

# ELEMENTAL ANALYSIS OF OAK AND HICKORY CHARCOAL USING NEUTRON ACTIVATION ANALYSIS

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## ABSTRACT

One-cm cubes of heartwood of white oak and shagbark hickory wood and charcoal were analyzed for selected inorganic elements using neutron activation analysis. A multi-element survey procedure with short (30-sec) and long (24-h) irradiation exposures was developed for use with the University of Missouri Research Reactor Facility. Output of this facility is 10 Megawatts, generating a flux of  $1 \times 10^{14}$  neutrons/cm<sup>2</sup>/sec. Matched wood samples were converted into charcoal utilizing (1) commercial process in a Missouri-type kiln, and (2) laboratory charring using specified time/temperature schedules.

Inorganic concentrations of Al, Ba, Br, Ca, Ce, Co, Cr, Eu, Fe, K, Mg, Mn, Na, Rb, and Zn were found to increase with charring temperature as a result of the reduced charcoal yield. The elements measured accounted for some 60% of the ash content, which was also shown to increase in inverse proportion to the charcoal yield.

**Keywords:** *Quercus alba*, *Carya ovata*, charcoal, ash, minerals, neutron activation analysis, chemical analysis.

## INTRODUCTION

Historically, the use of charcoal as fuel and as a source of pure carbon for metallurgy is well known, but recently its use in the chemical industry because of its carbon content and absorbent properties has become extensive. The amount and composition of the ash are quite significant factors in most forms of charcoal utilization. Ash removal is important when charcoal is used as fuel or in carbon bisulfide manufacture. In activated charcoal the composition of the ash can profoundly affect the absorbing properties of the material (Humphreys and Ironside 1974).

In contrast to wood, few studies have been made concerning inorganic constituents of charcoal. Stokes and Friedenstien (1952) give the ash content of commercial charcoal as ranging between 1.5 and 3.5% (based on the dry weight of charcoal). Humphreys and Ironside (1974) give the ash content from over fifty Australian species and report results of the ash analysis for nineteen of these

species. They state that their results may be used only as a guide as the sample was inadequate and analytical techniques were inferior to those currently employed.

Various analytical techniques have been used to determine quantities of inorganic elements in wood; these include gravimetric, spectrographic, flame photometry, spectrophotometry, and X-ray fluorescence. Most of these techniques require chemical separation, digestion, or otherwise cumbersome sample preparation.

Neutron activation analysis (NAA) permits nondestructive testing for qualitative and quantitative analysis of trace elements in wood. Sample preparation is quick and convenient; samples may be irradiated in the form of solid wood, sawdust, wood flour, or ash. Analysis of wood for its inorganic content has been greatly enhanced by improvements in gamma-counting equipment and high flux reactors. Developments in electronics such as the 4,096-channel analyzer and high resolution, solid-state gamma-counting detectors have made NAA the most sensitive means known at the present for the detection of the majority of elements in wood (Guinn and Lukens 1965).

The convenience and sensitivity of NAA have made its application to the study of inorganics in wood increasingly popular. Meyer and Langwig (1973) identified twenty-one inorganic elements from thirty-one domestic and tropical woods in a comprehensive study of the neutron activation analysis of wood. Lyon (1964) and Kruger (1971) have provided a more detailed treatment of the theory, practice, and limitations of NAA.

In this study, the inorganic elements of oak and hickory wood and charcoal were quantitatively determined using NAA. The elements of interest were all those measured using a multi-element survey procedure with two irradiation periods. Charcoal was formed by two processes: 1) commercial batch process in a Missouri-type kiln; and 2) laboratory charring using specified time/temperature schedules simulating those encountered in the Missouri-type kiln. In this manner not only could the effects of charring be studied, but also the accuracy of simulating commercial charcoal using laboratory conditions.

#### EXPERIMENTAL PROCEDURE

##### *Sample preparation*

Four matched sets of twenty samples each were prepared by cutting 1-cm cubes from a narrow tangential section of heartwood from white oak (*Quercus alba* L.) and shagbark hickory (*Carya ovata* Mill.) trees. One set was kept for inorganic analysis (control); one set was used for commercial charring; one set was used for laboratory charring; and one set was kept in reserve. Wood samples were sanded smooth, oven-dried, weighed, and stored over desiccant until inorganic analysis or charring.

##### *Charring procedure*

Designated wood samples were placed, one each, into forty perforated, one-inch-diameter pipes for commercial charring. Two such samples, one oak and one hickory, were placed at each of twenty locations, during loading, in a Missouri-type kiln. The pipes containing each pair of samples were wrapped with asbestos-insulated iron-constantan thermocouple wire to monitor the temperature

every 4 h from initial firing through the cooling cycle. The operation and design details of the Missouri-type kiln have been presented in works by Jarvis (1960) and the U.S. Forest Products Laboratory (1961).

Laboratory charring, under a nitrogen atmosphere, was done using ten schedules approximating the range of those observed previously in Missouri commercial kilns (McGinnes et al. 1971). Maximum temperatures and corresponding heating rates ranged from 250 to 800 C and 1.5° to 130°/h, respectively.

The charring procedure consisted of placing four oven-dried wood cubes (two oak, two hickory) on a vycor boat, which was then inserted into a horizontal furnace (550 watt), and the nitrogen flow rate was adjusted to 500 ml/min to purge the system of oxygen. A temperature programmer and cyclic timers were set for the required heating rate and the gas flow was reduced to 50 ml/min. During the run the temperature was recorded on a strip chart recorder. When the end point was reached, the heating system was shut off and the furnace tube permitted to cool. After commercial and laboratory charring, samples were oven-dried, weighed, and stored in cleaned polyethylene vials until inorganic analyses were undertaken.

#### *Neutron activation analysis*

A multi-element procedure using two irradiation periods was developed for use within the University of Missouri's 10 Megawatt Research Reactor. Irradiations were made in the reactor's graphite reflector, operating at a neutron flux of approximately  $1 \times 10^{14}$  neutrons/cm<sup>2</sup>/sec; samples were in sealed quartz vials for long periods and in high-density polyethylene vials for short irradiations. The University Research Reactor Facilities and instrumentation have been detailed in a technical report by the Nuclear Science Group at the University (Vogt 1970).

Wood and charcoal samples were placed, one each, in 4-dram polyethylene vials for 30-sec irradiations in the pneumatic tube facility. The sealed vial was positioned in a molded high-density polyethylene "rabbit" using a spacer to reduce variations in irradiation geometry. The irradiation timing cycle was controlled automatically from the laboratory station console using a Microflex Timer (0.1 sec/division).

Irradiated samples were transferred to nonradioactive counting vials, and after a decay of 10 min, they were counted for 500 sec on the Ge(Li) system using a scale of 1 Kev/channel for the 4,096 channels. To calibrate the spectrum, an NBS calibrated Ra<sup>226</sup> standard solution was counted for 200 sec. The 45 cm<sup>3</sup> coaxial Ge(Li) detector has a gamma-ray energy resolution of 2.5 Kev (FWHM for 1.33 Mev Co<sup>60</sup>), a peak-to-compton ratio of 28:1 and an efficiency [relative to NaI(Tl) for the 1.33 Mev Co<sup>60</sup> gamma-ray] of 9.4%.

The detector was coupled through a linear amplifier and baseline restorer to a 4,096 channel Packard 900-series pulse-height analyzer. Data readout from the analyzer was via incremental Kennedy 9-track, 800 bpi computer compatible magnetic tape with tag work identification. The tape was then analyzed on the University's IBM 370/165 computer network using the BARFF computer code, an adaptation of the M.I.T. GAMANL code (Harper et al. 1968).

Ample quantities of standard solutions were prepared containing similar concentrations of all the elements that were semi-quantitatively determined during procedure development. Standard concentrations for these elements, along with some of the properties that are important to this method, are shown in Table 1.

TABLE 1. Summary of radionuclides measured using two irradiation exposures.

Radio-nuclide	Gamma-ray (Kev)	Half-life	Std conc	
			Oak (μg/ml)	Hickory (μg/ml)
Short irradiation <sup>a</sup>				
Al-28	1,778.9	2.31 m	0.77	2.0
Ca-49	3,083	8.8 m	1,056	1,173
Cl-38	1,642	37.3 m	6.8	9.1
Mg-27	1,014.1	9.5 m	114	526.5
Mn-56	1,810.7	2.58 h	13.5	193.7
K-42	1,524.7	12.4 h	524	1,132
Na-24	1,368.4	15.0 h	7.4	10.4
Long irradiation <sup>b</sup>				
Ba-131	216.3	12 d	200.8 μg/.2 ml	
Br-82	554.2	35.5 h	2.93 μg/.2 ml	
Ce-141	145.6	33 d	10.06 μg/.2 ml	
Co-60	1,173	5.26 yr	1.95 μg/.2 ml	
	1,332			
Cr-51	319.7	27.8 d	4.02 μg/.2 ml	
Eu-152	344.2	13 yr	0.56 μg/.2 ml	
Fe-59	1,099	45.1 d	506.5 μg/.2 ml	
	1,292			
Rb-87	1,076.8	5 × 10 <sup>11</sup> h	99.5 μg/.2 ml	
Zn-65	1,115	243.6 d	40.2 μg/.2 ml	

<sup>a</sup> Samples were irradiated 30-sec, 10-min decay, and 500-sec count.<sup>b</sup> Samples were irradiated 24-h, 13-day decay, and 500-sec count. One standard was used for oak and hickory.

By preparing a mixed standard similar in concentration to the wood, the validity of using a direct ratio of sample activity to standard activity of a particular radionuclide is enhanced. In this way, fewer normalizations are required and additional sources of error are eliminated. Since the sample and standard have very similar gamma-ray spectra, errors are reduced caused by analyzer dead time in the measurement of radionuclides having short half-lives. Therefore, all the parameters affecting an observed count rate upon which an analysis is based were made identical for both sample and standard.

A 24-h irradiation was chosen for the quantitative measurement of long half-lived elements. Wood and charcoal samples were ashed before irradiation to prevent pressure build-up from evolved volatile compounds. Three matched sample sets (wood, commercial, and laboratory charcoal) were ashed in a muffle furnace at 550 to 600 C in a manner described by Browning (1967) to minimize any change in organic constituents. Ashed samples were cooled to room temperature in an efficient desiccator and were weighed to determine percent ash (based on the original oven-dried weight of the wood or charcoal sample). Ashed samples and long-irradiation time standards were heat-sealed in quartz vials, which were enclosed in an aluminum can and placed in the graphite reflector for 24 h. Following a decay of 13 days, the quartz vials were broken open, and samples and standards were transferred to nonradioactive vials for a 500-sec count on the Ge(Li) detector using a scale of 0.5 Kev/channel. A  $\text{Ra}^{226}$  standard was counted to calibrate the spectrum, and data readout was obtained by magnetic tape using the University computer network.

TABLE 2. *Ash content of oak and hickory wood and charcoal.*<sup>a</sup>

Sample	Number of replications	Oak	Hickory
wood	3 ea.	0.28 (.05) <sup>b</sup>	0.37 (.02) <sup>b</sup>
300S <sup>d</sup>	1	0.49 (.47) <sup>c</sup>	—
400S	1	—	1.00 (.95) <sup>c</sup>
400L	1	0.87 (.86) <sup>c</sup>	—
600L	1	—	1.54 (1.43) <sup>c</sup>
800M	1	—	1.54 (1.47) <sup>c</sup>
800L	1	0.91 (1.02) <sup>c</sup>	—
Commercial Char	3 ea.	1.04 (.83) <sup>c</sup>	1.14 (1.13) <sup>c</sup>

<sup>a</sup> Ash content was determined as percent of wood or charcoal precursor.<sup>b</sup> Standard deviation in parentheses for 3 replications of oak and hickory wood ash.<sup>c</sup> Normalized values in parentheses were calculated from wood controls and charcoal yields.<sup>d</sup> The letters S, M, and L refer to length of residence time at the indicated maximum temperature (degrees C) S = 0 hours, M = 12 hours, and L = 50 hours ( $\alpha$  400°, 100 hours ( $\alpha$  600°, and 114 hours ( $\alpha$  800°).

Gamma-ray spectra were calibrated using the known photopeaks of the Ra<sup>226</sup> standard to identify the channel number of the desired gamma-ray for each element (see Table 1). The sample activity was divided by sample weight to give counts/gram wood, and the standard activity was divided by the micrograms of the element that produced it. By utilizing a direct ratio of sample activity to standard activity, concentration of each element was determined:

$$\text{PPM} = \frac{\text{counts/gm wood}}{\text{counts}/\mu\text{g standard}} \cdot$$

## RESULTS AND DISCUSSION

### *Ash content*

The ash content of oak and hickory wood and selected charcoals is shown in Table 2. From the table it is apparent that the ash content of charcoal is greater than that of wood and is a function of the maximum charring temperature employed. The higher the temperature, the greater the ash content over the range of 300 to 800 C.

Normalized values in Table 2 were calculated by adjusting the ash content of the wood control for the charcoal yield of the sample. For instance, for oak charred to 300 C, the ash content of the matched wood control (0.24%) was divided by the fractional yield (0.505) to obtain the normalized value (0.47%). Statistical analysis of the paired observations (measured and normalized) revealed no significant difference at the 1% level. The percentage of ash in charcoal increased in inverse proportion to charcoal yield, which is temperature-dependent.

Chemical composition of ash was determined as oxides of all the elements quantitatively measured. Oxides of calcium, potassium, and magnesium comprised approximately 50% of wood and charcoal ash. For oak wood, levels of calcium (36%), potassium (14%), and magnesium (5%) were consistent with general amounts for ash components reported by Wise (1952). Ash from hickory wood had higher levels of magnesium (26%), and somewhat less calcium (18%) and potassium (5%). Excluding manganese (4%) in hickory, the remaining elements measured (Al, Ba, Br, Ce, Cl, Co, Cr, Eu, Fe, Na, Rb, and Zn) comprised less than 3% of the wood ash. In all, about 60% of the ash was accounted for in

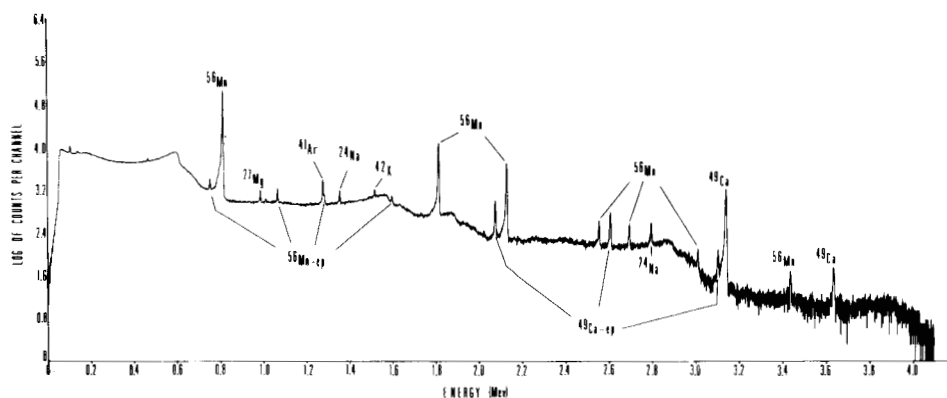


FIG. 1. Ge(Li) gamma spectrum of oak charcoal (52% yield) carbonized under laboratory conditions to 300 C.

this study. The bulk of unidentified ash constituents are probably common acid radicals such as carbonates, phosphates, silicates, and sulfates which Wise (1952) reported are always present in wood.

There was little significant change in the chemical composition of the ash upon charring. However, for charcoals formed in a Missouri-type kiln, the proportion of iron and zinc increased substantially, probably indicating contamination from the pipe used to hold the samples. This may contribute to the higher level of ash (than that predicted by normalization) in oak charcoal produced by the commercial process (see Table 2).

#### *Inorganic constituents*

In Figs. 1 and 2 the major peaks in the gamma-ray spectra of oak and hickory charcoal have been identified. Peak heights do not indicate relative elemental concentrations, since each radionuclide varies in its activity after irradiation. However, differences between species are reflected by slight variations in the

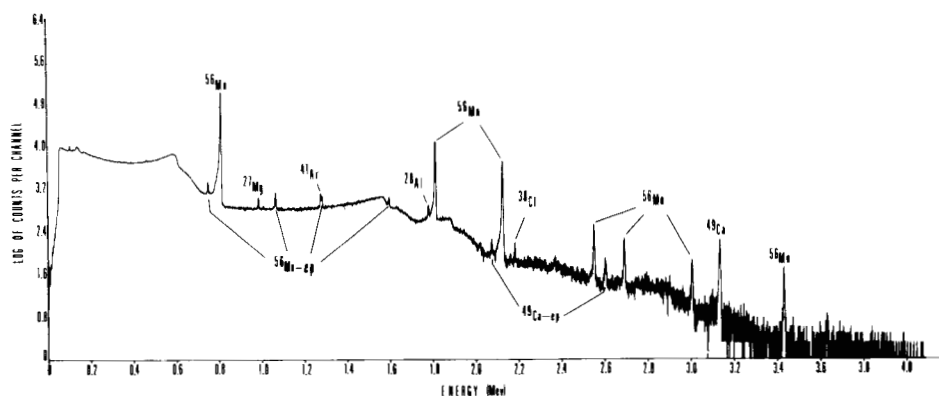


FIG. 2. Ge(Li) gamma spectrum of hickory charcoal (22% yield) carbonized under laboratory conditions to 800 C.

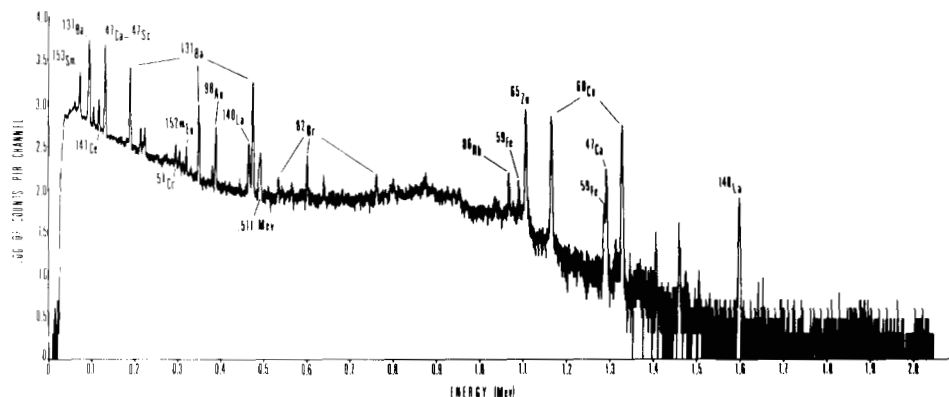


FIG. 3. Ge(Li) gamma spectrum of white oak wood irradiated for 24 h.

shape of the two gamma-ray spectra. For example, in Fig. 2, hickory has larger  $\text{Mn}^{56}$  peaks relative to the other elements, which would suggest a proportionately larger manganese concentration in hickory than oak. In fact, the activity of  $\text{Mn}^{56}$  in hickory was so intense that it prevented the measurement of potassium and sodium using the 30-sec irradiation procedure. Therefore, these elements were quantitatively determined in selected hickory samples using a 1-min irradiation, 24-h decay, and 200-sec count.

Gamma-ray spectra for the 24-h irradiation are shown in Figs. 3 and 4 for oak wood and commercial charcoal, respectively. The overall shape of the spectra was quite similar since ash composition was relatively unchanged by charring.

The results of the quantitative measurements of wood and charcoal are shown in Tables 3 and 4. The range of values is considerable and represents the wide variation of inorganic concentrations in wood. Elemental concentrations in charcoal were significantly higher than wood and generally increased with charring temperature. Normalized concentrations were determined for each charcoal sample by assuming no change in elemental amount, but an increase in concentration

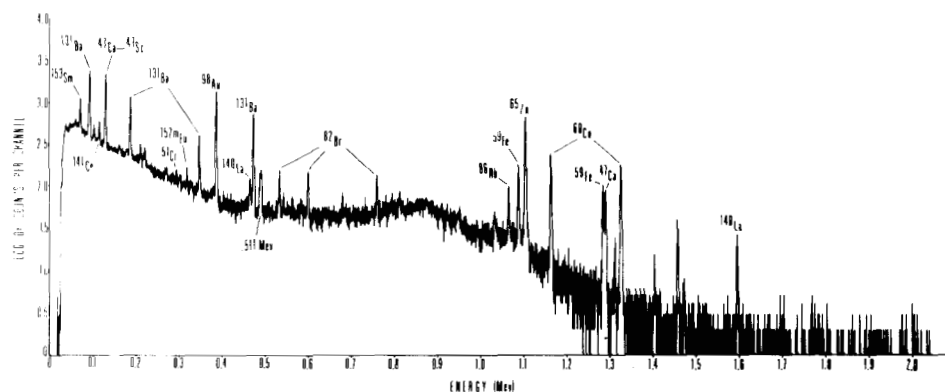


FIG. 4. Ge(Li) gamma spectrum of white oak charcoal (34% yield) formed in a commercial kiln. Sample irradiated for 24 hr.

TABLE 3. Levels of inorganic constituents in wood and charcoal determined by short irradiation.<sup>a</sup>

Sample <sup>b</sup>	Al	Ca	Cl	K	Mg	Mn	Na
White oak							
Wood	1.2 (42)	820 (20)	11 (36)	366 (28)	95 (16)	30 (17)	8.8 (40)
300°C	<1.8	1,672	<1.7	706	102	59	19
600°C	7.7	2,833	<3.4	1,294	320	117	30
800°C	6.2	3,212	<4.2	1,239	360	115	26
Commercial charcoal	2.0 (85)	2,978 (36)	12.3 (91)	1,218 (24)	308 (33)	104 (32)	25 (40)
Shagbark hickory							
Wood	—	408 (10)	—	155 (14)	529 (30)	117 (5)	6.4 (48)
300°C	—	548	—	183	642	134	6
600°C	—	1,618	—	594	1,535	413	22
800°C	—	1,886	—	910	2,232	502	13
Commercial charcoal	—	2,007 (48)	—	497 (7)	1,623 (35)	438 (47)	26 (65)

<sup>a</sup> Determinations are expressed in ppm (parts per million). Coefficient of variation is given in parentheses for wood and commercial charcoal.

<sup>b</sup> Values represent an average of 15–20 samples for wood and commercial charcoal (formed in a Missouri-type kiln). Charcoal formed under laboratory conditions is given by maximum charring temperature. There were 2–6 samples for each temperature.

due to mass loss on charring. Measured and normalized values were analyzed by pairing observations in a manner described by Dixon and Massey (1969).

There was no significant difference at the 1% level in measured and normalized concentrations of Al, Ba, Br, Ca, Ce, Co, Cr, Eu, Fe, Mg, Mn, Na, Rb, and Zn. For these elements there was no significant change in absolute amount, only an increase in concentration due to the mass loss of the charred wood. This is especially interesting for calcium since McGinnes et al. (1974) have shown that the middle lamella of wood fibers is eliminated as an anatomical feature by fusion of adjacent cell walls during charring. However, it must be remembered that calcium pectate is only a small proportion of the middle lamella and that loss of anatomical identity does not mean that chemical loss has necessarily occurred.

Only chlorine was substantially affected by the conversion of wood into charcoal. In oak there was a 69 and 89% loss of chlorine for commercial and laboratory chars, respectively.

The highly variable distribution of mineral components in wood was evidenced by coefficients of variation from 5 to 107%. Variability was even larger for most elements in commercial charcoal since values reflect a wide range of charring conditions and charcoal yields.

#### CONCLUSION

Sixteen elements in white oak and shagbark hickory wood and charcoal were determined quantitatively using neutron activation analysis. Inorganic concentrations in charcoal were temperature-dependent, increasing with charring temper-



TABLE 4. Levels of inorganic constituents in wood and charcoal determined by long irradiation.<sup>a</sup>

Sample <sup>b</sup>	Ba	Br <sup>c</sup>	Ce	b3Co <sup>c</sup>	Cr <sup>c</sup>	Eu <sup>c</sup>	Fe	Rb <sup>c</sup>	Zn
White oak									
Wood	12 (5)	60 (30)	0.06 (20)	77 (61)	30 (23)	4 (5)	5 (10)	213 (16)	2 (50)
400°C	29	220	0.13	44	33	10	7	573	3
800°C	60	507	0.30	301	138	25	22	913	3
Commercial charcoal	25 (24)	342 (60)	0.12 (75)	98 (76)	37 (22)	6 (10)	46 (93)	354 (64)	392 (87)
Shagbark hickory									
Wood	41 (71)	67 (107)	1 (50)	56 (29)	17 (76)	22 (64)	2 (15)	127 (79)	9 (33)
400°C	158	339	3	202	45	92	16	344	31
800°C	323	403	9	376	260	258	<3	788	<1
Commercial charcoal	202 (32)	648 (43)	4 (50)	308 (66)	121 (55)	121 (57)	58 (91)	431 (42)	51 (20)

<sup>a</sup> Coefficient of variation is given in parentheses for wood and commercial charcoal.<sup>b</sup> Values represent an average of 3 samples for wood and commercial charcoal. There was one sample for laboratory charcoal at each temperature.<sup>c</sup> Determinations are expressed in ppb (parts per billion), all other elements in ppm.

ature (except chlorine) as a result of the reduced charcoal yield. The elements measured accounted for some 60% of the ash content, which was also shown to increase in inverse proportion to the charcoal yield.

Inorganic analysis indicated the above relationships for charcoal produced in either a Missouri-type kiln or under laboratory conditions simulating commercial charring. Therefore in future studies concerning inorganic constituents of commercial charcoal, it may be desirable to simulate commercial charring conditions using carefully controlled laboratory processes.

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