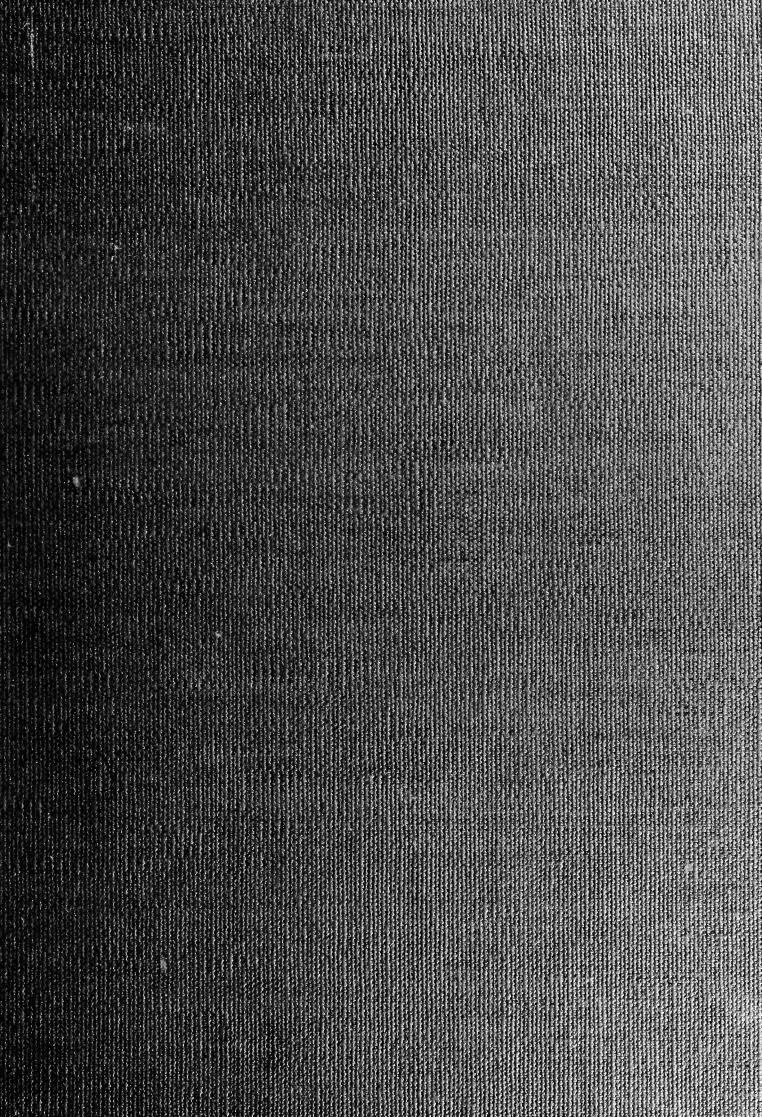
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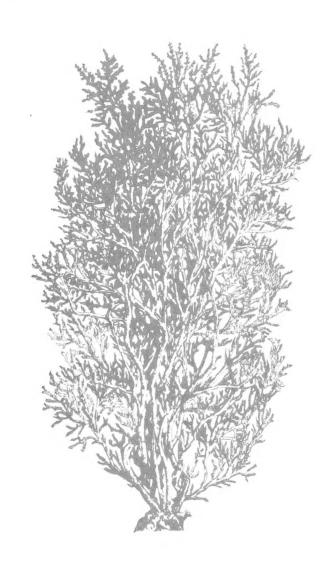
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SEASONAL CHANGES IN HEAT CONTENT AND ETHER EXTRACTIVE CONTENT OF CHAMISE

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CHARLES W. PHILPOT received his bachelor's and master's degrees in forestry from the University of California in 1961 and 1962, respectively. From 1960 to 1966 he studied fuel moisture and related variables as part of the Pacific Southwest Forest and Range Experiment Station's research on the factors that influence forest fire behavior. In 1966 he transferred to the Northern Forest Fire Laboratory, Missoula, Montana, where he is responsible for fuel chemistry research.

INTRODUCTION

Knowledge of the variations in heat content of wildland fuels is important in predicting fire behavior or assessing the relative flammability of different fuel complexes. The heat content of the fuel, and the availability of this heat content, partly determines the intensity with which the fuel burns. (Intensity is usually expressed as the rate of heat release per unit area per unit time; that is, B.t.u. per square foot per second.) Heat content availability also affects the fire's rate of spread. Studies are now underway to determine the effect of heat content changes on flammability. Several species are being sampled seasonally to acquire data on fuels that differ in heat content.

The relation of heat content to ether extractive content is a part of this study. "Ether extractives" is a broad term that covers various waxes, oils, terpenes, and fats present in most plant fuels in varying amounts. Because these compounds do not undergo the complex pyrolytic reactions prior to combustion that are characteristic of the carbohydrate constituents of fuels (primarily cellulose), the extractives are more readily available. Also, much of the extractive material appears to be deposited on or near the surface of the plant parts, especially the leaves. The extractives collectively contain about twice the heat con-

tent of the extracted fuel. All indications are that extractives could play an important role in fire spread and intensity and that their seasonal variation is partly responsible for variation in heat content of fuels.

The specific effect of extractive content on fire behavior and flammability is presently an open question. In a study of herbicidal treatment on fire intensity, the U.S. Forest Service, Rocky Mountain Forest and Range Experiment Station (1963), found that chemically dried manzanita (Arctostaphylos pungens H.B.K.) did not burn as readily as untreated manzanita, although its moisture content was much lower. The treated material contained about one-half as much ether extractives as the untreated material. On the other hand, Mutch (1964) found the ignition time for powdered ponderosa pine (Pinus ponderosa Laws.) to be much longer than that of powdered sphagnum moss (Sphagnum sp.), although the pine had over four times more extractives than the moss. (The higher density of the pine may have influenced these results.) Pilot ignition time for both fuels, however, was increased by the removal of extractives. Philpot and Mutch (1968) found that guava (*Psidium guajava* L.) leaves that had been treated with herbicide did not burn as fast as leaves that had died naturally. The treated leaves were found to have 18 percent less extractives, as well as other chemical differences.

¹Defined for these studies as a combination of ignitibility, combustibility, and sustainability.

Table 1. — The heat content of various species

Species	Anatomical portion	High heat value	Source
		B.t.u./lb.	·
Basswood (Tilia americana)	xylem	8,341	Fons et al. (1960)
Bitterbrush (<i>Purshia tridentata</i>) Spring Summer Fall	leaves	8,703 7,933 8,647	Short et al. (1966)
Longleaf pine (Pinus palustris)	xylem	8,771	Fons et al. (1960)
Magnolia (Magnolia grandiflora)	xylem	8,561	Fons et al. (1960)
Manzanita (Arctostaphylos viscida)	leaves twigs	9,208 8,676	Countryman (1964)
Manzanita (Arctostaphylos pungens)	leaves	9,070	Davis (1968)
Maple (Acer saccharum)	xylem	8,543	Fons et al. (1960)
Mountain mahogany (Cercocarpus montanos) Spring Summer Fall	leaves	8,483 8,309 8,395	Short et al. (1965)
Pinyon pine (Pinus monophylla)	leaves stems	$9,480 \\ 8,718$	Countryman (1964)
Ponderosa pine (Pinus ponderosa)	needles	9,449	Mutch (1964)
Sagebrush (Artemisia tridentata) Spring Summer Fall	leaves	8,527 8,777 9,094	Short et al. (1965)
Sphagnum moss (Sphagnum spp.)		7,918	Mutch (1964)
White fir (Abies concolor)	xylem	8,660	Fons et al. (1960)

The heat contents of most wildland fuels are quite similar, as shown in table 1. This fact has led many to conclude that chemical composition and heat content changes of fuels are relatively unimportant, compared to their physical properties. However, some studies have been made; Richards (1940) found an increase of 1,300 B.t.u./lb. for snowbrush (*Ceanothus velutinus* Dougl.) during the fire season (fig. 1). A corresponding increase in extractives from 5.2 percent in June to 11.5 percent in September was also noted. Richards concluded that the heat con-

tent change would have a minor effect on burning rate as compared with moisture changes. Several range ecology studies have also found corresponding seasonal trends in extractives, and heat content (Short, Dietz, and Remmenga 1966; Dietz, Udall, and Yeager 1962) (fig. 2). The relationship between heat content and extractives is supported by evidence that plant parts with high extractive content, such as pine needles or chaparral leaves, have higher heat contents than stems and xylem.

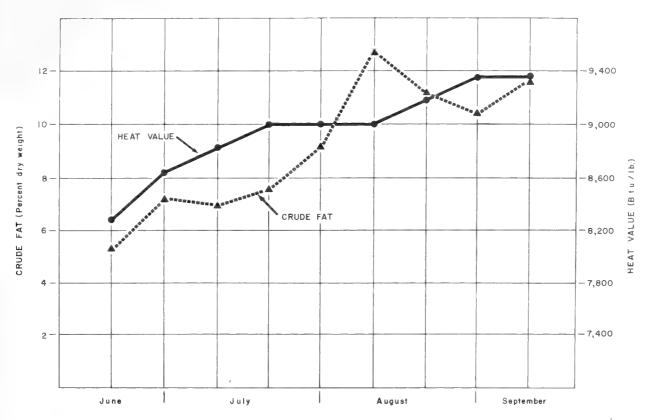


Figure 1. — The relationship between crude fat and heat of combustion of snowbrush. (Adapted from Richards.)

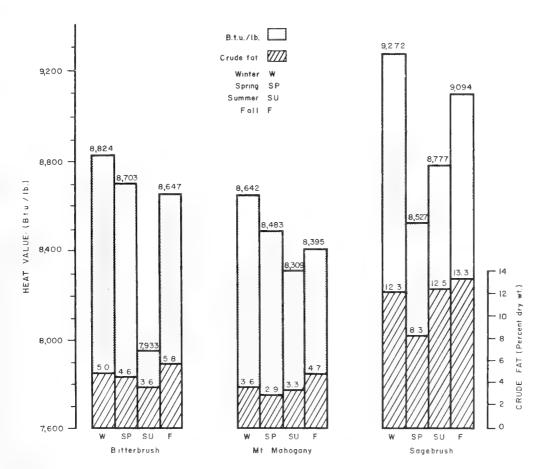


Figure 2. — Data from Dietz, Udall, and Yeager showing crude fat and heat content of three Colorado brush species.

CHAMISE

Chamise has been studied more extensively than most other wildland fuels. Because of its growth habit, physical makeup, moisture relations, and chemical characteristics, chamise is an extremely hazardous fuel — probably the most serious single fuel problem in California brushlands.

This species makes up about 50 percent of the chaparral fuel type in California and up to 70 percent in southern California (Leonard and Carlson 1957). Chamise often occurs in pure stands and deteriorates rapidly upon maturity and during periods of drought, losing its leaves and dying back. About one-third of mature chamise stands are dead material.

The needlelike leaves of chamise are arranged in groups of 10-15 per node on very small stems (fig. 3) and their surface area-to-volume ratio (σ) is 184 in.²/in.³ High values of σ imply rapid preheating and ignition and



Figure 3. — Chamise stem with leaves.

high burning rates. The leaves make up 67 percent of the total plant surface area but only 16 percent of the volume and 10 percent of the weight.² The form of the plant is generally conducive to rapid burning because several stems arise from the soil surface and branch into many smaller stems that support the leaves. All of this relatively small fuel becomes available for combustion under moderate burning conditions.

The seasonal moisture trends of this species were determined by Olsen (1960). He found the moisture content of the foliage to be highest during active growth and lowest during late September and fall months. This trend generally coincides with fire season severity (Buck 1951). The moisture content of all aerial parts of this plant falls as low as 60 percent dry weight in September (Dell and Philpot 1965).

The chemical characteristics of chamise have not been studied to any great extent. Its approximate heat content is known, but not how this changes with time and location. The extractive content of the leaves is quite high, and by our own measurements has reached 13 percent dry weight. The seasonal changes in inorganic constituents, which may indicate changes in flammability, are currently being investigated at the Northern Forest Fire Laboratory.

METHODS OF ANALYSIS

The chamise samples were obtained from the 4,500-ft. level, southwest exposure, on the North Mountain Experimental Area in southern California.³ Two sets of data are in-

cluded in this paper: the 1963 samples representing three dates and the much more complete 1966-67 samples representing eight dates. The leaves and stems (¼ inch or less) were clipped from each of three randomly picked plants in the same six subplots at each sample date during 1966-67 and were imme-

²Countryman, C. M., and C. W. Philpot. The physical characteristics of chamise as a wildland fuel. Pacific Southwest Forest and Range Exp. Station. (In preparation.)

³Cooperatively managed by the Riverside Fire Laboratory of the USDA Forest Service and the California Division of Forestry.

diately placed in a styrofoam box with dry ice and airshipped frozen to the Northern Forest Fire Laboratory. There the material was freeze-dried to prevent volatile loss and was ground to 40 mesh in a Wiley mill. For the 1963 sampling, the complete plants were harvested on each sample date and all of the leaves removed. A subsample of all dates was then taken for analysis. The mineral and ether extractive contents were determined by standard methods (ASTM 1956a, 1956b). I extracted the samples with diethyl ether at a rate of 10 siphonings per hour for 8 hours. The weight change of the thimble was found to be more reliable than the weight of the

flask because some extractives were apparently lost while the ether was being evaporated.

The heat content of the leaves and stems was determined for all of the 1963 samples and 14 of the 1966-67 samples. Heat contents for extracted leaves and stems were determined for only 14 of the 1966-67 samples picked at random. Heat content of extractives was determined directly (ASTM 1966) for some 1963 samples, but was calculated for the fourteen 1966-67 samples. All heat contents are expressed on an ash-free basis. Karl Fischer titrations were used for the moisture determinations necessary to convert data to a dry weight basis (ASTM 1962).

RESULTS

The extractive content of chamise leaves and small stems varied seasonally (figs. 4 and 5). The highest content for leaves (12 percent) was recorded for the fall and the lowest (8.5 percent) for the spring. A similar trend occurred in the stems, with a range of 4.3 percent to 8.9 percent. Duncan's New Multiple Range Test was used to test for significant dif-

ferences between means on different dates (Steele and Torrie 1960). The results of this test (table 2) show the seasonal trend to be significant at the 5 percent level. The 1963 data were tested separately and the October value was found to be different from that for May. Apparently the 1963 data show a relationship similar to the 1966-67 data.

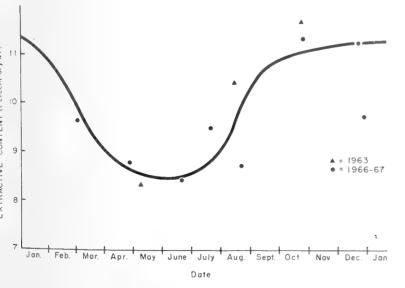


Figure 4. — Seasonal trend in ether extractives of chamise leaves.

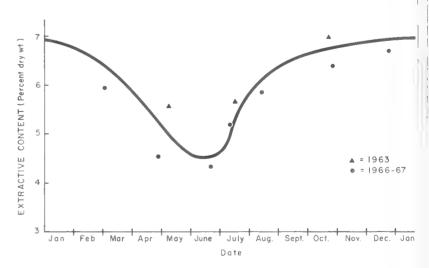


Figure 5. — Seasonal trend in ether extractives of chamise stems.

Table 2. — The significance of seasonal means for extractive content as determined by Duncan's New Multiple Range Test

Date of sampling	Code for sample	Samples having significant difference (P = 0.05) in mean extractive content				
		Leaves	Mean ¹	Stems	Mean ¹	
10/26/66	Α	BCDEFGH	11.34	DEFH	8.29	
12/22/66	В	ACDEFGH	11.24	DEFH	6.65	
3/ 2/67	C	ABE	9.66	DEH	5.94	
4/27/67	D	AB	8.80	ABCGH	4.54	
6/21/67	E	ABCFH	8.44	ABCFGH	4.33	
7/12/67	\mathbf{F}	ABE	9.57	ABEH	5.19	
8/12/67	G	AB	8.72	DEH	5.83	
12/28/67	Н	ABE	9.72	ABCDEFG	8.29	

¹Percent dry weight, ash free.

The regression between extractive content and heat content of the total fuel, ash free, was determined by using data from two out of the six samples per sample date. These subsamples were picked randomly; data for these are presented in table 3. A portion of the 1963 data is also included in this analysis. Figures 6 and 7 show the relationships for leaves and stems. The coefficient of determination,

 r^2 , is 0.72 for leaves and 0.58 for stems. The equations for the lines are

Leaves: $\overline{Y} = 8,000 + 169X$ Stems: $\overline{Y} = 8,800 + 101X$ where Y = high heat content(B.t.u./lb., ash free)

and X = ether extractive content (percent dry weight, ash free).

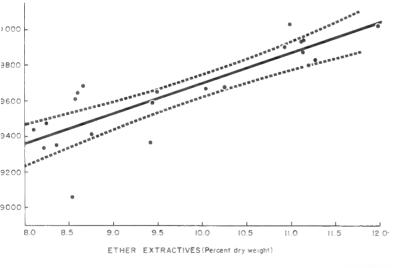


Figure 6. — The relationship between the extractive content of the leaves and total ash-free heat content.

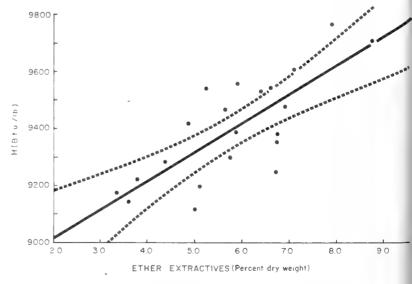


Figure 7. — The relationship between the extractive content of the stems and total ash-free heat content.

Table 3. — Data from randomly selected samples used for heat content determinations

Date of sample	Ether extractive content	High heat content, ash free (H _{tot})	Heat content of extracted fuel (H _{ex})	Difference H_{tot} and H_{ex} $(\triangle H)$	Heat content of extractives $(H_{ext})^1$
	Percent	B.t.u./lb.	B.t.u./lb.	B.t.u./lb.	B.t.u./lb.
		L	EAVES		
5/63 5/63 7/63 7/63 10/63 10/66	8.76 8.54 11.28 9.42 11.94 10.99	9,413 9,062 9,826 9,367 10,026 10,027 9,904	9,161	743	15,959
$10/66 \\ 12/66$	$\begin{array}{c} 11.14 \\ 11.14 \end{array}$	$9,871 \\ 9,937$	9,063 $9,194$	808 743	. 16,316
$\frac{12}{66}$	$11.14 \\ 11.20$	9,354	9,800	745 775	15,864 $15,945$
3/67 3/67 4/67 4/67 6/67 6/67 7/67 7/67 8/67	8.57 9.44 8.25 8.60 8.22 8.36 9.50 10.26 8.66 8.10	9,611 9,592 9,473 9,645 9,337 9,353 9,655 9,677 9,686 9,436	9,014 8,930 9,034 9,078 8,969 8,866 9,123 9,031 9,059 8,736	596 662 439 567 368 487 532 646 627 700	15,980 15,943 14,355 15,671 13,445 14,691 14,723 15,327 16,299 17,378
		•	STEMS		
5/63 5/63 7/63 7/63 10/63	5.87 5.01 6.72 6.74 5.75	9,387 9,118 9,249 9,353 9,300 9,709	o I EMB		
10/66 10/66 12/66 12/66	6.39 7.10 6.91 7.90	9,531 9,608 9,479 9,766	8,919 8,990 8,905 8,900	612 618 574 866	18,496 17,694 17,212 19,862
3/67 3/67 4/67 4/67 6/67	5.11 6.75 4.86 5.24 3.35	9,198 9,383 9,419 9,541 9,177	8,939 8,809 8,862 8,712 8,738	259 574 557 829 440	$14,007 \\ 17,313 \\ 20,323 \\ 24,533 \\ 21,871$
6/67 7/67 7/67 8/67 8/67	3.60 3.78 4.37 5.64 5.90	9,144 9,222 9,284 9,467 9,559	8,771 8,846 8,837 8,882 8,991	373 376 447 585 568	19,132 18,793 19,065 19,254 18,618

 $^{^{1}}$ Calculated from H_{tot} , H_{ex} , and extractive content.

The level of significance for both regression lines according to the F test is >99.5 percent for both sets of data. Dashed lines on the figures indicate 95 percent confidence bands.

The variability of these data prompted us to determine the heat content of the extracted fuel to see if a seasonal trend was present. These data are also presented in table 3. The extracted leaves gained approximately 171 B.t.u./lb. from spring to fall. The stems gained 148 B.t.u./lb.

Assuming that the difference between the heat content of the total fuel and the heat content of the extracted fuel, $\triangle H$, is due solely to extractives, we plotted $\triangle H$ against extractive content (figs. 8 and 9). The coefficient of determination, r^2 , is 0.60 for leaves and 0.44 for stems. The data were determined to fit a linear line and the equations are

Leaves: $\overline{Y} = 156 + 82.2X$ Stems: $\overline{Y} = 120 + 78.0X$.

The level of significance of the regression line is >99.0 percent according to the F test.

This relationship is complicated by the likelihood of seasonal variation in the heat content of the extractives themselves. Therefore it was necessary to determine this for the samples. The heat content of the ether extrac-

tives was calculated by the following relationship:

 $(1-{\rm fraction\ ext.})\cdot (H_{ex})$ + fraction ext. \cdot (H_{ext}) = H_{tot} where

fraction ext. = extractive content
(fraction dry weight)

Hex = heat content of the
extracted fuel (B.t.u./lb.)

 H_{ext} = heat content of the extractives (B.t.u./lb.) H_{tot} = heat content of the

total fuel (B.t.u./lb.).

Heat content of the extractives calculated from 14 samples was

Leaves: $\overline{X} = 15,564$

Range = 3,933 (13,445 - 17,378)

Stems: $\overline{X} = 19,012$

Range = 7,321 (17,212 - 24,533).

The average heat content of leaf extractives from three of the 1963 plants was found to be 15,679 B.t.u./lb. by actual measurement.

There is a direct relationship for leaves between extractive content and heat content of the total fuel (H_{tot}). This implies a seasonal trend in H_{ext} for leaves. For stems, the trend does not appear to be the same, since the values remain fairly constant during summer and fall.

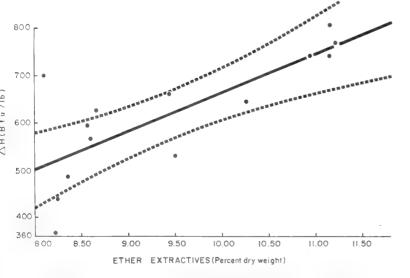


Figure 8. — The relationship between $\triangle H$ and the extractive content of the leaves.

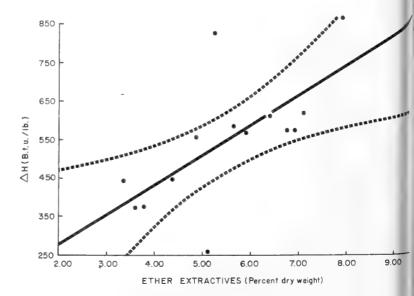


Figure 9. — The relationship between $\triangle H$ and the extractive content of the stems.

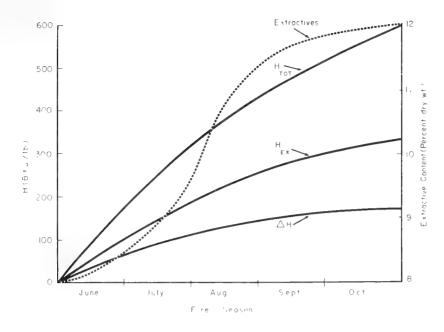


Figure 10. — Calculated heat content trends.

CONCLUSIONS

This study shows the following relationships for chamise:

- 1. The ether extractive content of the leaves ranged from a low of about 8.5 percent in the spring to about 12 percent in the fall for leaves and from 4.3 percent (spring) to 8.9 percent (fall) for stems. The dip at spring is probably partly due to new leaf flush and stem elongation. This new plant material has a lower extractive content.
- 2. The heat content of the total fuel, leaves, and small stems is directly related to their ether extractive content. The heat content of leaves increased 600 B.t.u./lb. and that of stems increased 465 B.t.u./lb. from May to October.
- 3. The heat content of the leaves and stems after extraction increased during the same period. Increase for leaves was about 171 B.t.u./lb.; and for stems, about 148 B.t.u./lb.
- 4. The computed heat content of the ether extractives was much higher from the

stems and varied with time of year. It was at its highest for leaves at the end of the fire season. Values as high as 17,378 B.t.u./lb. for leaves and 24,533 B.t.u./lb. for stems were found. This variation implies a significant compositional change with season in the compounds making up the extractives.

The change in heat content of the leaves during the fire season (June through October) can be summarized graphically using the equations and data from this study (fig. 10).

The effect of this change will not be known until further research establishes the relation between flammability and extractives. An increase in flammability would be expected because of the increase in heat content. We found a direct relation between extractive content and the burning rate of aspen leaves (Philpot 1969). Also, if part of the extractives added to the leaves is deposited on the surface, rate of spread may be enhanced. However, the change probably is not very important from a fire hazard standpoint if the added heat content is not more available than the rest of the fuel within a specific species.

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