FACTORS AFFECTING THE STABILITY OF SHELLED WALNUTS

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The effects of moisture on the stability of shelled walnuts was discussed at the Second Annual Research Conference of the Dried Fruit Industry Research Advisory Committee two years ago. It was reported that differences of less than 1% in moisture content influenced significant variations in kernel stabilities. Other small differences in physical or chemical characteristics may also modify kernel stabilities. For example, differences in skin color appear to be related to multifold variations in the shelf life of kernels (Table 1). The latter variations are impressive when it is recognized that the kernels employed were (a) part of a single lot of isogenetic nuts sharing a common agronomic history. Because of the relatively severe effects of small variables, some of which cannot be controlled completely, it is often difficult to obtain completely reproducible quantitative results, although qualitative effects are generally consistent within replicate experiments. Therefore, studies on the effects of single factors generally include controlled variations of other interdependent variables in order to define the limits of variation that may be expected from finite changes in the supplemental variables. For these reasons, it will be necessary to consider the effects of moisture and other factors in addition to the effects of radiation which will be the principal subject of the present discussion.

Effects of Radiation: Light and Heat

Most biological systems are subjected to a broad spectrum of electromagnetic radiations of which visible light is only a very small portion. In addition to very high and low frequency radiations, the sun radiates ultraviolet, infrared as well as visible light. It is generally recognized that visible light is a mixture of radiation frequencies which the human eye detects as the colors of the rainbow. Similarly, other types of radiation are generally mixtures of radiation frequencies. Heterogeneous radiations are generated by numerous man-made devices such as electric cooking ranges, radiant heaters, sun lamps, tungsten, neon, sodium vapor and mercury vapor light bulbs, fluorescent light fixtures and numerous other common appliances. Controlled investigations on the effects of radiation are possible only in those restricted portions of the electromagnetic sprectrum for which techniques and instrumentation are available. The biological effects of specific radiation frequencies have been studied in a limited manner. In recent years, a great deal of work has been done on the biological effects of high energy radiations of the type emitted by nuclear and thermonuclear devices. It has been shown that these types of radiations may affect the stability of unprotected walnut kernels. However, except under special unfavorable circumstances the low levels of these high energy radiations normally encountered do not significantly affect kernel quality. Radiations which affect kernel stability during normal processing and marketing operations include: sunlight, which is a source of broad spectrum radiations; tungsten light bulbs, which are primary sources of visible and infrared light; and fluorescent lights, which produce largely visible and ultraviolet light. Although the latter, man-made sources of radiation produce narrow spectrum, low intensity radiation, they are capable of affecting the stability of walnut kernels significantly.

Two simple equations aid in describing the manner in which radiation may influence biological systems. The Planck equation

$$E = hv$$

where E represents energy, h is a constant, and v is radiant frequency, states that the energy radiated is directly proportional to the type of radiation emitted. For the present purposes, it is only important to recognize that radiation is equivalent to energy. The second equation, illustrated in Figure 1, states that radiant energy is the sum of the reflected, transmitted and absorbed radiation. It is apparent that radiation which is completely transmitted, such as visible light through a pane of glass, or totally reflected, such as visible light from a silver mirror, does not add any energy to the pane of glass or mirror. However, radiation that is absorbed adds energy to the system. Absorbed radiation may be utilized in a number of ways, the most widely recognized being the production of heat or a rise in temperature. Most biological systems, including walnuts, absorb infrared radiation strongly, experiencing a temperature increase and accelerated chemical reactivities. In walnuts, these reactions are unfavorable leading to more rapid darkening and the development of rancidity. In the broadest sense, absorption of infrared radiation is equivalent to the absorption of heat. Therefore, storage at elevated temperatures may be considered equivalent to exposing kernels to relatively specific frequencies of infrared radiation. Constant product temperature is attained when the heat or infrared energy being absorbed is equivalent to the radiation being emitted by the product.

The effects of radiation may be related to both the quality (wave length) and the quantity absorbed. The quantity of radiation absorbed is dependent upon the radiation intensity and the time of exposure. It may be seen in Table 2 that storage of walnut kernels in the dark (absence of visible light) at 70° F. reduced the shelf life more than 20% compared with kernels held at 40° F. It is clear that walnuts absorb infrared energy strongly and are sensitive to relatively small changes in the quality of the radiation.

When visible and ultraviolet radiations were simultaneously imposed upon kernels held at 70° F, using ambient lighting, the shelf life of the kernels was reduced to less than half of that obtained for kernels held in the dark (Table 2). These effects were more pronounced when the kernel moisture was above the optimum moisture range. A further increase in storage temperature from 70° F. to 100° F. produced an analogous reduction in the acceptability of kernels (Table 3). When a rating of 5, on a hedonic scale of 10, was designated as the minimum acceptable flavor level, kernels held at 70° F. were rated 3.9 compared to 6.5 for kernels stored at 100° F.

It was of further interest that kernel quality was lost at a reduced rate when they were maintained in a vacuum. The primary effects of the vacuum was due to the absence of oxygen. Improved stability was also obtained when kernels were pretreated with antioxidant coatings. The rate of oxygen absorption by kernels was reduced significantly when an antioxidant was present (Table 4). A 50% reduction in the absorption of oxygen resulted in a three-fold increase or a 12 month enhancement in kernel stability.

Rancidity Mechanism

Basic investigations by many workers in different laboratories have produced a background of knowledge from which a mechanism has been outlined to explain the physico-chemical changes associated with the development of rancidity in shelled walnuts (Figure 2). Rancidity development may be initiated by ultraviolet radiation causing the formation of so-called free radicals. Secondary free radicals are propagated through a chain reaction without further irradiation. The free radicals combine with available oxygen forming a peroxide radical which in turn abstracts a hydrogen atom from a neighboring fatty acid or other molecule and forms a hydroperoxide and a new free radical in the molecule from which the hydrogen atom had been removed. Decomposition of the peroxides or hydroperoxides, catalyzed by metal ions and accelerated by heat, result in the formation of a variety of volatile carbonyl compounds. These compounds, which may include products such as acetaldehyde, hexanal, heptanal as well as other aldehydes and ketones appear to be responsible for the odors characteristic of rancid products.

Reversible and Irreversible Rancidity

On the basis of the proposed mechanism, it appeared reasonable to presume that the removal of carbonyl and other volatile products as they are evolved might inhibit or prevent the development of organoleptic rancidity. The results of a typical experiment designed to test this hypothesis are shown in Table 5. Air-packed kernels held at 80° F. in the presence of a small porous package of activated carbon remained acceptable for 10 months.

Similar kernels held under the same conditions without the carbonyl absorber were unacceptable. It is of interest that kernels held in an air-free vacuum had slightly better organoleptic ratings than the air-packed kernels containing the carbonyl absorber. However, the freshly-opened vacuum-packed kernels had a slightly fishy, metalic odor, whereas the air-packed kernels containing activated carbon were odorless.

These results suggested the possibility that preformed volatile products present in rancid kernels might be removed by incubation of the kernels with activated carbon and thereby restore them to an acceptable organoleptic level. Small packages of activated carbon were placed within screw-cap jars of kernels that had become rancid during storage for 18 months under ambient conditions. These samples were maintained in the dark at 70° F. together with unopened jars as well as similar jars of kernels which were opened and re-sealed without activated carbon. After 35 days each of the samples was evaluated organoleptically (Table 6). Kernels which contained 2.7% and 3.0% moisture were restored to within acceptable organoleptic limits. However, kernels stored at higher moisture levels did not respond to the treatment. These results suggested that rancidity development progresses in at least two distinguishable stages. The first, reversible process appears to involve the evolution of carbonyl and other offensive volatile compounds. The second, irreversible stage may have involved the re-absorption and reaction of the volatile carbonyl compounds with other constituents of kernels such as free amino acids, enzymes or other proteins and the formation of nonvolatile products which could not be absorbed by the activated carbon.

Packaging

The high susceptibility of walnuts to darkening and the development of rancidity under the influences of moisture and other physico-chemical effects imposed severe limitations upon the types of materials that could be employed for the production of an economical, attractive visible pack. The additional unfavorable effects of radiation, and particularly ultraviolet radiation, restricted more severely the choice of materials suitable for packaging kernels. Literally hundreds of types of packaging materials were surveyed and eliminated. Polyvinylidene chloride-polyvinyl chloride copolymer (Saran) film most closely filled the required specifications for low moisture and oxygen permeabilities, strength and resistance to insect penetration. When compounded with a suitable ultraviolet absorbing material, Saran had satisfactory ultraviolet light-shielding properties (Figure 3). The shelf life of commercial, stabilized kernels packaged in Saran film easily exceeded 12 months at ambient temperatures under the radiation received from sunlight and fluorescent light fixtures employed generally in modern markets.

Summary

Ultraviolet and infrared or heat radiation promote the deterioration of shelled walnuts. The influences of electromagnetic radiation is related interdependently to the effects of moisture, oxygen, metal ions and other physical and chemical factors. A plausible mechanism has been suggested to explain the relationships between these factors. On the basis of the proposed mechanism, experiments were initiated which supported the premise that rancidity development progresses in at least two stages. The first stage involves the light catalyzed, oxidative production of hydroperoxides, followed by the evolution of volatile carbonyl compounds which produce flavors characteristic of rancid kernels. The second stage of rancidity is visualized as an interaction between the volatile products and other constituents, producing off-flavors which, being non-volatile, are not removed by activated carbon. Further knowledge of these chemical reactions may provide a rational basis for inhibiting the production of irreversible off-flavors and lead to development of improved walnuts and other food products which would be more resistant to rancidity development.

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TABLE 1

Influence of Color Grade on the Stability of Walnut Kernels Stored in the Dark at 70° F.

GRADE	MOISTURE	ESTIMATED SHELF LIFE
	%	days
Light	3.8	280
Medium	3.6	110
Dark	3.8	90
Dark	4.7	20

TABLE 2

Influence of Moisture, Heat & Light on the Stability of Shelled Walnuts

MOISTURE	STORAGE CONDITIONS			ESTIMATED SHELF LIFE
	40° F. dark	70° F. dark	Ambient	
%				days
3.7	X			> 365
3.8		X		280
3.8			X	150
4.2		X		125
4.3			X	85

TABLE 3

Effects of Atmosphere and Temperature on Flavor and Color of Stabilized Walnut Kernels*

STORAGE TEMP.	FLAVOR SCORES INITIAL	FINAL		COLOR INCREASE	
		Vacuum	Air	Vacuum	Air
70	3.6	3.7	3.9	15	25
100	3.6	4.5	6.5	17	47

*Antioxidant-treated kernels held at 3.2% moisture in sealed tin cans for 5 months.

TABLE 4

Oxygen Absorption By Antioxidant-Treated and Untreated Walnut Kernels

STORAGE TIME	OXYGEN ABSORBED		FLAVOR SCORES	
mo.	Control %	Antiox. %	Control	Antiox.
0	0	0	4	4
1	9	5	3	3
4	14	10	3	3
6	28	16	4	3
13	47	21	6	4
18	71	30	7	4

TABLE 5

Stabilization of Walnut Kernels With Activated Carbon Adsorbent

STORAGE months at 80° F.	ATMOS.	CARBON	FLAVOR SCORES AT Moisture levels of 3.0%	3.4%	4.2%	ODOR
0	air	no	4.0	3.4	3.8	fresh
10	air	no	6.4	5.5	6.8	stale
10	air	yes	5.1	5.0	5.1	none
10	vacuum	no	4.8	4.2	4.6	sl. metal

TABLE 6

Reversible and Irreversible Rancidity in Shelled Walnuts

MOISTURE %	FLAVOR SCORES Initial	Final*	Plus 35 days, 70° F., dark Control	Carbon
2.7	4.0	7.7	-	5.2
3.0	3.4	6.0	5.8	4.5
3.5	3.6	7.3	7.0	6.8

*18 months at ambient temperature and light.

$$h\nu = E = \text{TRANSMISSION} + \text{ABSORPTION} + \text{REFLECTION}$$

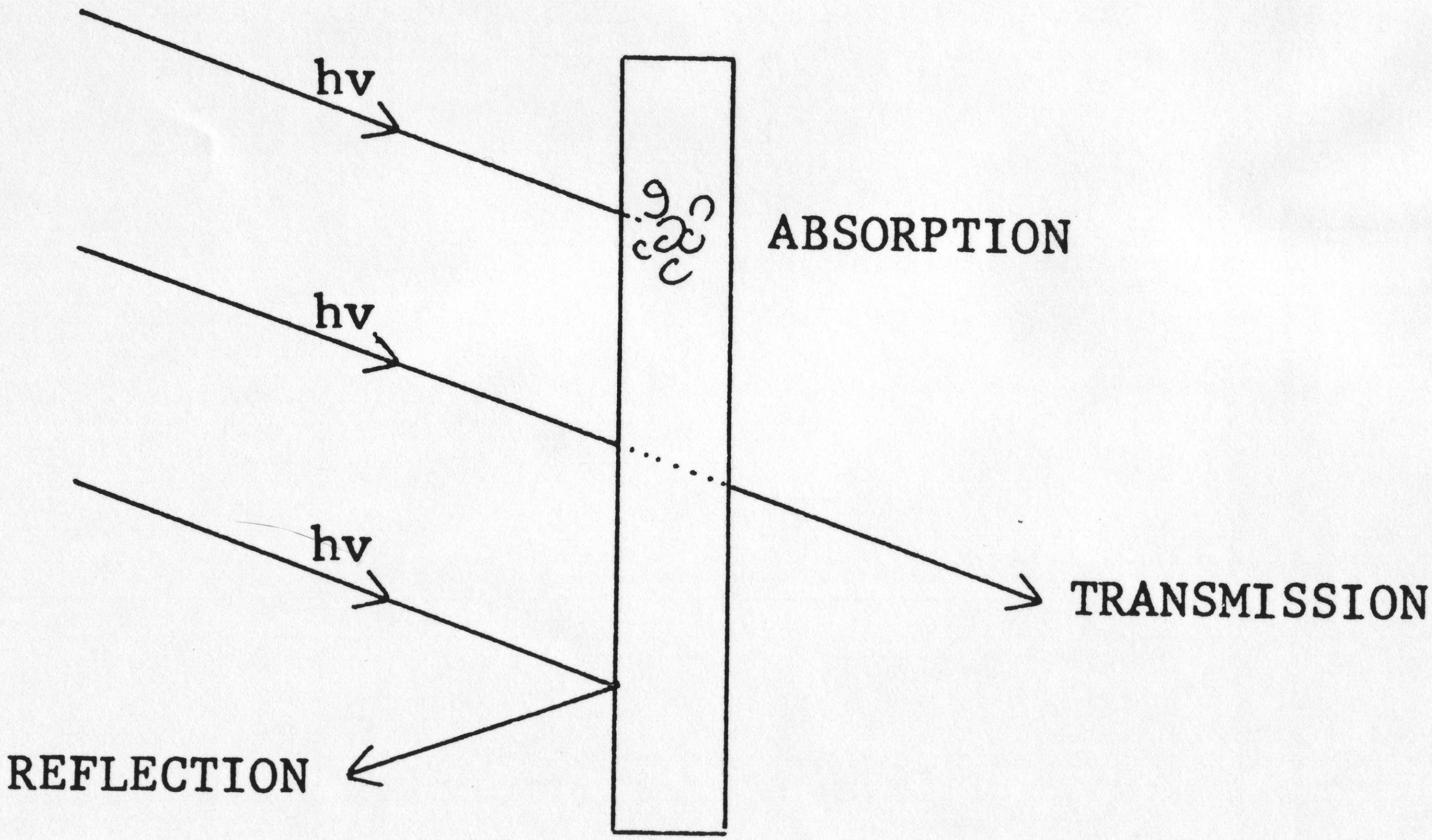

Figure 1. Dispersion of electromagnetic radiation

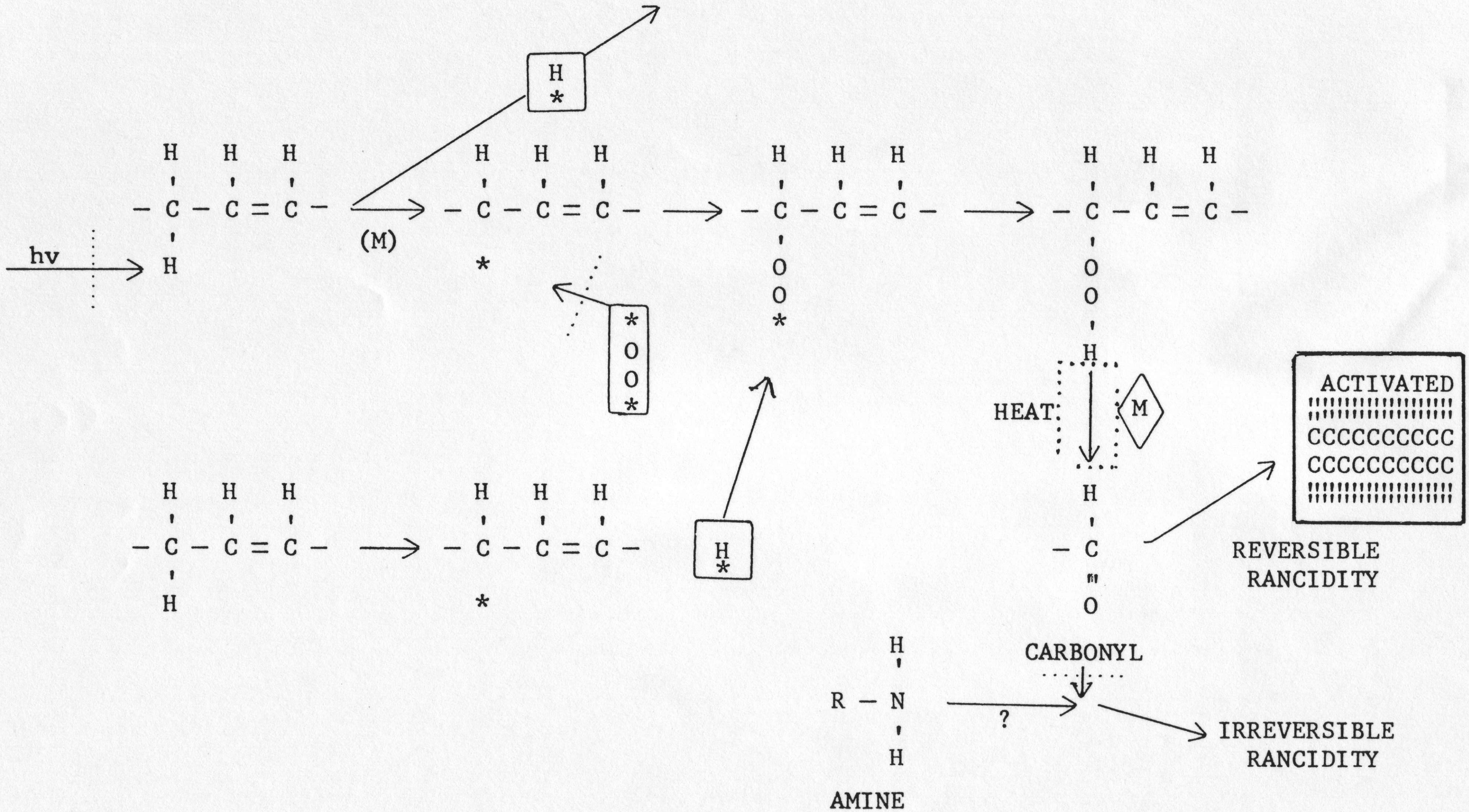

Figure 2. Schematic outline of proposed mechanism for the development of rancidity in walnut kernels.

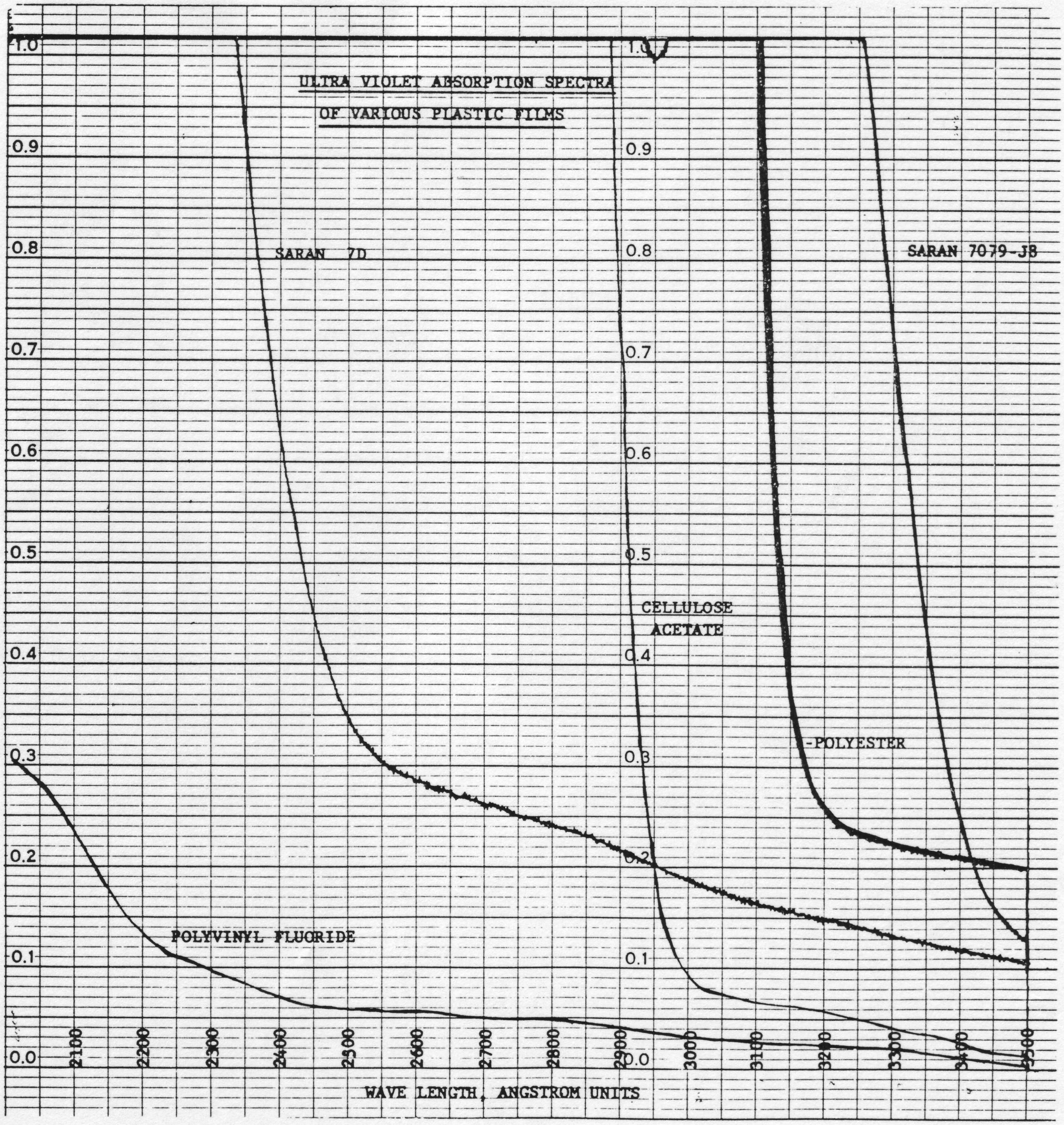

Figure 3. Ultra violet absorption spectra of various plastic films