

INORGANIC CONCENTRATIONS IN SELECTED WOODS AND CHARCOALS MEASURED USING NAA

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(Received 3 August 1979)

ABSTRACT

Neutron activation analysis was used to determine the levels of several inorganic elements in seven species of wood- and laboratory-prepared charcoals. The samples were exposed for 1 min to a thermal neutron flux of 1×10^{14} n/cm²-sec. Following a 10-min decay period, sample activity was measured for 500 sec. Concentrations of Al, Ca, Cl, K, Mg, Mn, and Na were measured. Ba, Cu, Sr, and V were also identified in several samples. Matched samples of southern pine earlywood and latewood contained similar amounts of *inorganics*.

Keywords: Inorganics, woods, charcoals, NAA, southern pine, earlywood, latewood.

While several techniques have been used to identify and quantify inorganics in wood, most of them require some sort of destructive sample pretreatment before actual measurements can take place. Neutron activation analysis (NAA) is a nondestructive method of elemental analysis well suited to both qualitative and quantitative analyses. Using NAA, wood may be analyzed in either solid or powder form. The limits of detection vary with the element under study and the irradiation conditions employed.

The theory and applicability of NAA to wood analyses have been reviewed and demonstrated previously. Young and Guinn (1966) used NAA to examine seven species of wood. They quantitatively measured five elements and determined detection limits for another seventy elements. Meyer and Langwig (1973) surveyed thirty-one domestic and tropical species of wood and identified twenty-one different inorganic elements. Osterhaus et al. (1975) reanalyzed some of these samples using more sophisticated instrumentation and reported similar results. Slocum et al. (1978) used NAA to analyze cubes of white oak and shagbark hickory that were charred in either a commercial charcoal kiln or a laboratory furnace. They detected sixteen inorganic elements and found that, with the exception of Cl, the concentration of an element in the ash was directly proportional to the charring temperature.

METHODS AND MATERIALS

Matched samples of 7 woods (shown in Table 1) were charred in a flowing N₂ atmosphere using the apparatus described by Beall (1977) at rates of 1 C/min, 10 C/min, and 50 C/min to temperatures of 250 C, 300 C, 350 C, 400 C, and 600 C. The gross physical behavior and properties of these samples have been described

TABLE 1. Elements detected in wood and char samples.

Species	
Southern pine	Al, Ca, Cl, K, Mg, Mn, Na
Douglas-fir	Al, Ca, Cl, Mg, Mn, Na
Redwood	Al, Ba, Ca, Cl, Cu, K, Mg, Mn, Na, V
Western redcedar	Al, Ca, Cl, Cu, K, Mg, Mn, Na, V
White oak	Al, Ba, Ca, Cl, Cu, K, Mg, Mn, Na
Basswood	Al, Ba, Ca, Cl, Cu, K, Mg, Mn, Na, Sr
Hard maple	Al, Ca, Cl, K, Mg, Mn, Na

by Beall (1977) and Beall et al. (1977). The wood and char samples were dried to constant weight *in vacuo* at 60 C, cooled in a desiccator containing CaCl₂, and weighed. Duplicate samples of each treatment combination were heat-sealed in individual 4-dram polyethylene (PE) vials.

A multi-element neutron activation analysis (NAA) procedure similar to that of Slocum et al. (1978) was used to quantitatively determine amounts of Al, Ca, Cl, K, Mg, Mn, and Na in the samples of the domestic woods. These elements account for the majority of the ash in wood (Ellis 1962, 1965; Humphreys and Ironside 1974).

The individual PE sample vials were placed in high-density PE "rabbits" with spacers to ensure reproducible sample positioning. Each sample was irradiated sequentially for one (1) min at a thermal neutron flux of 1×10^{14} n/cm²/sec using the pneumatic tube facility at the University of Missouri's 10 MW Research Reactor. The reactor facilities and instrumentation have been described in a technical report by the Nuclear Science Group at the University (Vogt 1970).

Following irradiation, each sample was transferred to a clean counting vial and, after a 10-min decay period, was counted for 500 seconds using a Ge(Li) gamma-ray spectrometer system described by Slocum et al. (1978).

Duplicate multi-element standard solutions for each wood species were prepared containing similar concentrations of the elements determined semi-quantitatively during preliminary runs. These solutions were frozen and stored until needed. Aliquots of standard solutions were irradiated and counted in the same manner as the samples.

Gamma-ray spectra were recorded on computer compatible magnetic tape to facilitate data reduction using a modified version of the GAMANL spectrum analysis code (Harper et al. 1968). Integrated peak areas for all significant gamma-ray peaks in the spectra are generated by this code.

The gamma-ray spectra were calibrated using known energy photopeaks of an NBS calibrated RA²²⁶ standard to identify the channel number of the desired inorganic elements. Concentrations, in parts per million (ppm), of the individual elements in the samples were determined using:

$$\text{PPM} = \frac{\text{Peak area activity/gm wood sample}}{\text{Peak area activity}/\mu\text{g standard}} \quad (1)$$

Standard analytical methods were used for statistical analyses.

TABLE 2. *Inorganic concentrations in wood (ppm).*

Element	White oak	Basswood	Hard maple	Southern pine			Douglas-fir	Redwood	Western redcedar
				EW	LW	Wholewood			
Al	6 ^a	15	1	10	17	6	13	(170) ^c	2
Ca	674	1,125	1,064	743	589	764	295	(481)	1,013
Cl	8	93	82	102	23	48	67	(40)	12
K	780	543	990	n.d. ^b	117	39	n.d.	(274)	229
Mg	11	117	140	132	138	110	41	(265)	76
Mn	2	11	36	134	111	97	25	(10)	1
Na	3	74	29	49	34	28	44	(90)	10

^a Determined directly using NAA techniques.

^b n.d. = not detected.

^c Redwood control sample missing. Values estimated using Eq. 2.

RESULTS AND DISCUSSION

Eleven inorganic elements were positively identified using the 1-min irradiation, 10-min decay, and 500-sec counting scheme in the gamma-ray spectra of the various wood and chars (Table 1). The nondetection of an element does not imply complete absence, but that, if it is there, it is below the detection limits of the system under the above conditions. Undoubtedly, additional elements could have been identified if additional irradiation-decay-counting schemes had been used.

Aluminum (Al), calcium (Ca), chlorine (Cl), magnesium (Mg), manganese (Mn), and sodium (Na) were detected in the wood char of each species in this study, while potassium (K) was detected in all but Douglas-fir. Copper (Cu) was identified in four species; redwood, western redcedar, white oak, and basswood. Vanadium (V) was found in redwood and western redcedar. Barium (Ba) was found in redwood, white oak, and basswood, while strontium (Sr) was found only in basswood. Analyses of variance indicated no significant difference among charring rates for any of the inorganic elements quantified. Therefore, values given in the text and tables are average values.

The elemental concentration in the uncharred wood samples (Table 2) indicates a broad range of values among species. For example, Mn values vary from 1 ppm

TABLE 3. *Radiation parameters for elements observed.*

Element	Radionuclide observed	Gamma-ray energy (keV)	Activation cross-section (barns)	$t_{1/2}$
Al	Al-28	1,778.9	0.232	2.29 m
Ba	Ba-139	165.8	0.350	1.37 h
Ca	Ca-49	3,083.0	1.10	1.42 h
Cl	Cl-38	1,642.0	0.43	6.21 h
Cu	Cu-66	1,039.0	2.30	5.10 m
K	K-42	1,524.7	1.30	12.49 h
Mg	Mg-27	1,014.1	0.03	9.49 m
Mn	Mn-56	1,810.9	13.30	2.58 h
Na	Na-24	1,368.5	0.53	15.00 h
Sr	Sr-87m	388.4	0.80	2.80 h
V	V-52	1,434.4	4.80	3.80 m

in western redcedar to 134 ppm in southern pine earlywood. Manganese had the largest activation cross-section (Table 3) of the elements identified and is easily activated. Previous workers had found that the Mn-56 photopeak activity was so intense that it masked peaks of other elements with smaller activation cross-sections (Loos 1965; Galligan et al. 1965). The increased resolution of the Ge(Li) solid-state gamma-ray detectors has enabled much of this masking to be eliminated (Osterhaus et al. 1975).

As pointed out by other authors, there is a lack of published information regarding inorganic concentrations in wood. Galligan et al. (1965) reported 2 to 30 ppm Mn in Douglas-fir. The Douglas-fir wood sample examined in this research contained 25 ppm.

With regard to white oak, the measured concentrations in Table 2 agree reasonably well with values in the literature with the exception of Mg. Slocum et al. (1978) reported 95 ppm Mg, and Osterhaus et al. (1975) found 305 ppm Mg in their white oak samples. The white oak used in this study contained 11 ppm Mg. This points out the extreme variability that may be encountered. All the elements quantified in oak became more concentrated as temperature increased including Cl.

Osterhaus et al. (1975) reported that basswood contained 137 ppm Ca, 88 ppm Cl, 2819 ppm K, 345 ppm Mg, and 6.3 ppm Na. This contrasts significantly with the data in Table 2 where we found 1125 ppm Ca, 93 ppm Cl, 544 ppm K, 118 ppm Mg, and 74 ppm Na. They did not report any levels of Mn using NAA, whereas we found 12 ppm Mn in the samples.

Ellis (1965) reports finding 878 ppm Ca, 274 ppm K, and 170 ppm Na in the sapwood of sugar maple. In a mineral streak area, he found 7621 ppm Ca, 120 ppm K, and 218 ppm Na. The hard maple analyzed in this study contained 1065 ppm Ca, 991 ppm K, and 300 ppm Na.

The samples of southern pine provided an opportunity to compare elemental concentrations in earlywood samples and latewood samples (Table 2 and Fig. 1). The earlywood and latewood samples were taken from a single growth ring of a board showing fast growth. The whole-wood samples were taken from a slow-grown tree and encompassed several growth rings. The data shown in Table 2 are reasonably consistent with previously published values. McMillin (1970) found that loblolly pine earlywood averaged 1141 ppm Ca, 116 ppm K, 326 ppm Mg, 121 ppm Mn, and 230 ppm Na, while latewood contained 885 ppm Ca, 98 ppm K, 240 ppm Mg, 102 ppm Mn, and 180 ppm Na. Choong et al. (1974) found that inorganic concentrations in unfertilized loblolly pine ranged from 476 to 789 ppm Ca, 249 to 429 ppm K, 197 to 281 ppm Mg, 67 to 91 ppm Mn, and 111 to 130 ppm Na.

Temperature vs. concentration

As previously noted, Slocum (1978) indicated that there were positive correlations between charring temperature and inorganic concentrations. Beall (1977) had indicated that weight loss accompanying pyrolysis was best described using a nonlinear relationship with temperature. Our data were analyzed to find which pattern fit the inorganic accumulation data best. Plots of the data suggested that a logarithmic relationship might produce acceptable results (Fig. 1). However, the correlation coefficients produced using a logarithmic equation were less than

TABLE 4. Simple correlation coefficients for charring temperature and inorganic concentrations in seven species.

Element	White oak	Basswood	H. maple	Southern pine			Douglas-fir	Redwood	W. Redcedar
				EW	LW	Wholewood			
Al	0.644* ^a	0.409*	0.587*	0.564*	0.726*	0.509*	0.049	0.831*	0.395
Ca	0.759*	0.862*	0.635*	0.814*	0.851*	0.857*	0.728*	0.872*	0.794*
Cl	0.773*	0.434*	0.005	0.516*	0.176	0.138	0.107	0.242	0.691*
K	0.829*	0.849*	0.456*	0.945*	0.078	0.769*	n.d. ^b	0.461*	0.825*
Mg	0.896*	0.809*	0.838*	0.594*	0.740*	0.730*	0.704*	0.920*	0.777*
Mn	0.761*	0.863*	0.855*	0.760*	0.847*	0.874*	0.693*	0.877*	0.578*
Na	0.688*	0.603*	0.687*	0.679*	0.450*	0.045	0.158	0.795*	0.821*

^a * Indicates significance at the $P \geq 0.05$ level.

^b n.d. = not detected.

the coefficients of simple linear regression. Table 4 shows the inorganic concentrations for wood and char as linear functions of charring temperature. The accumulation patterns for inorganics in the southern pine EW, LW, and wholewood samples (Fig. 1 and 2) are typical of the results for other species. The concentrations of Ca, Mg, and Mn are positively correlated with temperature for each species. Aluminum, potassium, and sodium were usually well correlated with temperature while chlorine behaved erratically. Aluminum has a low activation cross-section (0.232 barns) and a short half-life (2.29 min), and the measured photopeak is fairly close to a very intense manganese photopeak (1778.9 keV for Al; 1816.9 keV for Mn). When "large" concentrations of Mn are present, the very large cross-section of Mn (13.3 barns) may produce enough activity to mask the 1178.9 keV of Al peak. Both Galligan et al. (1965) and Loos (1965) had observed this phenomenon. Chlorine is reasonably volatile and is probably driven off during charring process.

When linear and nonlinear equations were examined to see how well they described the data at 20 C, the results were misleading. Frequently negative inorganic concentrations were indicated. An alternative method of describing the effect of temperature on inorganic accumulations was evaluated using the weight loss at various charring temperatures. The elemental composition data obtained from the various charring levels were corrected to 0% weight loss (the uncharred wood) using the following formula:

$$\text{PPM}_{0\%} = \left(1 - \frac{\% \text{ wt. loss at } X^{\circ}\text{C}}{100} \right) \text{PPM}_{X^{\circ}\text{C}} \quad (2)$$

This equation had been previously used to correct chemical composition in decayed wood (Cowling 1961; Cutter and Murphey 1970). Some of the weight loss data were previously described by Beall (1977) and Beall et al. (1977).

The use of this relationship to estimate inorganic concentrations in wood from char concentrations appears to be reasonable. This is particularly helpful since the redwood control samples were missing from the data set, but we feel that the estimates for inorganic levels in the wood shown in Table 2 are quite reasonable. The use of this equation results in very good agreement for the more stable elements—Ca, K, Mg, Mn—and reasonable values for Al, Cl, and Na. To illus-

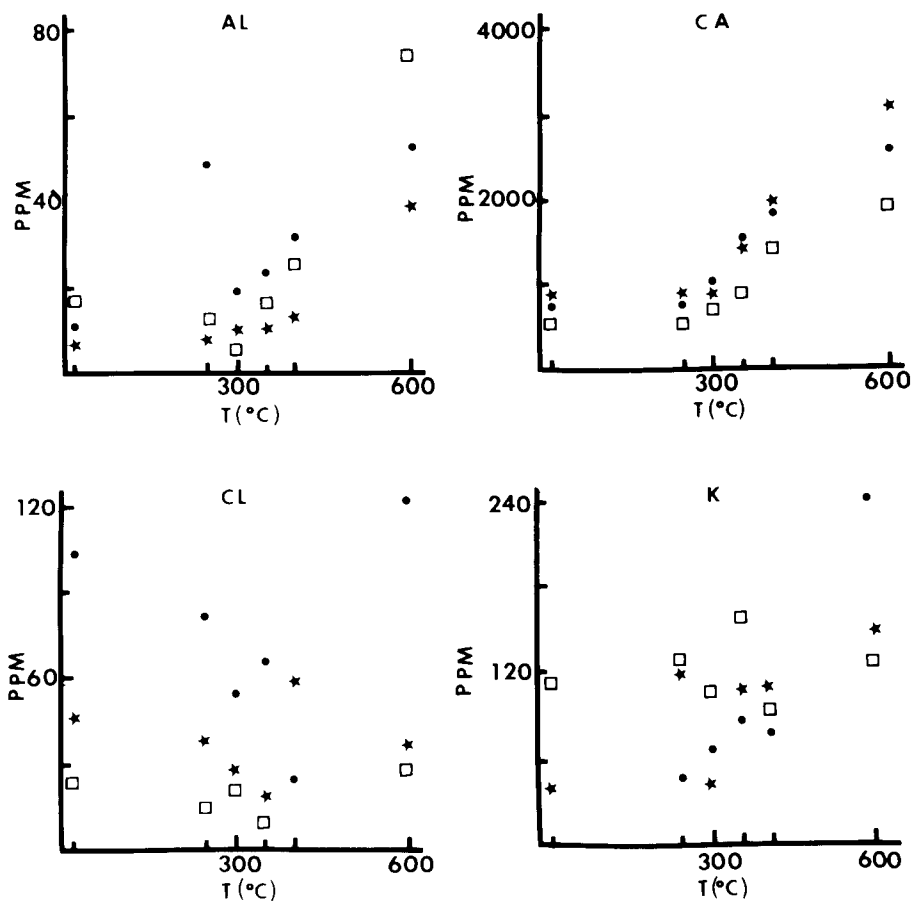


FIG. 1. Accumulation patterns for Al, Ca, Cl, and K in southern pine earlywood (dot), latewood (square), and wholewood (star) as functions of charring temperature.

trate, the levels of Ca, K, Mg, and Mn in basswood wood were found to be 1125, 543, 117, and 11 ppm, respectively (Table 2). Using Equation 2, the estimated levels are Ca, 1069; K, 538; Mg, 124; and Mn, 11 ppm. The detected and estimated levels of the other inorganic elements are as follows: Al, 15 vs. 19 ppm; Cl, 93 vs. 37 ppm; and Na, 74 vs. 96 ppm.

Although in some cases, no peaks were detected for certain elements, it is still possible to estimate the concentration at which a discernible peak would be observed using Eq. 3

$$\text{Detection limit (ppm)} = \frac{2\sigma(\text{peak width})/\text{gm wood sample}}{\text{activity}/\mu\text{g sample}} \quad (3)$$

where σ is equal to the square root of the average background activity detected in the channels defining the peak width. The peak width is a whole number from 6 to 10. In the case of Douglas-fir, no K activity was detected. However, application of Eq. 3 indicates that there was less than 5 ppm K in the wood.

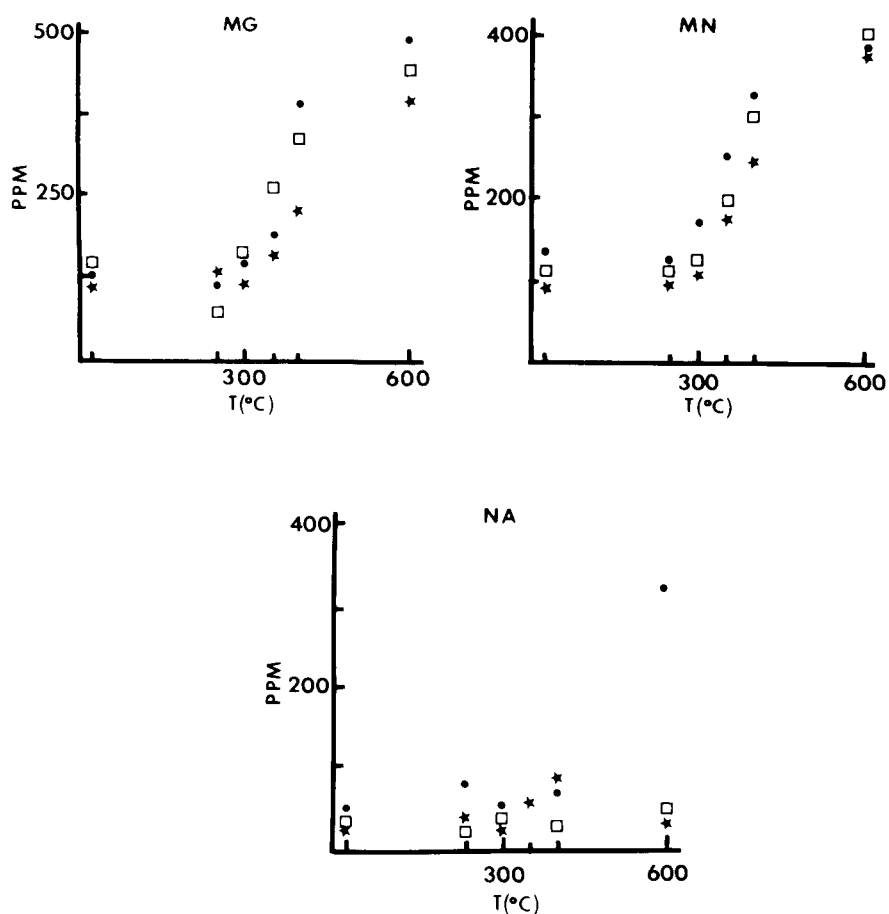


FIG. 2. Accumulation patterns for Mg, Mn, and Na in southern pine earlywood (dot), latewood (square), and wholewood (star) as functions of charring temperature.

SUMMARY AND CONCLUSIONS

Neutron activation analysis was used to determine the concentration of selected inorganic elements in the wood char of seven species. Matched samples were exposed to a thermal neutron flux of 1×10^{11} n/cm²/sec for 1 min. Following a 10-min decay period, the activity of the samples was measured for 500 sec using a Ge(Li) spectrometer system.

Eleven inorganic elements were positively identified: Al, Ba, Ca, Cl, Cu, K, Mg, Mn, Na, Sr, and Na. A wide range of values was evident among the various wood species: white oak, basswood, hard maple, southern pine earlywood and latewood, Douglas-fir, redwood, and western redcedar. Individual ranges were found to be: Al, 1 to 17 ppm; Ca, 295 to 1124 ppm; Cl, 8 to 102 ppm; K, 39 to 990 ppm; Mg, 11 to 140 ppm; Mn, 1 to 134 ppm; and Na, 3 to 74 ppm. Since no information is available concerning the history of the specific samples prior to preparation, no comments can be made regarding possible environmental influences on inorganic content.

The inorganic content of the chars increased proportionally with charring temperature. There were consistent positive significant correlations between charring temperature and the levels of Ca, Mg, and Mn. Al, K, and Na levels were usually well correlated with charring temperature, while the correlation between temperature and Cl content was very erratic.

While there were significant linear correlations between inorganic concentration and charring temperature, the relationship between weight loss and inorganic content allowed indirect estimation of inorganic levels in wood. Estimates developed using this relationship appear quite reasonable.

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