographic detection were discussed and solutions were evaluated. Fluorine, Cl, and S determination in solid waste incinerator residues using oxidative high pressure digestion was carried out in a special bomb with the inner surface coated by an auto-regenerating catalysts (Belavi and Mönch 2000). For fluorine determination in coal, oxygen flask combustion with WO_3/Sn as a catalyst was developed (Geng et al. 2007). Determination of halogens has been performed using ion-selective electrodes (ISE) by direct detection (Dressler et al. 2002; Geng et al. 2007) and standard addition (Wood, Dale, and Riley 2003; Sredović and Rajaković 2010), non-suppressed ion chromatography (IC) (Fung and Dao 1995, 1996), IC with conductivity detection (Belavi and Mönch 2000; Cortes-Pena et al. 2002; Flores et al. 2008), and inductively coupled plasma mass spectrometry (ICP-MS) (Gao et al. 2007; Sun et al. 2010).

Combustion in closed vessels has been used for coal digestion due to the low residual carbon content of the digests and suitability for determination by potentiometric or chromatographic techniques. The official methods proposed by American Society for Testing and Materials (ASTM) recommend combustion bombs as the digestion technique for subsequent determination of chloride and fluoride in coal (ASTM D2361-02 2002; ASTM D3761-96 2002).

In general, combustion techniques allow efficient coal digestion with almost complete matrix destruction due to the high temperatures (Flores et al. 2008). Combustion may be performed in open or closed systems. In open systems, oxidation is performed by continuously supplying oxygen to the reaction. For closed systems, in general, the resulting pressure and temperatures are dependent upon the sample mass, oxygen pressure, vessel dimensions, and reaction rate between the sample and oxygen (Cortes-Pena et al. 2002). Closed combustion systems employ combustion bombs and oxygen flasks.

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Downloaded by [University of Otago] at 10:25 05 July 2015

In general, the decomposition of organic matter is effective and may be performed in few minutes. The sample mass for decomposition in combustion bomb is relatively high, usually greater than 0.5 gram. The entire procedure, including combustion and cooling, may be completed in less than thirty minutes. Contamination risks may be associated with the absorbing solutions, although this problem is be more pronounced with trace metal determination in the digests due to probable contamination from metallic parts of the vessels. Although residual carbon concentrations are low, only one sample at a time may be processed, resulting in relatively low sample throughput (Flores et al. 2007).

Although the combustion bomb may be considered as an old technique, it is still in use and recent applications (after 2000) have been described in the literature showing its suitability, especially as pretreatment for halogen and sulfur determination (Belavi and Mönch 2000; Cortes-Pena et al. 2002; Souza et al. 2002). Organic halogen group parameters, such total organic halogens, absorbable organic halogens, volatile organic halogens, and extractable organic halogens, are well known and used for monitoring drinking water (Kristiana et al. 2009), surface water (Putschew, Mania, and Jekel 2003), wastewater (Vinder and Simonič 2012), soil (Pereira et al. 2011), and sediments (Niemirycz, Kaczwarzyk, and Blazejowski 2005).

In this paper, a method for total coal halogen determination is reported. The group parameter, denoted as total halogens, was used to express halogen concentration in coal. The influence of method variables on halogen release from coal during combustion in an oxygen bomb and the absorption of gases were examined using an experimental design approach. Methodology in statistical experimental design involves the development a small number of experiments in which the relevant factors are simultaneously and systematically varied. Fractional factorial design was for screening to identify the factors influencing the total halogen determination. Optimal

Accepted Manuscript

conditions for total halogen determination were defined by the use of the surface methodology response.

Experimental

Samples and Reference Materials

Fractional factorial and response surface experiments were performed with in-house prepared composite coal samples from Serbia's largest coalfield, Kolubara. The samples were collected and ground in a mixer mill and in an agate mortar to obtain particle sizes less than or equal to 220 mesh. Fluorine and chlorine concentrations in the sample denoted as Kolubara Field 1 were 167 and 66 milligrams per kilogram; in the sample denoted as Kolubara Field 2, the concentrations were 150 and 145 milligrams per kilogram. The combustion-IC method was validated by halogen determination in coal certified reference materials BCR 460 (European Commission, Measurements and Testing Programme) and NIST 1632c (National Institute of Standards and Technology, USA).

Instrumentation

A self-contained bomb calorimeter with a water-jacketed bucket chamber and automatic temperature controls (1108 Oxygen combustion bomb, Parr instrument company, USA) was used for sample preparation. Combustion was carried out in a high pressure stainless steel oxygen bomb with an internal volume of 340 milliliters. Ignition of the sample was carried out by heating and melting down the nickel alloy fuse wire (Ref. 45C10, Parr instrument) immersed in sample pellets placed in a stainless steel combustion capsule.

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

The concentrations of halogen ions in the absorption solution were measured using a Metrohm 761 compact IC system (Metrohm ion analysis, Herisau, Switzerland). An anion-exchange column (Metrosep A supp 1 (250 × 4.6 millimeters), with a capacity of 34 micromoles Cl^- was in series with a guard column (Metrosep A supp 1), followed by the Metrohm suppressor module with fully automatic regeneration, and a thermostated conductivity detector. The IC system was PC-controlled and equipped with high-pressure isocratic pump. Metrodata IC Net 2.3 software was used to control the instrument, as well as for recording and evaluating chromatograms. The eluent was 3.0 moles per liter Na_2CO_3 at a flow rate of 1.0 milliliter per minute.

Chemicals and Reagents

Reagent grade water, with a specific resistance of 18.2 megaohms centimeter, was obtained from a Milli-Q system (Millipore Corp., USA). All other chemicals (NaOH, H_2O_2, and Na_2CO_3), were of analytical reagent grade (Merck, Darmstat, Germany). All standard solutions, eluents, and reagents were prepared in deionized water, degassed under vacuum, and passed through 0.45 µm regenerated cellulose membrane filters (Phenomenex Inc., USA) prior to use. An anion multicomponent standard solution included fluoride, chloride, bromide, nitrate, phosphate, and sulfate (Multi-Component Anion Mix 2, IC-MAN-02-1, AccuStandard, USA). The working calibration solutions were prepared by serial dilutions of the multicomponent standard with deionized water.

Analytical Procedure

Combustion in oxygen bomb provides a simple procedure for extraction of halogens from solids. Several experimental parameters were found to be important for the success of this method. In this paper, the influence of six parameters was investigated. The tested parameters were oxygen

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

pressure, the catalyst, type of absorption solution, H_2O_2 as reducing reagent, bomb cooling time, and the use of a combustion aid. Two composite coal samples were used that were designated as Kolubara Field 1 and Kolubara Field 2.

Dried samples (500 milligrams) were measured with a precision of ±0.1 milligram before pelleting. A nickel alloy fuse wire was immersed in coal during the pelleting. When a catalyst was used, the coal and catalyst were mixed before pelleting. The coal pellet was placed in combustion capsule and the nickel alloy fuse wire was connected to two electrodes for subsequent ignition. 5 milliliters of H_2O_2 and 5 milliliters of absorbing solution (H_2O or NaOH) were placed on the bottom of the combustion bomb to absorb the volatile elements. When H_2O_2 or NaOH were not used, 5 milliliters of deionized water were added to the bomb to provide a total volume of 10 milliliters. In some experiments, a combustion aid was added to the sample pellet after connecting the fuse wire to electrodes and before closing the bomb.

After the assembly, the bomb was purged with oxygen for two minutes before the pressure inside the bomb was set at the designated value. Ignition was performed by an electric current that heated the metal wire and initiated the combustion (Mester and Sturgeon 2003). Since the oxygen bomb is under pressure, safety provisions were taken into account. Because the combustion may heat the decomposition vessel (50–55 degree celsius) (Souza et al. 2002), the bomb was submersed in a water bath during combustion for rapid release of heat from the vessel. After combustion, bomb was transferred to an ice water bath and cooled to allow condensation and absorption of the volatile compounds in the solution. After cooling, the residual gases were carefully released through a valve so that the pressure was reduced to atmospheric level. After opening, the absorption solution was removed. The bomb and all parts of its interior, including the combustion capsule, valve passages, and electrodes, were washed with deionized water. The

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

washings were collected, added to absorption solution, and diluted to 50 milliliters. The oxygen bomb and its parts were rinsed and dried for the next sample. A blank for coal samples consisted of catalyst, mineral oil, or catalyst/oil mixture. A blank was prepared prior to sample combustion in in the bomb for each experiment.

The concentrations of halogen ions in the absorption solution were measured by IC. Prior to injection, the samples were passed through 0.45 micrometers regenerated cellulose syringe membrane filters. The injection volume was 20 microliters. At least three replicate injections of each sample were made and the results are the average of the replicates.

Fractional Factorial Design

Experimental design may identify the most influential factors (variables and parameters), the synergy between the factors, and the optimal conditions (Vera Candioti et al. 2014). The primary applications of the experimental design are screening, in which the factors that influence the experiment are identified, and optimization, in which the best conditions for an experiment are found (Hanrahan et al. 2005; Mutihac and Mutihac 2008). A full factorial design provides sufficient information to evaluate the whole set of primary effects as well as their interactions. As the number of factors in factorial design increases, the number of trials required for a full replicate of the design rapidly increases. Factorial designs are widely used in experiments involving many factors where it is necessary to study the impact of the factors or their combinations. Fractional factorial design is an alternative to full factorial design, especially in the initial stage of investigation, and is considered a representative subset of full factorial design (Hanrahan and Lu 2006).

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

In this work, the influence of six factors (variables) on halogen release during coal combustion in an oxygen bomb was investigated. The oxygen bomb combustion parameters were evaluated by applying fractional factorial design to establish an accurate, precise, and reliable method for determination of total halogens in coal.

The 2^{6-2} fractional factorial design consisted of nineteen experimental runs including three replicates of the central point. The investigated factors were tested at two levels (low and high). The matrix for six analyzed factors was obtained according to the selected fractional factorial design using MINITAB (Release 15, Minitab Inc., State College, PA). In order to ensure that uncontrolled factors did not affect the results, the experiments were performed randomly.

In combustion reactions, organic matrices decompose in a reaction with oxygen at high temperature or with oxygen radicals and excited oxygen plasmas (Flores et al. 2007). Combustion in an oxygen bomb is performed with an excess of oxygen as an oxidant; hence, 1.5 and 2.5 megapascals were chosen for low and high level. As a demonstrated catalyst, V_2O_5 was added to the sample to investigate its influence on coal decomposition in the oxygen bomb and the halogen release. In order to evaluate the effect of the catalyst on total halogen analysis, the catalyst to coal mass ratio was varied from 0 (low level) to 0.5 (high level). During combustion, halogens are dominantly released as hydrogen halides. Instead of N_2H_4 (Nadkarni and Pond 1983), H_2O_2 was added as a reducing agent to the absorption solution to convert halogen species into the corresponding halide. Hydrogen peroxide was selected since it exhibits oxidizing and reduction properties, depending on the conditions. The influence of H_2O_2 as the reducing agent was investigated from 0 to 1 wt percent. After combustion, analytes were present as gases or volatile compounds and the combustion products were dissolved in a suitable solution before determination. The gaseous products of coal combustion were absorbed in deionized H_2O (low

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

level) or 1 mole per liter NaOH (high level). The time of bomb cooling after the combustion was measured because the solubility of gases increases with decreasing temperature. The oxygen bomb was cooled between 5 (low level) and 25 (high level) minutes in ice bath. The use of a combustion aid may be necessary for an efficient decomposition for some samples, depending upon the texture, the combustible portions, and calorific values (Souza et al. 2002). Lignite coals used in this research have high calorific values and moderate mineral concentrations. Therefore, coal combustion and halogens release were investigated with (high level) and without (low level) the combustion aid. Mineral oil (100 milliliters) (Fluka, Germany) was used as the combustion aid.

Results and discussion

Fractional Factorial Design

Experimental design is the methodology of conducting and planning experiments in order to extract the maximum amount of information from the data in the fewest number of experiments. Since the main effects and the lower-order interactions are usually the most significant terms, fractional factorial design may be performed in these cases (Montgomery, Runger, and Hubele 2007; Chen et al. 2009; Sánchez, Sarabia, and Ortiz 2012). The goal of fractional factorial design was to identify the most influential factors on halogen release during coal combustion in the oxygen bomb. Assuming that higher-order interactions may be neglected, nineteen experiments were performed and the concentrations of halides in the absorption solution were determined. **Figure 1** shows a representative chromatogram of a composite coal. Subsequently, total halogen concentrations were evaluated by converting fluorine and bromine concentrations to corresponding chlorine concentrations using the ratio of molar masses. The results were

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

statistically analyzed. The confidence interval of each individual factor and their combinations at 95 percent of the confidence level were evaluated.

In order to establish the relationship between investigated factors and total halogen determination, the data were graphically displayed using Pareto charts (**Figure 2**). Estimated effects and regression coefficients, presented in **Table 1**, and ANOVA were used to determine the effects of factors upon the total halogen determination. The standard error for each estimated regression coefficient, listed in **Table 1**, was 7.66 percent. For the center point, the standard error for estimated regression coefficient was 19.29 percent.

Changes in the level of a factor influence the system response, which represents the effect of the factor. The Pareto chart compares absolute values and the significance of effects. **Figure 2** shows the Pareto chart resulting from the statistical analysis of total halogen concentration obtained by combustion-IC. The most significant factors were the catalyst and the type of absorption solution. All other investigated variables, as well as their two- and three-way interactions, were not statistically significant.

The relative magnitudes of the process variables were determined on the basis of the factor effect and corresponding *p*-value. High negative effects for the catalyst and type of absorption solution indicated that these factors had negative influences on halogen release during coal combustion. V_2O_5 has been shown to be an active catalyst for the decomposition of solid samples (Dressler et al. 2002). These results confirm that this catalyst has high negative effects on extraction of halogens from coal (Sredović and Rajaković 2010). Standard ASTM methods recommend alkaline solutions for absorption (ASTM D2361-02 2002; ASTM D3761-96 2002). In this work, an increase in the solution alkalinity decreased the solubility of released gaseous compounds.

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Downloaded by [University of Otago] at 10:25 05 July 2015

The extraction of halogens from coal during combustion in the oxygen bomb increased with oxygen pressure and the volume of mineral oil. Combustion of an organic substance is a complex and exothermic reaction that results largely in CO_2 and H_2O production. The ignition process occurs when the oxidation reaction is accelerated and reagents are quickly consumed and is commonly accompanied by light emission (Barnard and Bradley 1985). For closed vessels, if the rate of energy released by chemical reaction exceeds the rate at which it is lost to the vessel walls, the temperature increases, causing the reaction rate and the rate of energy release to increase rapidly (Razus et al. 2006; Razus, Movileanu, and Oancea 2007). Thus, the reaction rate is accelerated indefinitely, leading to a pressure increase with a rapid self-acceleration of the reaction. After ignition occurs, the reaction continues until the supply of reactants is exhausted. As an oxidant, it was expected that oxygen pressure had a higher influence on halogen release during coal combustion than the combustion aid. Contrarily, according to the obtained regression coefficients and *p*-values (**Table 1**), it was concluded that the mineral oil was more significant than the oxygen pressure. Mineral oil was used because lignite coal with a moderate ash content was employed. The ash content corresponds to the mineral content, and this combustion aid enhances complete decomposition. The estimated regression coefficient and corresponding *p*-value of 0.659 indicated that after fifteen minutes, cooling had no effect on solubility of the released gases. The addition of H_2O_2 as a reducing reagent also had no significant influence.

ANOVA provided information on two- and three-way interactions between investigated factors: by comparing the estimated *p*-values and established criterion ($p = 0.05$), there were no interactions that significantly influence the determination of total halogens. The only two-way interaction was observed between oxygen pressure and combustion aid: at low oxygen pressure (1.5 megapascals), the concentration of halogens increased with the volume of mineral oil.

Accepted Manuscript

Optimization and Validation of the Combustion-ion Chromatography Method

In order to further investigate the influence of oxygen pressure and the addition of combustion aid on the determination of total halogens using combustion, these two factors were additionally investigated using response surface methodology. Response surface design methodology is often used to refine models, after important factors have been determined using factorial design. The main objective of response surface methodology is to determine the optimal operational conditions or to determine the area that meets the operating specification (Mutihac and Mutihac 2008). The difference between a response surface equation and the equation for a factorial design is the addition of quadratic terms that allow model curvature in the response, making them useful for understanding how changes of input factors influence the response of interest, finding the levels of input factors that optimize the response, and selecting the operating conditions to meet the specifications (Hanrahan et al. 2005). Central composite design is a response surface methodology that is often used when the design calls for sequential experimentation because this approach may incorporate information from a properly planned factorial experiment (Sahu, Acharya, and Meikap 2009; Ghasemi, Raofie, and Najati 2011). In order to optimize the total halogens extracted from coal, the experiment was conducted with total halogen recovery as the response variable in the central composite design. Total halogen recovery was calculated as the ratio of the measured and certified values. The oxygen pressure and combustion aid were chosen as independent factors for additional experiments. The low, middle, and high levels of each factor were employed with five central points resulting in a matrix of thirteen experiments obtained by statistical software. The influence of oxygen as a fuel for coal combustion was investigated at 2.0, 2.5, and 3.0 megapascals. Since the combustion aid affected halogen release

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

from coal during combustion according to screening experiments, this parameter was investigated by the addition of 50, 100, or 150 microliters.

According to the results obtained from the fractional factorial design, it was concluded that catalyst and alkaline solution negatively influenced the total halogen determination. Therefore, the catalyst was not used in subsequent experiments and deionized water was used as the absorption solution. Since the change of the concentration of H_2O_2 as reducing agent from low to medium level had no effect, its concentration was employed at 0.5 wt percent. Sufficient dissolution of gases was achieved after fifteen minutes of cooling the oxygen bomb.

Response surface methodology consists of a group of mathematical and statistical techniques that are based on the fitting of empirical models to the experimental data obtained in relation to the experimental design (Bezerra et al. 2008). **Table 2** summarizes the estimated regression coefficients from linear, square, and interaction models. The combustion aid, as well as oxygen pressure × oxygen pressure, and oxygen pressure × combustion aid interactions, according to *p*-values, were statistically significant on the total halogen determination. The coefficient of variation was $R^2 = 93.72$ percent, indicating a high degree of correlation between the response variable and independent factors and a high degree of fitting. The results shown in **Table 3** (analysis of variance) and response surface plot shown on **Figure 3** confirmed that the combustion aid improved the recovery and the accuracy of halogen determination in coal. The volume of the combustion aid was set at 150 microliters and the oxygen pressure at 2.5 megapascals.

Parameters for entire procedure are listed in **Table 4**. The accuracy of the combustion-IC method for total halogen determination was evaluated by using in-house prepared coal samples from

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Kolubara, Tamnava-West field, one of the largest lignite coal depositions in Serbia. Total halogen recovery was also investigated by fortified in-house coal samples. The total halogen concentrations in coal were increased by 50 percent (spike 1) and by 100 percent (spike 2) by adding a standard containing sodium salts of fluoride, chloride, and bromide. A small volume of the concentrated standard was added to coal pellets in the sample capsule. The sample was carefully dried, assembled in the oxygen bomb, and combusted.

The results shown in **Table 5** indicated that halogen recovery ranged from 96 to 104 percent, and the relative standard deviations were less than 3.5 percent. All determined concentrations of total halogens presented in **Table 5** are given with the confidence intervals, calculated from the standard deviation for five measurements and Student's distribution. Student's *t* was adopted for four degrees of freedom at a 95 percent confidence interval. The limits of detection and quantification were determined as $3sk^{-1}$ ratio and $10sk^{-1}$, respectively, where *s* is standard deviation for blank and *k* is the slope of calibration curve (Harris 2007). The limits of detection were 0.84 milligram per kilogram for chlorine and 0.4 milligram per kilogram for fluorine, while corresponding limits of quantification were 2.8 and 1.3 milligrams per kilogram. The higher values were employed for analytical purposes.

The accuracy of the method was also investigated on coal certified reference materials (BCR 460, NIST 1632c). The results for these samples are listed in **Table 6** with the confidence intervals. The relative standard deviations were less than 4 percent, indicating that the precision was satisfactory. **Table 6** shows that the total halogen recovery was 95 percent for the NIST and 109 percent for the BCR coal. A low recovery of 87 percent (not included in **Table 6**) was obtained for NIST coal sample during the early measurements probably due to the high total halogen and sulfur content in the NIST coal and in absorption solution, *i.e.* which was greater

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

than the IC column capacity. This problem was eliminated by five-fold dilution of the absorption solution prior to injection, and acceptable recovery (95 percent) for the NIST sample was achieved.

Conclusions

Fractional factorial design was used in screening experiments to determine the most influential factors upon the determination of total halogens in coal using an oxygen bomb. The 2^{6-2} fractional factorial design, with nineteen experimental runs, was successfully applied. The results of fractional factorial design showed that the catalyst and the absorption solution strongly influenced the total halogen determination. Response surface methodology was employed to optimize the results obtained from fractional factorial design. The oxygen pressure and combustion aid were chosen as independent factors for additional experiments and central composite design methodology was applied.

The optimal combustion parameters for determination of total halogens were 500 milligrams of coal, an oxygen pressure of 2.5 megapascals, 5 milliliters of H_2O as the absorption solution, 5 milliliters of 0.5 wt percent H_2O_2 as the reducing reagent, 150 microliters of mineral oil as the combustion aid, and a cooling interval of fifteen minutes after combustion. Halide concentrations in the absorption solution were measured by IC. The limits of detection and quantification for total halogens were 0.84 and 2.8 milligrams per kilograms, respectively, for 500 milligrams of coal.

The satisfactory recoveries and relative standard deviations indicate that the method is suitable for total halogen determination. The method was sensitive, with good reproducibility and accuracy, as confirmed through validation using certified reference materials. The method has

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

advantages that include simple and available instrumentation, since oxygen bomb combustion is a conventional method for determining halogens in coal. Compared to pyrohydrolytic methods and to microwave-induced combustion techniques followed by inductively coupled plasma - mass spectrometry, the oxygen bomb is easy to operate and the analysis is more economical and environmentally friendly.

Acknowledgments

This study was supported by Ministry of Education, Science and Technologic Development of the Republic of Serbia, Project No III43009.

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

References

ASTM D2361-02. 2002. *Standard test method for chlorine in coal*. W. Conshohocken, PA, USA: ASTM International.

ASTM D3761-96. 2002. *Standard test method for total fluorine in coal by the oxygen bomb combustion/ion selective electrode method*. Reapproved. W. Conshohocken, PA, USA: ASTM International.

Barnard, J. A., and J. N. Bradley. 1985. *Flame and combustion*. New York: Chapman and Hall

Belavi, H., and H. Mönch. 2000. Simultaneous determination of fluorine, chlorine and sulfur in incinerator residues by oxidative high pressure digestion and ion chromatography. *Analusis* 28: 988–94. doi:10.1051/analusis:2000166

Bezerra, M. A., R. E. Santelli, E. P. Oliveira, L. S. Villar, and L. A. Escaleira. 2008. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta* 76: 965–77. doi:10.1016/j.talanta.2008.05.019

Chen, Y., C.-J. Liu, G. Jones, S. Fu, and H. Zhan. 2009. Enhancing biodegradation of wastewater by microbial consortia with fractional factorial design. *Journal of Hazardous Materials* 171: 948–53. doi:10.1016/j.jhazmat.2009.06.100

Chen, J., G. Liu, Y. Kang, B. Wu, R. Sun, C. Zhou, and D. Wu. 2013. Atmospheric emissions of F, As, Se, Hg, and Sb from coal-fired power and heat generation in China. *Chemosphere* 90: 1925–32. doi:10.1016/j.chemosphere.2012.10.032

Cortes-Pena, M. A., L. V. Perez-Arribas, E. M. Leon-Gonzalez, and L. M. Polo-Diez. 2002. Determination of chlorine and bromine in automotive shredder residues by oxygen bomb and ion chromatography. *Waste Management & Research* 20: 302–07. doi:10.1177/0734242x0202000311

Domazetis, G., M. Raoarun, B. D. James, J. Liesegang, P. J. Pigram, N. Brack, and R. Glaisher. 2006. Analytical and characterization studies of organic and inorganic species in brown coal. *Energy & Fuels* 20: 1556–64. doi:10.1021/ef0502251

Dressler, V. L., D. Pozebon, E. L. M. Flores, J. N. G. Paniz, and E. M. M. Flores. 2002. Potentiometric determination of fluoride in geological and biological samples following pyrohydrolytic decomposition. *Analytica Chimica Acta* 466: 117–23. doi:10.1016/S0003-2670(02)00550-0

Finkelman, R. B. 2004. Potential health impacts of burning coal beds and waste banks. *International Journal of Coal Geology* 59: 19–24. doi:10.1016/j.coal.2003.11.002

Flores, E. M. M., J. S. Barin, M. F. Mesko, and G. Knapp. 2007. Sample preparation techniques based on combustion reactions in closed vessels – A brief overview and recent applications. *Spectrochimica Acta Part B: Atomic Spectroscopy* 62: 1051–64. doi:10.1016/j.sab.2007.04.018

Flores, E. M. M., M. F. Mesko, D. P. Moraes, J. S. F. Pereira, P. A. Mello, J. S. Barin, and G. Knapp. 2008. Determination of halogens in coal after digestion using the microwave-induced combustion technique. *Analytical Chemistry* 80: 1865–70. doi:10.1021/ac8000836

Fung, Y. S., and K. L. Dao. 1995. Oxygen bomb combustion ion chromatography for elemental analysis of heteroatoms in fuel and wastes development. *Analytica Chimica Acta* 315: 347–55. doi:10.1016/0003-2670(95)00317-S

Fung, Y. S., and K. L. Dao. 1996. Elemental analysis of chemical wastes by oxygen bomb combustion-ion chromatography. *Analytica Chimica Acta* 334: 51–56. doi:10.1016/S0003-2670(96)00320-0

Gao, Y.-C., Q.-F. Gao, M.-X. Sun, Z.-X. Zhu, and Z.-H. Chen. 2007. Simultaneous measurements of arsenic, bromine, and iodine in coal and coke by inductively coupled plasma-mass spectrometer. *Chinese Journal of Analytical Chemistry* 35: 1175–78. doi:10.1016/S1872-2040(07)60077-2

Geng, W., T. Nakajima, H. Takanashi, and A. Okhi. 2007. Determination of total fluorine in coal by use of oxygen flask combustion method with catalyst. *Fuel* 86: 715–21. doi:10.1016/j.fuel.2006.08.025

Ghasemi, E., F. Raofie, and N. M. Najati. 2011. Application of response surface methodology and central composite design for the optimisation of supercritical fluid extraction of essential oils from *Myrtus communis* L. Leaves. *Food Chemistry* 126: 1449–53. doi:10.1016/j.foodchem.2010.11.135

Guo, S., J. Yang, and Z. Liu. 2006. The fate of fluorine and chlorine during thermal treatment of coals. *Environmental Science & Technology* 40: 7886–89. doi:10.1021/es0604562

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Hanrahan, G., and K. Lu. 2006. Application of factorial and response surface methodology in modern experimental design and optimization. *Critical Reviews in Analytical Chemistry* 36: 141–51. doi:10.1080/10408340600969478

Hanrahan, G., F. Tse, S. Gibani, and D. G. Patil. 2005. Chemometrics and statistics: experimental design. In *Encyclopedia of analytical science*, 2nd ed., ed. P. J. Worsfold, A. Townshend, and C. F. Poole, Oxford: Elsevier.

Harris, D. C. 2007.*Quantitative chemical analysis*. 7th ed. New York: W.H. Freeman and Company.

Kristiana, I., H. Gallard, C. Joll, and J.-P. Croué. 2009. The formation of halogen-specific TOX from chlorination and chloramination of natural organic matter isolates. *Water Research* 43: 4177–86. doi:10.1016/j.watres.2009.06.044

Mester, Z., and R. Sturgeon. 2003. *Sample preparation for trace element analysis*. Amsterdam: Elsevier.

Montgomery, D. C., G. C. Runger, and N. F. Hubele. 2007. *Engineering statistics*, 4th ed. New York: J. Wiley and Sons.

Mutihac, L., and R. Mutihac. 2008. Mining in chemometrics. *Analytica Chimica Acta* 612: 1–18. doi:10.1016/j.aca.2008.02.025

Nadkarni, R. A. 1980. Multitechnique multielemental analysis of coal and fly ash. *Analytical Chemistry* 52: 929–35. doi:10.1021/ac50056a036

Nadkarni, R. A., and D. M. Pond. 1983. Application of ion chromatography for determination of selected elements in coal and oil shale. *Analytica Chimica Acta* 146: 261–66. doi:10.1016/S0003-2670(00)80614-5

Niemirycz, E., A. Kaczwarzyk, and J. Blazejowski. 2005. Extractable organic halogens (EOX) in sediments from selected Polish rivers and lakes – a measure of the quality of the inland water environment. *Chemosphere* 61: 92-97. doi:10.1016/j.chemosphere.2005.03.071

Peng, B., D. Wu, J. Lai, H. Xiao, and P. Li. 2012. Simultaneous determination of halogens (F, Cl, Br, and I) in coal using pyrohydrolysis combined with ion chromatography. *Fuel* 94: 629–31. doi:10.1016/j.fuel.2011.12.011

Pereira, J. S. F., C. M. Moreira, C. N. Albers, O. S. Jacobsen, and E. M. M. Flores. 2011. Determination of total organic halogen (TOX) in humic acids after microwave-induced combustion. *Chemosphere* 83: 281–86. doi:10.1016/j.chemosphere.2010.12.068

Putschew, A., M. Mania, and M. Jekel. 2003. Occurrence and source of brominated organic compounds in surface waters. *Chemosphere* 52: 399–407. doi:10.1016/S0045-6535(03)00195-4

Ratafia-Brown, J. A. 1994. Overview of trace element partitioning in flames and furnaces of utility coal-fired boilers. *Fuel Processing Technology* 39: 139–57. doi:10.1016/0378-3820(94)90177-5

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Razus, D., C. Movileanu, V. Brinzea, and D. Oancea. 2006. Explosion pressures of hydrocarbon–air mixtures in closed vessels. *Journal of Hazardous Materials* 135: 58–65. doi:10.1016/j.jhazmat.2005.10.061

Razus, D., C. Movileanu, and D. Oancea. 2007. The rate of pressure rise of gaseous propylene–air explosions in spherical and cylindrical enclosures. *Journal of Hazardous Materials* 139: 1–8. doi:10.1016/j.jhazmat.2006.05.103

Sahu, J. N., J. Acharya, and B. C. Meikap. 2009. Response surface modeling and optimization of chromium(VI) removal from aqueous solutions using tamarind wood activated carbon in batch process. *Journal of Hazardous Materials* 172: 818–25. doi:10.1016/j.jhazmat.2009.07.075

Sánchez, M. S., L. A. Sarabia, and M. C. Ortiz. 2012. On the construction of experimental designs for a given task by jointly optimizing several quality criteria: Pareto-optimal experimental designs. *Analytica Chimica Acta* 754: 39–46. doi:10.1016/j.aca.2012.10.014

Souza, G. B., E. N. V. M. Carrilho, C. V. Oliveira, A. R. A. Nogueira, and J. A. Nóbrega. 2002. Oxygen bomb combustion of biological samples for inductively coupled plasma optical emission spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy* 57: 2195–201. doi:10.1016/s0584-8547(02)00180-5

Sredović, I., and Lj. Rajaković. 2010. Pyrohydrolytic determination of fluorine in coal: A chemometric approach. *Journal of Hazardous Materials* 177: 445–51. doi:10.1016/j.jhazmat.2009.12.053

Sun, M., Y. Gao, B. Wei, and X. Wu. 2010. Determination of iodine and bromine in coal and atmospheric particles by inductively coupled plasma mass spectrometry. *Talanta* 81: 473–76. doi:10.1016/j.talanta.2009.12.026

Vera Candioti, L., M. M. De Zan, M. S. Cámara, and H. C. Goicoechea. 2014. Experimental design and multiple response optimization. Using the desirability function in analytical methods development. *Talanta* 124: 123–38. doi:10.1016/j.talanta.2014.01.034

Vinder, A., and M. Simonič. 2012. Removal of AOX from waste water with mixed surfactants by MEUF. *Desalination* 289: 51–57. doi:10.1016/j.desal.2012.01.007

Wang, W., Y. Qin, J. Wang, J. Li, and D. J. Weiss. 2010. A preliminary method for determining acceptable trace element levels in coal. *Energy* 35: 70–76. doi:10.1016/j.energy.2009.08.028

Warych, J., and M. Szymanowski. 2001. Model of the wet limestone flue gas desulfurization process for cost optimization. *Industrial & Engineering Chemistry Research* 40: 2597–05.

Wood, R. A., L. S. Dale, and K. W. Riley. 2003. A borate fusion method for the determination of fluorine in coal. *Fuel* 82: 1587–90. doi:10.1016/S0016-2361(03)00090-5

Wu, D., H. Deng, W. Wang, and H. Xiao. 2007. Catalytic spectrophotometric determination of iodine in coal by pyrohydrolysis decomposition. *Analytica Chimica Acta* 601: 183–88. doi:10.1016/j.aca.2007.08.041

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Xu, M., R. Yan, C. Zheng, Y. Qiao, J. Han, and C. Sheng. 2003. Status of trace element emission in a coal combustion process: A review. *Fuel Processing Technology* 85: 215–37.

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Table 1. Estimated effects and regression coefficients for fractional factorial design

Term	Effect	Coefficient	*T*-value	*p*-value
Constant		333.06	43.45	0.001
Oxygen pressure	26.13	13.06	1.70	0.231
Catalyst/coal ratio	–113.63	–56.81	–7.41	0.018
Absorption solution	–95.37	–47.69	–6.22	0.025
H_2O_2	–18.13	–9.06	–1.18	0.359
Cooling time	7.88	3.94	0.51	0.659
Combustion aid	38.63	19.31	2.52	0.128
Oxygen pressure × Catalyst/coal ratio	–8.13	–4.06	–0.53	0.649
Oxygen pressure × Absorption solution	–2.38	–1.19	–0.15	0.891
Oxygen pressure × Hydrogen peroxide	18.88	9.44	1.23	0.343
Oxygen pressure × Cooling time	26.37	13.19	1.72	0.228
Oxygen pressure × Combustion aid	–42.87	–21.44	–2.80	0.108
Catalyst/coal ratio × Hydrogen	20.62	10.31	1.35	0.311

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

peroxide				
Catalyst/coal ratio × Combustion aid	18.38	9.19	1.20	0.353
Oxygen pressure × Catalyst/coal ratio × Hydrogen peroxide	14.13	7.06	0.92	0.454
Oxygen pressure × Catalyst/coal ratio × Combustion aid	17.38	8.69	1.13	0.375
Center Point		4.60	0.24	0.834

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Table 2. Estimated regression coefficients for response surface design

Term	Coefficient	Standard error of the coefficient	*p*-value
Constant	87.231	1.520	0.000
Oxygen pressure	1.433	1.494	0.369
Combustion aid	9.433	1.494	0.000
Oxygen pressure × Oxygen pressure	–14.859	2.202	0.000
Combustion aid × Combustion aid	1.341	2.202	0.562
Oxygen pressure × Combustion aid	–6.775	1.830	0.008

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Table 3. Analysis of variance (ANOVA) for response surface model (coded units)

Source of variation	Degrees of freedom	Sequential sum of squares	Adjusted sum of squares	Adjusted mean of squares	*F*-value	*p*-value
Regression	5	1399.89	1399.89	279.979	20.90	0.000
Linear	2	546.25	546.25	273.127	20.39	0.001
Square	2	670.04	670.04	335.018	25.01	0.001
Interaction	1	183.60	183.60	183.603	13.71	0.008
Residual error	7	93.78	93.78	13.397		
Lack-of-fit	3	58.98	58.98	19.659	2.26	0.224
Pure error	4	34.80	34.80	8.700		
Total	12	1493.67				

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Table 4. Optimized parameters for the combustion ion chromatography method

Parameters	Values
Oxygen pressure (megapascals)	2.5
Catalyst/Coal mass ratio	0
Absorption solution	H_2O
Hydrogen peroxide (wt percent)	0.5
Cooling time (minutes)	15
Combustion aid (microliters)	150

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Table 5. Determination of total halogens in composite coal by combustion ion chromatography

Sample	Total halogens (milligrams per kilogram)		Relative standard deviation (percent)	Recovery (percent)
	Certified/Expected value	Determined value		
Kolubara Field 1	457	443 ± 10.5	1.90	97
Kolubara Field 1 Spike 1	670	673 ± 25.6	3.10	104
Kolubara Field 1 Spike 2	934	893 ± 24.0	2.16	96
Kolubara Field 2	346	334 ± 5.80	1.40	97
Kolubara Field 2 Spike 1	529	544 ± 12.3	1.82	103
Kolubara Field 2 Spike 2	711	689 ± 14.8	1.73	97

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

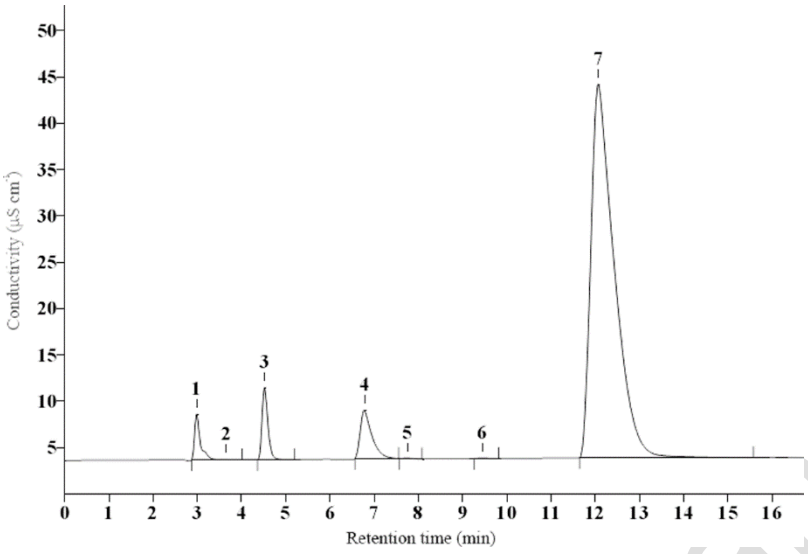
Table 6. Recoveries of total halogens in coal certified reference materials by combustion ion chromatography

Sample	Total halogens (milligrams per kilograms)		Relative standard deviation (percent)	Recovery (percent)
	Expected value	Determined value		
BCR 460	479 ± 19.7	523 ± 24.9	3.83	109
NIST 1632c	1283 ± 41.6	1219 ± 23.8	2.05	95

Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

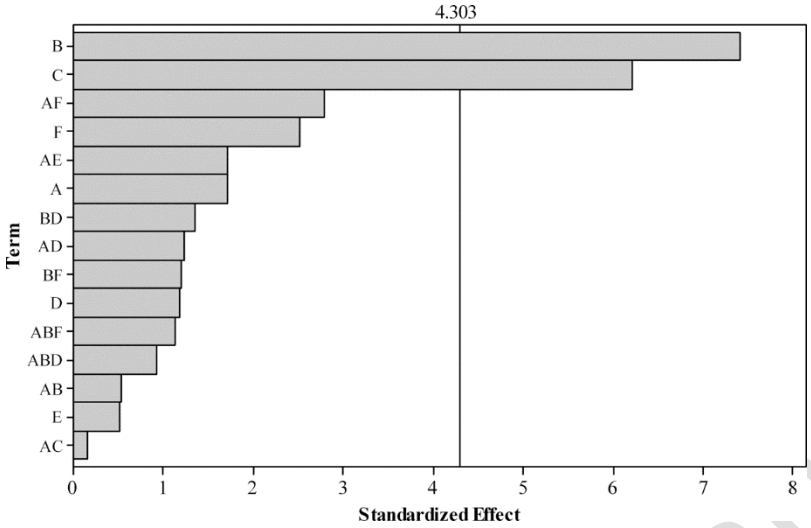
Figure 1. Chromatogram of coal. Conditions: oxygen pressure 2.5 megapascals; no catalyst; H2O as absorption medium; 1 wt percent H2O2, 100 microliters of combustion aid, and twenty-five minute cooling. Peaks: (1) fluoride, (2) unidentified, (3) chloride, (4) nitrate, (5) bromide, (6) unidentified, and (7) sulfate.



Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

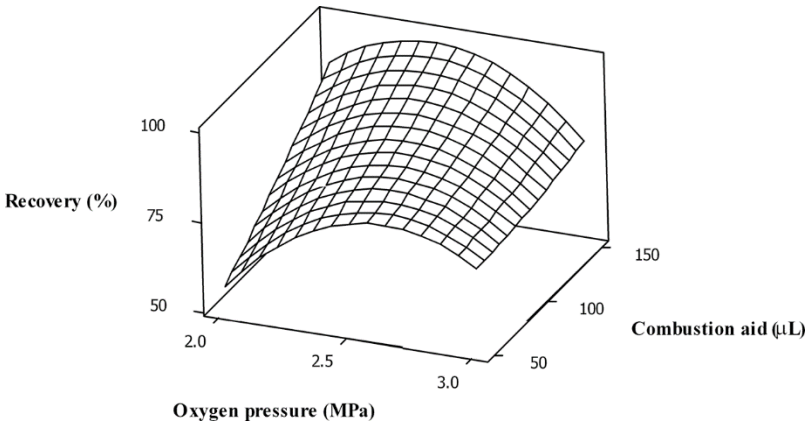
Figure 2. Pareto chart of the standardized effects for determination of total halogens by combustion ion chromatography. The vertical line defines the 95 percent confidence interval. Factor abbreviations: (A) oxygen pressure, (B) catalyst/coal mass ratio, (C) absorption solution, (D) hydrogen peroxide, (E) bomb cooling time, and (F) combustion aid.



Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript

Figure 3. Response surface plot of the total halogen recovery as a function of oxygen pressure and combustion aid.



Downloaded by [University of Otago] at 10:25 05 July 2015

Accepted Manuscript