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HISTORICAL CLIMATOLOGY

Leona M. Libby

R and D Associates

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FINAL TECHNICAL REPORT

Leona M. Libby

October 1972

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13. ABSTRACT			

The research program in Historical Climatology has the general purpose to show feasibility of determining global climate in the past, by determining past trends in surface temperature of the earth. The method being studied involves measuring past temperatures using isotope "thermometers" in bio-organic data bases. For example, isotope ratios in tree rings being formed are expected to change if the temperature changes; thus tree rings formed long ago may exhibit different ratios than those being formed today. Lower limits on the temperature coefficients have been computed, and compared favorably with experimental coefficients. New measurements of these coefficients have been undertaken in water plants. Feasibility of measurement of the isotope ratio by neutron activation for oxygen has been demonstrated and feasibility of measurement of D/H, C^{13}/C^{12} and O^{18}/O^{16} has been demonstrated by elastic backscatter of low energy protons. The variations of isotope ratios in two trees have been measured and the correlation with historic weather records is being studied. The principle and application of multiple thermometry is being patented.

II

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I

ANNUAL TECHNICAL REPORT
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The research program in Historical Climatology has the general purpose to show feasibility of determining the global climate in the past, determining past trends in surface temperature of the earth. The method being studied involves measuring past temperatures using "isotope thermometers," which may be understood in the following way. When bio-organic material is formed, such as cellulose, in trees, the isotope ratios of elements in the bio-organic material may differ from those in the inorganic material from which the living organism was formed and, if so, the difference depends on the local temperature. For example, the stable isotope ratios of O^{18}/O^{16} , C^{13}/C^{12} and D/H in cellulose may differ as a function of the radius of the ring or age of the tree, indicating that from time to time in the life of the tree, the climate varied.

As a first step in initiating this research, computation was made of the magnitude of effect to be expected; that is, the temperature coefficients of isotope ratios of oxygen, hydrogen, and carbon were computed in cellulose assuming that it is manufactured at equilibrium with water, carbon dioxide, and oxygen in the surroundings. If, instead, manufacture does not occur in an equilibrium process, then the actual temperature coefficients should be larger than those computed for equilibrium. Thus, from this calculation, we should obtain lower limits of the effects to be expected. The report of these calculations, entitled "Multiple Thermometry in Paleo Climate and Historic Climate," by Leona Libby, January 1972, has been published in the Journal of Geophysical Research 77, 4310-17, (1972).

The temperature coefficient for C^{13}/C^{12} in cellulose was computed to be 0.36 parts per thousand per degree C for equilibrium formation. It is in agreement with an experimental value measured in the laboratory for water plants by Degans, et al., "Metabolic Fractionation of Carbon Isotopes in Marine Plankton," Deep Sea Research, 15, 1-9 (1968).

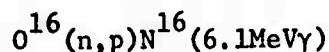
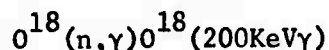
The temperature coefficient for D/H was computed to be 2.4 parts per thousand per degree C. Shortly after completion of the calculation, data from which an experimental value for D/H in peat could be estimated was published by W. E. Schiegl, "Deuterium Content of Peat as a Paleo-Climate Recorder," Science 175, 512-513 (1972), amounting to 3.0 parts per thousand per degree C, compatible with the calculated value.

With the help of Louis Pandolfi, a graduate student in the Chemistry Department of UCLA, an experiment to determine the temperature coefficients in water plants has been undertaken. In an outdoor pond of 800 liters volume, water plants were grown and the new growth was harvested at various constant temperatures. Dried of external moisture, the plant material was freeze-dried in a vacuum system, and analyzed for isotope ratios of carbon, hydrogen and oxygen by mass spectrographic methods. The measurements are being analyzed and a report will be prepared for publication when the analysis is complete, expected to occur in the second year of this research.

We have analyzed the tree rings of an American Bristlecone Pine and of a European Oak in a similar way for stable isotope ratios, and we are presently undertaking correlation of the observed variations with historic weather records at stations near where these trees grew. A report on this work will be prepared for publication when it is complete.

A second part of this research interests itself in the possibility of determining isotope ratios by neutron activation, as an alternative to mass spectroscopy. In the latter method, before the isotope ratio can be measured, many chemical reactions are involved in any one of which isotope fractionation might occur. Thus, using an alternate method for determination of the ratio would be important as a check on the method of mass spectroscopy.

To this end, determination of the ratio O^{18}/O^{16} to the required accuracy has been demonstrated to be feasible by measuring the activities:



induced by neutrons, the first by slow neutrons and the second by neutrons of more than 10 MeV. Activation should be made in a reactor with a sufficiently high flux of fast neutrons, such as the Gulf General Atomic TRIGA reactor. This method is non-destructive of the sample. Likewise, feasibility of measurement of the stable isotope ratios of carbon, hydrogen, and oxygen to sufficient accuracy by elastic back-scattering of low energy protons has been demonstrated. If this latter method is to be non-destructive, then it requires 30 keV protons from a tandem Van der Graaf so that reasonably thick targets can be used.

The ratio O^{18}/O^{16} has been measured to 6 parts in 10,000 by this method in about 40 minutes. It is expected that soon the method will be reduced to a routine measurement in shorter times and with, perhaps, somewhat better accuracy. A report is being prepared for publication.

A patent is being applied for concerning the principle of multiple thermometry of stable isotopes as a research tool to study past climates, and to identify and correlate sedimentary layers on a world wide basis. More particularly, we intend to patent the use of this principle for oil prospecting and prospecting of uranium and radium, and for mapping deformations of sedimentary layers caused by ice loading and mountain building. The patent search has been completed and the patent instrument is being prepared.

APPENDICES

Appendix I:

Multiple Thermometry in Paleo Climate and Historic Climate, by
L. M. Libby, J. Geo. Phy. Res. 77, No. 23, 4310-4317 (1972).

Appendix II:

Feasibility of Measurement of O^{18}/O^{16} Ratio by Activation Using
a Fast Neutron Reactor, by S. F. Bankert, S. D. Bloom, L. M. Libby
and H. R. Lukens.

Appendix III:

Determination of Isotopic Abundances of C, N, and O in Organic
Samples Using Nuclear Techniques by K. W. Jones and H. W. Kraner.

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MULTIPLE THERMOMETRY IN
PALEO CLIMATE AND HISTORIC CLIMATE

Leona M. Libby

January 1972

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ABSTRACT

The principle of isotope thermometry is that isotope ratios are temperature dependent. It is proposed that isotope ratios in bio-organic material may have independent temperature coefficients, so that by measuring ratios for several elements, e.g. hydrogen, carbon and oxygen, it may be possible to show that a temperature change occurred. Assuming that cellulose is formed almost at equilibrium, temperature coefficients for C, H and O are computed and found to be of measurable size. The coefficients computed for C^{13}/C^{12} and D/H agree with measured values. Thus indications are that temperature changes in past climates may be measured in old tree rings, using this principle of multiple thermometers.

I. INTRODUCTION

The principle of isotope thermometry is that the isotopic ratios are temperature dependent. There are two kinds of temperature dependence, kinetic and equilibrium. The theory of kinetic isotope separation is well established. For example, in the gaseous diffusion process for separation of the uranium isotopes, separation is caused by a difference in the rates with which the two species pass through holes in a barrier. In case of equilibrium, separation is caused by a difference of differences, namely the difference between separation by the forward rate and separation by the reverse rate, the two rates being equal. Distillation of liquid in a closed container is an example of separation at equilibrium, while vaporization into a vacuum is kinetic.

In distillation of a liquid containing two or more elements in the molecule, the corresponding isotope thermometers are functionally related because the corresponding vapor pressure ratios, which determine the separations on evaporation and condensation, depend on the same force constants tying them together.

In bio-organic material however, there may be at least three useful isotope thermometers, namely D/H , C^{13}/C^{12} , and O^{18}/O^{16} . The basic reaction is photosynthesis with production of cellulose, here written schematically as a basic module, $H - \overset{\overset{|}{\text{C}}}{\underset{\underset{|}{\text{C}}}{\text{C}}} - OH$, or CH_2O , according to $CO_2 + H_2O \rightarrow CH_2O + O_2$. In this reaction all three elements may yield isotope thermometers, and they may be independent of each other. That is, the ratio O^{18}/O^{16} is no longer functionally related to D/H because diatomic oxygen is being evolved and so rotational and vibrational energies of the $O-O$ bond are involved and because in cellulose

oxygen is bound to carbon as well as hydrogen. For the same reason, the temperature coefficient of O^{18}/O^{16} and C^{13}/C^{12} may be not functionally related. And finally, the ratio C^{13}/C^{12} should be independent of D/H because carbon and hydrogen are initially in different molecules, with differing vibrational frequencies.

In case variations are measured for only one isotope ratio the relation to paleo temperature is not proven. But if ratios are measured for two, three, or more independent isotopes in the same organic material, it is possible that the relation to temperature can be firmly established and quantified, and this is the principle point of the present discussion.

Over the small temperature interval ($0^{\circ}C < t < +30^{\circ}C$) within which climate could have varied without killing terrestrial life as we know it, the dependences of isotope ratios on temperature may be assumed to be linear for bio-organic material. That is, for isotope ratios δ^j , where $j = 2, 13, 15, 18, 34, 41, \dots$ referring to D, C^{13} , N^{15} , O^{18} , S^{34} , K^{41} , \dots the temperature dependence may be written as

$$\delta^j = a^j t + b^j, \quad (a^j \text{ and } b^j \text{ constants})$$

where a^j is the temperature coefficient and t is temperature. Then, a change Δt is related to a change $\Delta \delta^j$ by, (for a given compound),

$$\Delta t = \frac{\Delta \delta^2}{a_2} = \frac{\Delta \delta^{13}}{a_{13}} = \frac{\Delta \delta^{15}}{a_{15}} = \frac{\Delta \delta^{18}}{a_{18}} = \dots$$

The multiple over-determination of temperature by using a set of many thermometers may make it possible to show with some level of confidence that a temperature change did occur. It is also possible that new effects, not caused by temperature, will be demonstrated by the method of multiple thermometry, if some of the above ratios, but not all of them, show equality. Probably the specific relations to temperature will have to be calibrated at each geographical position to take into account local variations in water and CO₂.

Finally, bio-organic data bases can be radiocarbon dated, so that if evidence for temperature changes is stored in them, the dates when the changes occurred can be evaluated.

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II. EXPERIMENTAL EVIDENCE FOR TEMPERATURE DEPENDENCE OF ISOTOPE RATIOS IN BIO-ORGANIC MATERIAL

Although animal bio-organic material is not directly derived from photo-synthesis, nevertheless animals are largely what they eat, so that bio-organic material from both plants and animals may be useful in isotope thermometry. Some of the evidence⁽¹⁾ on isotope thermometers in bio-organic material is as follows.

The C^{13}/C^{12} ratio in combustible organic matter in cores from sea bottoms shows variations of as much as 6 parts per thousand with depth. These have been measured and attributed to temperature variation in the sea surface with time, by Rogers and Koons.⁽²⁾ Also, in a study of marine plankton, by Sackett et al,⁽³⁾ the C^{13} concentration was found depleted by 6 per mil where surface waters are near 0°C relative to samples collected where surface temperatures are about 25°C. These observations on both plant and animal plankton suggest that the temperature coefficient of C^{13}/C^{12} in bio-organic material is ~0.24 parts per thousand per degree C in the temperature range 0 - 25°C.

In further work by Degens et al,⁽⁴⁾ the temperature coefficient of C^{13}/C^{12} in marine phytoplankton grown in laboratory cultures was measured as ~0.35 parts per thousand per degree C between 10 - 30°C.

While shell carbonate is not, strictly speaking, bio-organic material, nevertheless, for completeness we note here that variations in the O^{18}/O^{16} ratio in foraminifera shells from Caribbean Sea cores have been measured by several workers and interpreted in terms of paleotemperature variations.⁽⁵⁾ This in fact was the first isotope thermometer, as developed by H. C. Urey.⁽⁶⁾

It may be that other isotope ratios in bio-organic material are temperature dependent, such as N^{15}/N^{14} and S^{34}/S^{32} , perhaps increasing the number of independent thermometers in bio-organic data bases to five or six. This possibility should be investigated.

III. THE QUESTION OF EQUILIBRIUM

In the following paper an attempt is made to estimate the magnitudes of the temperature coefficients of the several isotope thermometers in bio-organic data bases. This can be done using thermodynamic considerations, if one assumes that the organic material is manufactured in equilibrium with its surroundings. This is of course a major assumption, but one which does not seem too unlikely. For example, in experiments in the laboratory the isotopic composition of $CaCO_3$ slowly formed from aqueous solution, was found to be the same as in the shells produced by aquatic organisms at the same temperature.⁽⁷⁾ In any case, this assumption can be tested for plants and animals grown in laboratory conditions.

In the wild state, in coastal waters and estuaries, the carbon and oxygen isotopic composition of shell carbonate has been shown to be in isotopic equilibrium with bicarbonate dissolved in the water.⁽⁸⁾ The life span of the shell fish is about one year, so it would seem equilibration in self-manufacture might take place rapidly, say in less than or about a day. Equilibration between CO_2 gas and sea water is known to occur in less than 48 hours,⁽⁹⁾ and between CO_2 gas, water and precipitated CaCO_3 in less than 6 days.^(10,11) In living animals, tritiated water is known to equilibrate with blood serum of rats in 6 days or less.⁽¹²⁾ Thus the evidence, although meager, is that equilibration takes place rapidly compared with the relevant life spans.

It should be pointed out that in shells the carbon and oxygen are not independent thermometers because they are tied by the same vibrations in the C-O bond. But there is also organic material in the shell matrix which could provide a set of multiple thermometers, and furthermore could be ~~radiocarbon dated.~~

The question of the degree to which equilibrium obtains in formation of cellulose is interesting in itself. If equilibrium seems to apply, the assumption could be extended to computations of production of other substances. If equilibrium does not obtain, and instead the processes of isotope fractionation are kinetic, then the temperature coefficients should be even larger than those estimated by assuming equilibrium.

CALCULATION OF PARTITION FUNCTION FOR CELLULOSE

For a reaction in which there is isotope exchange, the equilibrium constant K_{eq} can be expressed in terms of the total partition functions Q^* and Q for molecules containing the heavy and light isotopes respectively, as follows. We define Q as the product of rotational, vibrational and translational parts, neglecting vibrational-rotational coupling:

$$Q = Q_{rot} Q_{vib} Q_{tr} \quad (1)$$

For solids and liquids, $Q_{tr} = 1$, and Q_{vib} is given by

$$Q_{vib}(T) = \sum_j \sum_n g_j \exp \left(-v_j n \frac{h}{kT} \right) \exp(-\Delta \epsilon_j / kT) \quad (2)$$

$$(n = 0, 1, 2, \dots)$$

which may be written as,

$$Q_{vib}(T) = \prod_j g_j [1 - \exp(-h\nu_j / kT)]^{-1} \exp(-\Delta \epsilon_j / kT) \quad (3)$$

We shall be computing partition functions at $\sim 300^\circ\text{K}$ so that the harmonic oscillator approximation, is reasonably good. Here k is the Boltzman constant, t is the absolute temperature, ν_j is the frequency of the j^{th} appropriate vibration of degeneracy g_j and n is the vibrational quantum number. and $\Delta\epsilon_j$ is the difference in zero point energy between the isotopes. In cellulose the barriers preventing free internal rotation are high, so that rotations deteriorate into torsional oscillations or bending vibrations. In the present treatment these will be included in Q_{vib} as part of the vibrational partition function.

The stretching and bending vibrations appropriate to cellulose, which is a chain molecule of module (H - C - OH), are listed in Tables I and II. Their frequencies differ slightly for molecules containing different isotopes because the isotopic mass enters into the reduced mass, μ , of the appropriate oscillator from which the particular frequency is computed, according to:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \quad (4)$$

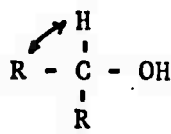
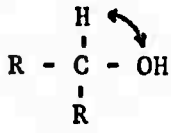
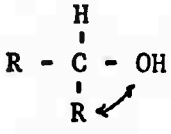
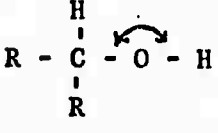
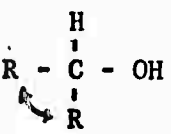
where K is the force constant of the particular vibration. Substituting in (3) the frequencies from Table I, and noting that the torsional frequency, 920 cm^{-1} , is 3-fold degenerate, one computes $Q(273^\circ\text{K}) = 1.2302$ and $Q(298^\circ\text{K}) = 1.2981$ for the module {H - C - OH}. In principle, the D-H isotope effect in cellulose involves two possible substitutions: namely substitution of a deuteron for the hydrogen linked to the carbon atom and

Table I

Bond	Stretching Vibration
$\begin{array}{c} \\ - \text{C} - \text{H} \\ \end{array}$	2960 cm^{-1}
$\begin{array}{c} \quad \\ - \text{C} - \text{C} - \\ \quad \end{array}$	900 cm^{-1}
- O - H	3680 cm^{-1}
$\begin{array}{c} \\ - \text{C} - (\text{OH}) \\ \end{array}$	(1200 cm^{-1})*
$\text{O}^{16} - \text{O}^{16}$	1580 cm^{-1} $B = 1.44560 \text{ cm}^{-1}$

* Calculated from a force constant taken as 1/2 of force constant for C = O, see G. Herzberg, Infrared and Raman Spectra, D. Van Nostrand & Co., Inc., New York, 1945, Table 51, pg. 195, and see also Table 89.

Table II

Bending Vibration	Bending Frequency
	920 cm ⁻¹
	920 cm ⁻¹
	920 cm ⁻¹
	(700 cm ⁻¹)*
	(375 cm ⁻¹)**

* See Herzberg, Infrared and Raman Spectra, op. cit., page 196, and Tables 51 and 89.

** See Herzberg, Infrared and Raman Spectra, op. cit., Tables 118 and 119.

secondly substitution of the hydrogen attached to oxygen. In the case of R and R' attached to the pivotal carbon, the appropriate reduced mass is insensitive to substitution of H by D because the masses of R and R' are almost infinitely large relative to H or D. The partition functions computed for the various isotopic substitutions of the cellulose module are given in Table III.

Because of the crudeness inherent in assuming bond frequencies for cellulose to be equal to those known in rather small organic molecules, we neglect anharmonic corrections, and complications such as hydration in solution, effect of hydrogen bond formation, etc.

The fractionation ratios may be written as follows. For the oxygen isotopes, there are three equilibria corresponding to isotopic exchange between cellulose and each of the three oxygen-containing molecules involved in the reaction:

$$K^{18}(O_2) = \frac{Q^*(CH_2O^{18})}{Q(CH_2O^{16})} \frac{Q(O_2^{16})}{Q^*(O^{16}O^{18})} \quad (5a)$$

$$K^{18}(CO_2) = \frac{Q^*(CH_2O^{18})}{Q(CH_2O^{16})} \frac{Q(CO_2^{16})}{Q^*(CO^{16}O^{18})} \quad (5b)$$

$$K^{18}(H_2O) = \frac{Q^*(CH_2O^{18})}{Q(CH_2O^{16})} \frac{Q(H_2O^{16})}{Q^*(H_2O^{18})} \quad (5c)$$

where Q^* is the partition function for the heavier isotope.

Table III

	Partition Functions for the Module of Cellulose (H - C - OH) and Its Isotopic Modifications				
	Q(HCOH)	Q*(DCOH)	Q*(HCO ¹³ D)	Q*(C ¹³ H ₂ O)	Q*(CH ₂ O ¹⁸)
273°K	1.2302	40.850	35.014	1.4240	1.5620
298°K	1.2981	32.695	28.086	1.4844	1.6659

For the hydrogen isotopes, two equilibria enter so that

$$K(\text{HCO}) = \frac{Q^*(\text{HCO})}{Q(\text{CH}_2\text{O})} \cdot \frac{Q(\text{H}_2\text{O})}{Q^*(\text{HDO})} ; \quad K(\text{DCO}) = \frac{Q^*(\text{DCO})}{Q(\text{CH}_2\text{O})} \cdot \frac{Q(\text{H}_2\text{O})}{Q^*(\text{HDO})} \quad (6)$$

and for the carbon isotopes, only one equilibrium enters, that with CO_2 , so,

$$K^{13} = \frac{Q^*(\text{C}^{13}\text{H}_2\text{O})}{Q(\text{C}^{12}\text{H}_2\text{O})} \cdot \frac{Q(\text{C}^{12}\text{O}_2)}{Q^*(\text{C}^{13}\text{O}_2)} \quad (7)$$

but what the chemist actually measures⁽⁶⁾ is an isotopic fractionation, α . For example for oxygen the fractionation factor corresponding to equation 5a is:

$$\frac{\{2[\text{O}_2^{18}] + [\text{O}^{18}\text{O}^{16}]\}}{\{[\text{O}^{18}\text{O}^{16}] + 2[\text{O}_2^{16}]\}} \cdot \frac{[\text{CH}_2\text{O}^{16}]}{[\text{CH}_2\text{O}^{18}]} = \alpha^{-1} \quad (8)$$

Considering the reaction,



the equilibrium constant is 4, neglecting a tiny correction for isotope effect⁽⁶⁾

$$4 = \frac{[\text{O}^{18}\text{O}^{16}]^2}{[\text{O}_2^{18}][\text{O}_2^{16}]} \quad (10)$$

because O_2^{18} and O_2^{16} , being symmetrical, have only half as many rotational states as the asymmetrical molecule $O^{16}O^{18}$. Substituting (10) into (8), the fractionation factor reduces to:

$$a^{18}(O_2) = \frac{Q[O_2^{16}]^{1/2}}{Q^*[O_2^{18}]^{1/2}} \frac{Q^*[CH_2O^{18}]}{Q[CH_2O^{16}]} \quad (11)$$

Correspondingly CO_2^{18} and CO_2^{16} , being symmetric, have only half the rotational states as $CO^{18}O^{16}$, so that

$$a^{18}(CO_2) = \frac{Q[CO_2^{16}]^{1/2}}{Q^*[CO_2^{18}]^{1/2}} \frac{Q^*[CH_2O^{18}]}{Q[CH_2O^{16}]} \quad (12)$$

but for $a(HCOD)$ and $a(DCOH)$ the isotope effect is large so,

$$a(HCOD) = \frac{Q^*[HCOD]}{Q[CH_2O]} \left\{ \frac{[2Q[H_2O] + Q[HDO]]}{[Q[HDO] + 2Q[D_2O]]} \right\} \quad (13)$$

$$a(DCOH) = \frac{Q^*[DCOH]}{Q[CH_2O]} \left\{ \frac{2Q[H_2O] + Q[HDO]}{Q[HDO] + 2Q[D_2O]} \right\}$$

Here, while H_2O and D_2O are symmetric, none of the deuterated or hydrogenated cellulose modules are. Finally because $C^{13}O_2$ and $C^{12}O_2$ have the same number of rotational states, also H_2O^{16} and H_2O^{18} , the fractionation factors are

$$a^{18}_{(H_2O)} = \frac{Q(H_2O^{16})}{Q^*(H_2O^{18})} \cdot \frac{Q^*(CH_2O^{18})}{Q(CH_2O^{16})} \quad (14)$$

$$a^{13} = \frac{Q(C^{12}O_2)}{Q^*(C^{13}O_2)} \cdot \frac{Q^*(C^{13}H_2O)}{Q(C^{12}H_2O)} \quad (15)$$

For the isotope ratios D/H, C^{13}/C^{12} , and O^{18}/O^{16} , we may now compute the partition function ratios $(Q^*/Q)_{CH_2O}$. The partition function ratios for $(Q^*/Q)_{\text{oxygen}}$ are taken from Urey (Ref. 6), those for $(H_2O)_{\text{liq.}}$ are taken from computations of Bottinga⁽¹³⁾ and those for $(CO_2)_{\text{gas}}$ from Bottinga⁽¹³⁾ and for HDO and D₂O from Urey⁽⁶⁾

The ratios appropriate for each isotope exchange are listed in Tables IV, V and VI. By substituting these in equations (11) through (15) the fractionation factors have been calculated for 273°K and 298°K. The corresponding temperature coefficients are listed in Table VII.

The temperature coefficient so calculated for C^{13}/C^{12} of 0.36 ppt/°C, agrees with the coefficient measured for C^{13}/C^{12} in plant and animal material by Sackett and his co-workers,^(3, 4) so that the assumption of equilibrium appears to be more or less valid and one can hope that the like calculations for oxygen and hydrogen may be meaningful.

From Ref. 6, at equilibrium the temperature coefficient of HDO/H_2O is -312‰ per degree C, namely much larger than that of the (D/H) ratio calculated for cellulose, so that measuring it in a geographical distribution of the same kind of trees would measure the

Table IV

Partition Function	273°K	298°K	Comment
$Q^*[\text{DCOH}]/Q[\text{HCOH}]$	33.206	25.187	Table III
$Q^*[\text{HCOH}]/Q[\text{HCOH}]$	28.462	21.636	
$\{Q^*[\text{D}_2\text{O}]_{\text{gas}}/Q[\text{H}_2\text{O}]_{\text{gas}}\}^{1/2}$	16.503	12.543	H. C. Urey (Ref. 6)*
$Q^*[\text{HDO}]_{\text{gas}}/Q[\text{H}_2\text{O}]_{\text{gas}}$	32.7400	24.9460	

* The partition function ratio for liquid is obtained by multiplying the partition function ratio for gas by the D/H ratio in liquid divided by that for gas. It is taken here as 1.104 at 273°K, and as 1.074 at 298°K, where the numbers in parentheses refer to partition of tritium, see Ref. 22.

Table V

Partition Function	273°K	298°K	Comment
$Q^*[\text{C}^{13}\text{H}_2\text{O}]/Q[\text{C}^{12}\text{H}_2\text{O}]$	1.1575	1.1435	Table III
ln $Q^*[\text{C}^{13}\text{O}_2]/Q[\text{C}^{12}\text{O}_2]$ (gas)	0.19732	0.17558	Y. Bottinga ⁹
$Q^*[\text{C}^{13}\text{O}_2]/Q[\text{C}^{12}\text{O}_2]$ (gas)	1.2181	1.1919	

Table VI

Partition Function	273°K	298°K	Source
$Q^*[\text{CH}_2\text{O}^{18}]/Q[\text{CH}_2\text{O}]^{16}$	1.2697	1.2833	This paper
$[Q^{**}(\text{O}_2^{18})/Q(\text{O}_2^{16})]_{\text{gas}}^{1/2}$	1.0923	1.0818	Urey (Ref. 6)
$1/2 \ln\{Q^*[\text{CO}_2^{18}]_{\text{gas}}/Q[\text{CO}_2^{16}]_{\text{gas}}\}$	0.12530	0.11108	Bottinga, (Ref. 13)
$\{Q^*[\text{CO}_2^{18}]/Q[\text{CO}_2^{16}]\}^{1/2}_{\text{gas}}$	1.1336	1.1175	
$\ln\{Q^*[\text{H}_2\text{O}^{18}]_{\text{gas}}/Q[\text{H}_2\text{O}^{16}]_{\text{gas}}\}$	0.06822	0.06164	Bottinga, (Ref. 13) See comment below
$Q^*[\text{H}_2\text{O}^{18}]/Q[\text{H}_2\text{O}^{16}]_{\text{gas}}$	1.0706	1.0635	

Comment: The partition function ratio for liquid water is obtained by multiplying the partition function ratio for water vapor with the $\text{O}^{18}/\text{O}^{16}$ ratio in liquid water divided by the ratio in the vapor. This correction is taken as 1.01150 at 273° and as 1.00930 at 298°K; (Ref. 13, page 806)

Table VII

	273°K	298°K	Temperature Coefficient	
$a^{18}(\text{O}_2)$	1.1624	1.1863	+0.96	°/° per °C
$a^{18}(\text{CO}_2)$	1.1200	1.1484	+1.14	°/° per °C
$a^{18}(\text{H}_2\text{O})$	1.1725	1.1956	+0.92	°/° per °C
a^{13}	0.9503	0.9594	+0.36	°/° per °C
$a(\text{HCO}_2)$	1.5881	1.5983	+0.4	°/° per °C
$a(\text{DCOH})$	1.8095	1.8606	+2.0	°/° per °C

The computed temperature coefficients listed above agree very well with the value 0.35 ppt per °C measured for $\text{Cl}^{13}/\text{Cl}^{12}$ by Degens et. al., Ref. 4, and with the value 3.0 ppt per °C measured for D/H by W. E. Schiegl, Science 175, 512-513, (1972), "Deuterium Content of Peat as a Paleo-Climate Recorder."

distribution in D/H ratios of rain water, and measuring it in a chronological sequence would measure time dependence of the rain water.

Our naive assumptions are mainly as follows. We have assumed that cellulose is formed in solution, that in cellulose rotations have degenerated into torsional vibration, that its vibrations are like those in small organic molecules, and that manufacture of cellulose in plants is an almost equilibrium process.⁽¹⁴⁾

The intent of the present computation is to show that all three of the isotope ratios D/H, C^{13}/C^{12} , and O^{18}/O^{16} may well be thermometers, and that their temperature coefficients may have measurable magnitudes in bio-organic plant residues, and so may give information about climate variation in the past.

For example, we may measure these ratios in a chronological sequence of tree rings. The results of Parker⁽¹⁵⁾ are that (1) different plant species growing side by side in a marine estuary can have different percentages of C^{13} in total carbon content, and (2) individuals of the same species have about the same percentage of C^{13} . So in evaluating past climates from isotope thermometers we should measure changes in a single species of tree and we should measure a chronological sequence consisting of several individuals, of the same kind of tree, having overlapping life spans. By measuring trees of overlapping life spans, and trees that grow in sparse environments such as mountain slopes, one may avoid spurious effects caused by the relatively greater removal of CO_2 from air near the ground by abundant low growing plants.

From Ref. 6, the temperature coefficient of oxygen in rain water could be as large as -0.36% per degree C. Also important is the fact that CO_2 mixes rapidly through the entire global atmosphere in a time of ~ 5 years, and with the oceans⁽¹⁶⁻¹⁹⁾ in about 15 years, so that at any time the atmospheric carbon isotope ratios reflect the temperature-dependent isotope separation in the sea, which has a coefficient of $-0.21 \text{ ppt}/^\circ\text{C}$ for oxygen (Ref. 10), and $-0.11 \text{ ppt}/^\circ\text{C}$ for carbon (Ref. 11).

One may ask whether there is isotope exchange between the hydrogens bound in old cellulose and in new sap. As shown in Table I, both hydrogens are bound very tightly, even more so than the C-C bonds, so that, knowing that radio-carbon dates in tree cellulose mainly agree with the tree ring dates, meaning that in heart wood carbon does not exchange, we can hope the same to be true of hydrogen in heart wood. But this point should be tested. When cellulose is prepared in a thin layer or finely ground, and repeatedly wetted and dried, there is some exchange,⁽²¹⁾ but these conditions are quite different from cellulose in sound heart wood.

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FEASIBILITY OF
MEASUREMENT OF O^{18}/O^{16} RATIO BY ACTIVATION
USING A FAST NEUTRON REACTOR

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PRINCIPLE OF THE METHOD

Preliminary measurements indicate the feasibility of using fast-neutron reactors to measure O^{18}/O^{16} isotope ratios with an accuracy of $1/10^4$, by neutron activation. A fast reactor is necessary because its total neutron flux is $10^{13}/\text{cm}^2 \text{ sec}$ or more and because its ultra fast neutron flux, F_u , and slow neutron flux, F_s , are comparable. The O^{18} , with a 0.2% natural abundance, is activated by thermal neutrons via the (n,γ) reaction, while the O^{16} is activated via the (n,p) reaction by ultra-high energy neutrons ($\geq 10 \text{ MeV}$) in the high energy tail of the fission neutron spectrum.

Both oxygen activities are measured simultaneously following activation, and ideally should have approximately equal numbers of decays or counts, for optimum determination of the ratio $R = O^{18}/O^{16}$. This equality can be achieved because the thermally activated isotope happens to be the rare one (O^{18}), so that its low abundance is compensated by a flux of thermal neutrons larger than the fast flux.

The characteristics of these activities are as follows:

(a) $O^{16}(n,p)N^{16}$; threshold neutron energy = 10.25 MeV,

$$\sigma_{16}(n,p) = 40 \text{ mb}, t_{16} \text{ (mean life)} = 10.3 \text{ sec}$$

$$E_{\gamma} = 6.14 \text{ MeV (68\%)}$$

(b) $O^{18}(n,\gamma)O^{19}$; formed by thermal neutron capture,

$$\sigma_{18}(\gamma,n) = 0.22 \text{ mb}, t_{18} \text{ (mean life)} = 41.8 \text{ sec}$$

$$E_{\gamma 1} = 1.37 \text{ MeV (60\%)}, E_{\gamma 2} = 200 \text{ KeV (100\%)}$$

For long irradiation times ≥ 60 sec, equilibrium is achieved, and the ratio R_{EQ} of the total decays detected is given by

$$R_E = a \frac{F_s}{F_u} \frac{\sigma_{18}}{\sigma_{16}} \frac{t_{18}}{t_{16}} \frac{\epsilon_{18}}{\epsilon_{16}} =$$

where $a = 2 \times 10^{-3}$ (abundance of O^{18}); ϵ_{18} and ϵ_{16} are efficiencies of detection of the photo peak for the respective gamma rays, with a ratio $\epsilon_{18}/\epsilon_{16} \sim 10$ for a 3" x 3" NaI detector crystal (Harshaw Chemical Company catalog, "Scintillation Phosphors," 1962). With these figures

$$R_{EQ} = 4.6 \cdot 10^{-4} F_s/F_u$$

For short irradiations ≤ 7 sec, the ratio R_s of accumulated counts is

$$R_s = t_{16} R_{EQ}/t_{18} = 1.1 \cdot 10^{-4} R_{EQ}$$

The optimal ratios of ultra fast to slow flux for R_{EQ} and R_s unity are respectively $2.2 \cdot 10^3$ and 10^4 . These flux ratios are approximately obtainable in the TRIGA fast reactor at Gulf General Atomic Corporation (GGA) in La Jolla, California. Accordingly, one of us, Dr. Richard Lukens, manager of activation analysis of GGA, verified the simultaneous and observable production of both oxygen activities by neutron activation. These results, shown in Figure 1, display clearly both the 200 KeV and the 6 MeV gamma rays in both wood and water. The conditions of his experiment allow a great deal of improvement to be made for the accurate measurement of R.

Based on the successful proof, achieved in the GAA experiment, that R can be measured by neutron activation, in the present report we analyze steps for improvement of measurement. The accuracy which is

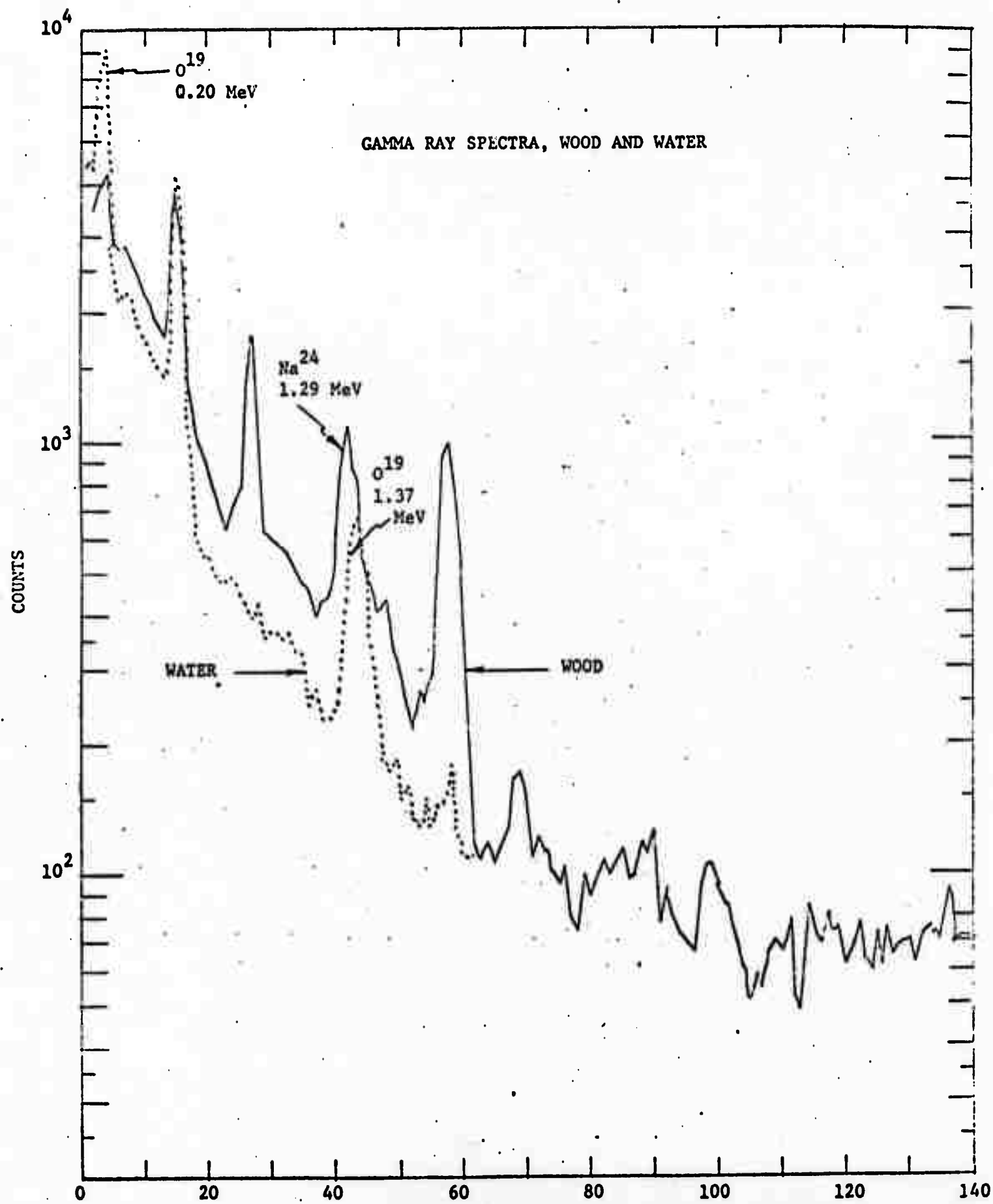


Fig. 1 -

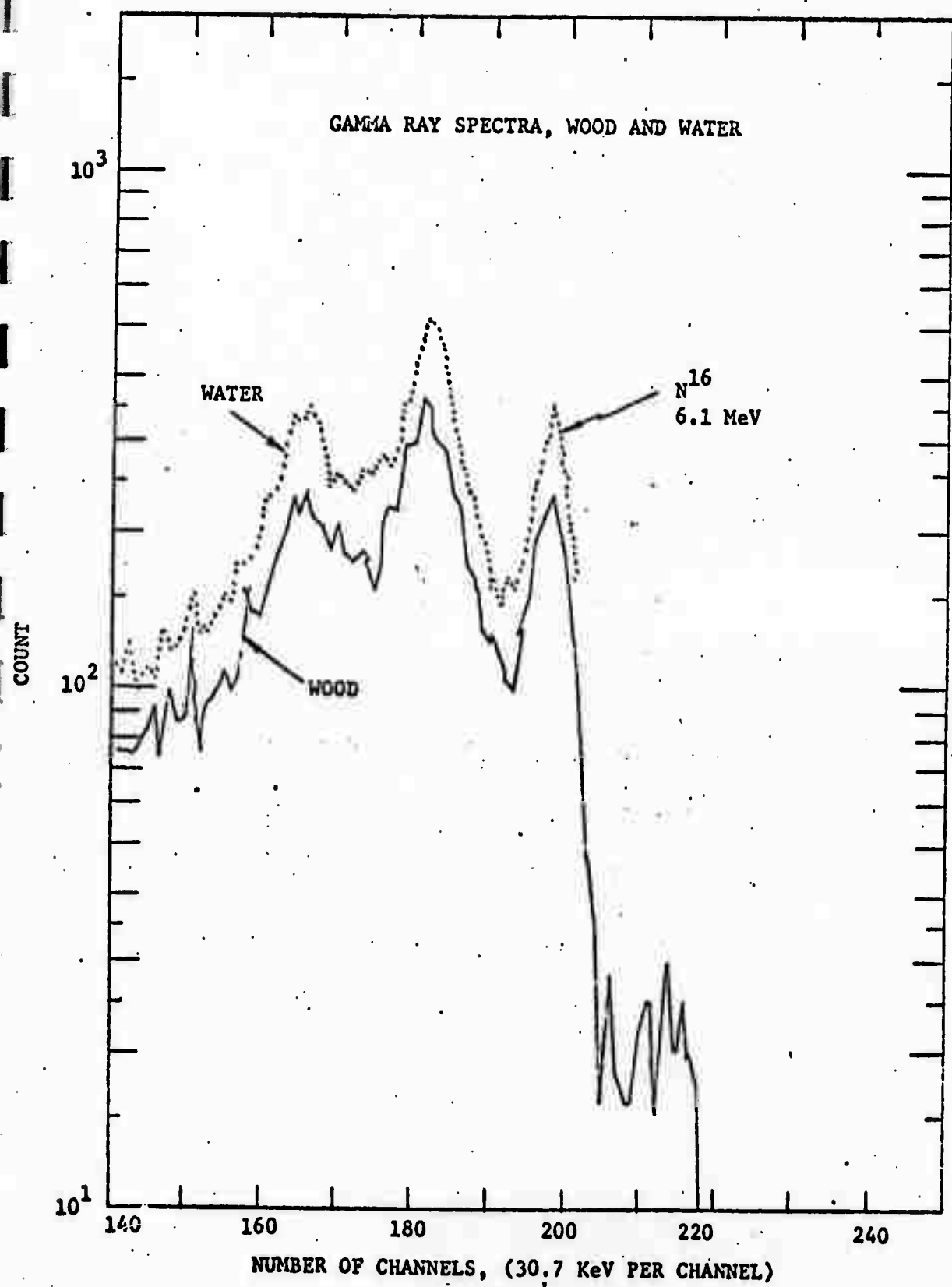


Fig. 1 (cont'd)

ultimately desired is $1/10^4$, this being the accuracy advertised for mass spectrometers (MS). However, the MS measurements are made on CO_2 , prepared and purified by several successive steps in some of which isotope fractionation is an uncomfortable possibility.

If the requisite accuracy can be achieved, measuring R by neutron activation may offer the advantages of checking on the mass spectrograph results by an alternate method and avoiding possible chemical and mechanical fractionation. Non-destructive measurement of the sample may also be a possibility. So this new method might be very valuable. Once developed and standardized, a number of practical applications are expected to follow.

METHOD AND NUMERICAL ESTIMATES

In designing a method of measuring the $\text{O}^{18}/\text{O}^{16}$ ratio by neutron activation, there are three main problems. The first is to find a distinct means of identification for each isotope. Then come the two related problems of interfering activities and of statistical accuracy. The identification tags for the O^{16} and O^{18} isotopes could consist of three different gamma rays produced by neutron activation, two for O^{19} (from the $\text{O}^{18}(\text{n},\gamma)$ reaction) and one for N^{16} (from the $\text{O}^{16}(\text{n},\text{p})$ reaction). Figure 2 gives the detailed decay schemes for O^{19} and N^{16} [3]. Here we concentrate on the 6.143 MeV (N^{16}) and 0.200 MeV (O^{19}) γ -rays. The reason for this is that the 1.37 MeV gamma ray is completely obscured in water by traces of sodium and in wood by sodium and other elements. (See

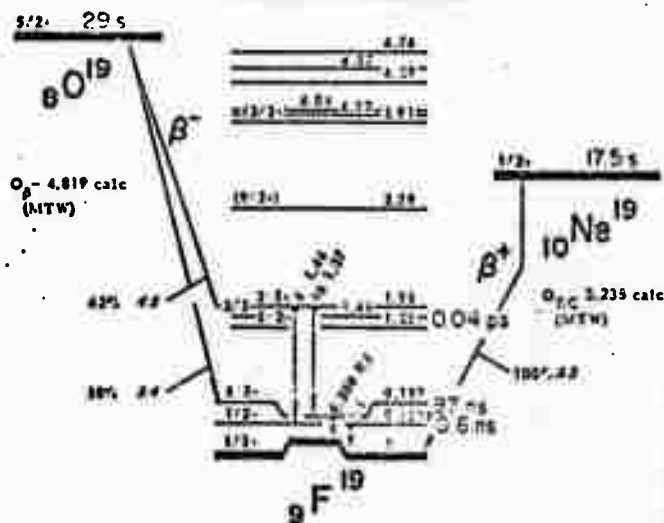
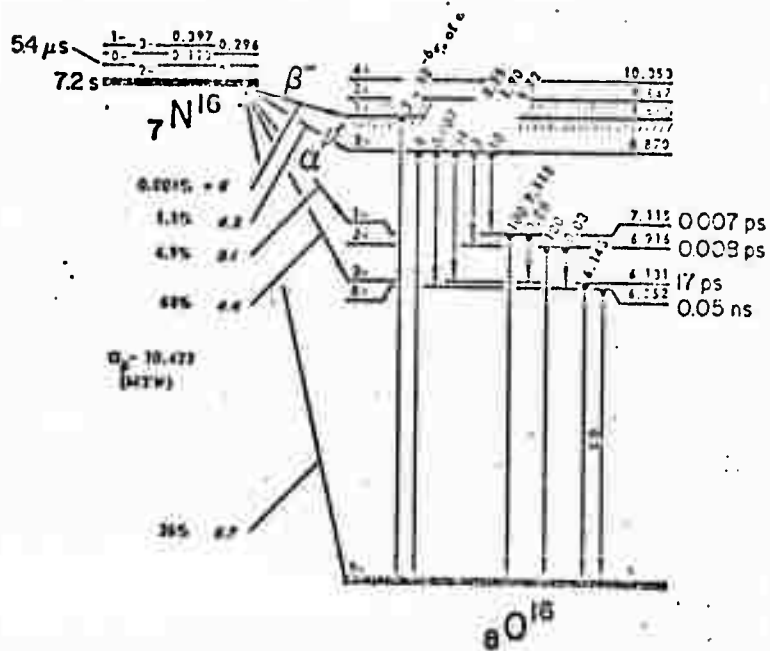
N^{16} (7.2 s): ρ^- : ρ_1 10.44 (25%), ρ_2 4.27 (58%) mag spect (AlbuD59a) ρ_1 10.40 (25%), ρ_2 4.4 mag spect (BruckG55) γ : γ_4 6.124, γ_5 7.112 semicond spect (CrePA65) γ_4 6.13 (I_γ 100), γ_5 7.10 (I_γ 2) pair spect (MillG51); scint spect (BosNS7) γ_4 (I_γ 100), γ_5 7.12 (I_γ 7) scint spect (TopB56a) γ_1 1.72 (I_γ 0.15), γ_2 1.90 (I_γ 0.05), γ_3 2.75 (I_γ 1.3), γ_4 (I_γ 100), γ_6 8.87 (I_γ 0.12) scint spect, $\gamma\gamma$ coinc, 3 cryst pair spect (WilksD56, AlbuD59a) α : 1.7 (broad peak) semicond spect (SegR61, SegR61b) others (KauW61, AlbuD61) O^{19} (29 s): ρ^- : 4.60 (42%), 3.25 (58%) mag spect (AlbuD59a) γ : 0.112 (I_γ 2.7), 0.200 (I_γ 2.7), 1.37 (I_γ 5.9), 1.44 (I_γ 2.7) (JohnCMP59) others (JonG54) $\gamma\gamma$ (9): (JohnCMP59)Figure 2 Decay schemes for ^{19}O and ^{16}N Reproduced from
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Figure 1) By chance, neutron activation of sodium, which is a persistent impurity, produces a gamma ray at 1.36 MeV, unresolvable from the O^{18} radiation at 1.37 MeV. This obscuration was noted in an initial experiment made with the medical reactor at Brookhaven National Laboratory (BNL), with Dr. Hobart Kraner, (described in RDA-MR-031-NMO, March 31, 1972).

As already noted, measuring R requires both a copious ultra-fast neutron flux ($E > 10.2$ MeV) and a thermal flux whose total should be $\sim 10^{13}/\text{cm}^2 \text{ sec}$ or more, so that the required statistical accuracy can be achieved in a reasonable time. The point we make now is that the identification and measurement of O^{16} and O^{18} by their respective γ peaks using NaI crystal detectors has been shown to be possible in the GGA experiment.

We shall concentrate on wood because of its importance to the study of climatology; namely the variation of isotopic ratios of such elements as C, O, H, N, S, ---, in tree rings, is expected to depend on the ambient air temperature when the tree ring was formed, and therefore to have recorded variations of climate.

The major elements of interest in wood are, of course, C, H, and O. We consider interference in measurement of R caused by activation of trace elements in wood, such as F, Mn, N, S, K, which may vary in abundance from one species of tree to another. However, interference caused by trace elements can be minimized (except for sodium). For example, consider Mn^{55} activated by thermal neutrons with properties as follows:

$Mn^{55}(n,\gamma)Mn^{56}$, thermal neutron capture; $\sigma(n,\gamma) = 13.3b$;

$T_{1/2} = 2.6h$; $E_{\gamma} = 0.845 \text{ MeV}(100\%)$; abundance of manganese in wood $\approx 1.5 \times 10^{-4}$.

Since O^{18} must be determined by measuring the 200 KeV radiation, there will be significant interference at ~ 200 KeV caused by Compton scattering of the 0.845 MeV γ -ray into the 200 KeV region. Indeed, in the preliminary experiment at BNL, the 200 KeV gamma peak in irradiated wood was completely masked by the high manganese content. But in the BNL experiment the irradiation time was long (90 sec) and there was considerable delay after extraction of the wood sample from the reactor before counting the 200 KeV gamma, both of which factors enhanced the Mn activity relative to O^{18} . A third factor was that the NaI detector was 3" x 3" so that the signal to noise ratio was poor at 200 KeV.

Two of these parameters were improved in the successful GGA experiment. Namely the irradiation time was decreased to 30 sec (still not the optimal time of ~ 10 sec), and the delay before counting was almost minimized. However, the NaI detector still had a too great thickness of 3 in. The efficiency for detection of the Mn gamma ray of 845 KeV which has been Compton-scattered into the 200 KeV region can be decreased by about a factor of 10 in a thin NaI crystal, without decreasing the efficiency of measurement of the 200 KeV γ ray emitted by oxygen. A thin NaI crystal will be used in the next experiment at GGA to achieve this enhancement.

The GGA reactor can be pulsed at $\sim 10^{17}$ neutrons/cm² sec flux for $\sim 7 \times 10^{-3}$ sec for a total flux of $7 \cdot 10^{14}$ neutrons/cm², as compared with the total flux of $\sim 10^{13}$ neutrons/cm² used in obtaining the data of Figure 1.11. Two advantages may result from irradiation by pulsing, namely, the short irradiation time minimizes the effect of impurities which have long lived activities, and secondly, the fast neutron flux is enhanced,

which increases the $O^{16}(n,p)N^{16}$ activity relative to the O^{18} activity.

Pulsed activation will be explored as a method to improve measurement of R.

Interfering Activations: Radio-active N^{16} can be produced by other reactions than activation of O^{16} , causing the measured value of R to be too low. These reactions are listed in Table I.

Table I
ACTIVATION REACTIONS PRODUCING RADIOACTIVE N^{16}

	Production Cross section	Isotopic Abundance	Threshold Energy
${}^9F^{19}(n,\alpha)N^{16}$	$2 \times 10^{-27} \text{ cm}^2$ at 5-6 MeV	100%	1.5 MeV
${}^8O^{17}(n,d)N^{16}$	-	.037%	11.5 MeV
${}^8O^{18}(n,t)N^{16}$	-	.204%	13.3 MeV
${}^7N^{15}(n,\gamma)N^{16}$	$\sim 2 \times 10^{-29} \text{ cm}^2$.37%	0

We must ask whether the radio- N^{16} produced from any of these reactions by irradiation of wood in a reactor can increase N^{16} by more than 10^{-4} of the production from $O^{16}(n,\gamma)N^{16}$.

According to Figure 1, the ratio R measured in the GGA experiment is about 10 (instead of the desired value of ~ 1), but if the irradiation time which was 30 sec had been shortened to the desired time of 10 sec,

and if the waiting time before counting had been decreased from 30 to 10 sec, the ratio R would have been close to unity, so that $F_s/F_u \sim 10^4$ in the TRIGA reactor for fast neutrons of ≥ 10 MeV. We may guess the relative flux of neutrons at the intermediate energy of 5 MeV to be 30 times greater. Then the N^{16} activity produced from $F^{19}(n,\alpha)N^{16}$ relative to that from $O^{16}(n,p)N^{16}$ is approximately less than or equal to

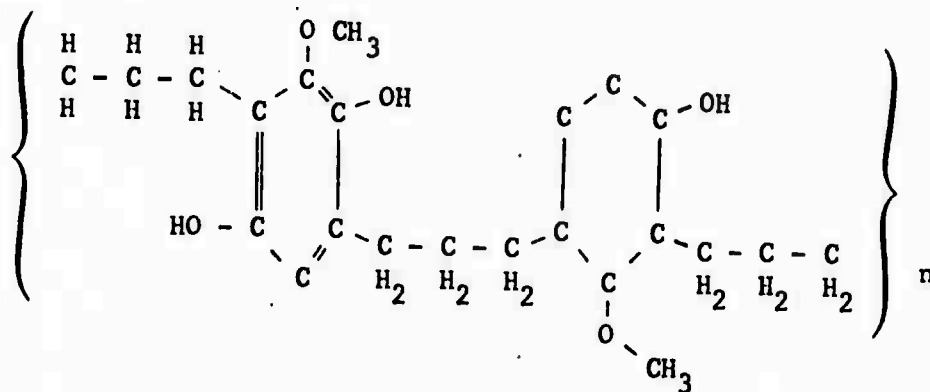
$$30 \left\{ \frac{10 \times 10^{-6}}{0.5} \right\} \left\{ \frac{2 \times 10^{-27}}{4 \times 10^{-26}} \right\} \sim 3 \times 10^{-5}$$

where the first bracket is the ratio of abundances of fluorine and oxygen, the second is the ratio of cross sections

Thus, the fluorine content of wood should not be a nuisance. For experimental evidence of the fluorine content we may look for the reaction $F^{19}(n,\gamma)F^{20}$, $T_{1/2} = 11$ sec, $E_\gamma = 1.63$ MeV, which should appear at channel ~52 in Figure 1 as a peak in wood (but not in water), with an intensity of 10 relative to N^{16} , however, no peak is there. In fact, wood and water are not perceptibly different. The answer may be that fluorine is less than 10 ppm in this particular kind of wood.

The basic formula for cellulose is $(C_6H_{10}O_5)_x$ present in wood to (Fig. 3) about 70%. Lignin, with composition $(C_{10}H_{10}O_3)_x$, is present to about 25%, and resins, $(C_{15}H_8O_2)_x$, to a few percent. The elemental impurities of interest are present in amounts typically as follows: N at ~0.2%, 10 ppm for S, 100 ppm for K, 10 ppm for F, 20 ppm for Al, 40 ppm for Na, and 150 ppm for Mn.

Because of the high energy threshold for $O^{17}(n,d)N^{16}$, the ratio of N^{16} it produces is given by


$$\left\{ -O-C \begin{array}{c} \text{H} \diagup \text{O} \\ \text{H} \diagdown \text{C} \\ \text{C} \diagup \text{OH} \end{array} \begin{array}{c} \text{O} \text{---} \text{C} \\ \text{H} \diagdown \text{H} \\ \text{C} \diagup \text{OH} \end{array} \right\}_n$$
$$\left\{ \begin{array}{c} \text{H} & & \text{H} & & \text{H} \\ | & & | & & | \\ -\text{C} & & \text{C} & & \text{C}- \\ | & & | & & | \\ \text{H} & & \text{H} & & \text{H} \end{array} \begin{array}{c} \diagup & & \diagdown \\ \text{C} & & \text{C} \\ | & & | \\ \text{C} & & \text{C} \\ \diagdown & & \diagup \\ \text{C} & & \text{C} \end{array} \begin{array}{c} \diagdown & & \diagup \\ \text{C} & & \text{C} \\ | & & | \\ \text{C} & & \text{C} \\ \diagup & & \diagdown \\ \text{C} & & \text{C} \end{array} \begin{array}{c} \diagup & & \diagdown \\ \text{C} & & \text{C} \\ | & & | \\ \text{C} & & \text{C} \\ \diagdown & & \diagup \\ \text{C} & & \text{C} \end{array} \right\}_n$$

Figure' 3

$$\frac{\sigma(\text{mb})}{40} \frac{3.7 \times 10^{-4}}{0.5} \times 1 = 2 \times 10^{-5} \sigma(\text{mb})$$

so that for a reasonable cross-section of a few mb or less, this reaction is negligible. The ratio for ${}^8\text{O}^{18}(\text{n}, \text{t})\text{N}^{16}$, with a similarly high energy threshold, is given by

$$\frac{\sigma(\text{mb})}{40} \left\{ \frac{2 \times 10^{-3}}{0.5} \right\} \{1\} = 10^{-4} \sigma(\text{mb})$$

and even with a grossly overestimated cross-section of ≈ 1 mb the contribution of this reaction would be tolerable.

Next, let us consider ${}^7\text{N}^{15}(\text{n}, \gamma)\text{N}^{16}$, produced by thermal neutrons. Nitrogen occurs in the nucleic acid attached to lignin, to an amount which could be as large as 0.2% of the mass of wood. The N^{16} activity it produces is given by, relative to the activity from O^{16}

$$(3.7 \times 10^{-3}) \left\{ \frac{(2 \times 10^{-3})}{0.5} \right\} \left\{ \frac{2 \times 10^{-29}}{4 \times 10^{-26}} \right\} 10^4 \approx 7 \cdot 10^{-5}$$

where the first bracket is the isotopic abundance of N^{15} , the second is the ratio of elemental abundance of N and O in wood, the third is the cross section ratio and the fourth is the appropriate ratio of neutron fluxes.

The only contributor to the 200 keV O^{19} peak is F^{19} from the $\text{F}^{19}(\text{n}, \text{p})\text{O}^{19}$ reaction. The ratio of its contribution to the $\text{O}^{18}(\text{n}, \gamma)\text{O}^{19}$ contribution is given by

$$\left(\frac{1}{2.2 \times 10^{-3}}\right) \left(\frac{10^{-5}}{0.5}\right) \left(\frac{30 \text{ mb}}{0.22 \text{ mb}}\right) \left(\frac{10^{-3}}{1}\right) \approx 1 \times 10^{-3},$$

making it a significant contributor to the error. If however one utilizes the 1.63 MeV gamma ray from the $F^{19}(n,\gamma)F^{20}$, $\tau_{1/2} = 11 \text{ sec}$ reaction, one can relate the number of counts in the 1.63 MeV peak to the contribution of F^{19} to the 200 keV peak and subtract it. The ratio of the $F^{19}(n,p)O^{19}$ reaction to the $F^{19}(n,\gamma)F^{20}$ reaction need only be known to 1/10 (from an independent measurement in the system) to reduce the $F^{19}(n,p)O^{19}$ contribution ratio to 10^{-4} . It is possible to measure the fluorine reaction ratio to at least $1/10^3$ thereby making the fluorine (n,p) contribution insignificant.

So it seems that measurement of O^{18}/O^{16} in wood may possibly be made non-destructively by neutron activation.

The statistical error in the measurement of the O^{18}/O^{16} ratio is the error in the total number of counts under each of the gamma peaks of interest. This error for 10^7 counts is $\sim 1/2000$.

The problem that must be solved, in the nuclear activation method for determining the O^{18}/O^{16} ratio with an accuracy of $\approx 3/10^4$, is recording high count rates without encountering unacceptable losses in count rate. This problem arises because N^{16} has a half-life of 7.2 sec so that the effective data collection time is $\approx 15 \text{ sec}$. To collect 10^7 counts in this time requires an initial count rate of $\approx 2-3 \times 10^6 \text{ sec}$ in the peak of interest. The technology of counting at megacycle rates exists, namely using fast, solid state discriminators, and this problem we are next attacking.

APPENDIX III

Determination of Isotopic Abundances of C, N, and O in Organic
Samples Using Nuclear Techniques *

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ABSTRACT

The determination of isotopic abundances of C, N, and O in organic samples by techniques involving the use of charged particle beams from a Van de Graaff accelerator is discussed. The accuracy and convenience of the method are considered and an example of a method for measuring ^{16}O - ^{18}O ratios is given.

*Work performed under the auspices of the U.S. Atomic Energy Commission.

I. Introduction

Radioactive isotopes have been used for many years as tracers in biological and medical experiments. The activity, of course, is used as a tag to trace the progress of the isotope through the sample. While this technique is very powerful it does have the disadvantage in some cases that the dosage can produce undesirable radiation damage effects in the sample or patient and that great care in handling of the radioactive isotope is required.

A possible alternative approach would be to use compounds which are enriched in some isotope present in the normal element in only a small percentage.⁽¹⁾ This might be particularly advantageous for carbon, oxygen, and nitrogen where the radioactive isotopes either have relatively short lifetimes, or in the case of ^{14}C , a long lifetime with a soft β -ray, and thus requires relatively large amounts of activity and special care in the processing and counting techniques. One of the major and limiting difficulties in the use of the stable isotope technique is to achieve adequate sensitivity for the detection of small changes in the isotopic abundance of each element.

Many approaches to this problem can be envisaged, but here the discussion will be limited to the determination of C, N, and O isotopic abundance ratios in organic samples by nuclear techniques which involve the use of charged particles easily available from a 4.0 MV Van de Graaff accelerator. This type of accelerator is chosen for consideration since many are available for use and the operating costs are modest. Naturally, accelerators capable of producing higher energy particles could also be used. The following sections consider the

suitability and ease of application of the various nuclear reactions which can be induced by these particle beams. Generally, the experimental techniques are fairly standard in nuclear physics, but it should be emphasized that some care and skill will be necessary for their successful application, i.e. the user is not completely free from responsible knowledge of nuclear techniques.

II. General Considerations

The concepts from nuclear physics which are needed for the determination of isotopic abundances are rather simple and have been discussed many times in the literature. For convenience and clarity a brief discussion will be given here.

.. The identification of a particular element is made by bombarding a target with a beam of particles and then measuring the energy of the particle scattered by the target or the energy of some reaction product. The kinematics of nuclear reactions and scattering are well discussed by Marion and Young. (2)

The energy release in a nuclear reaction $M_2(M_1, M_3)M_4$ is denoted by Q and is defined by:

$$Q = (M_1 + M_2 - M_3 - M_4)c^2 \quad 1)$$

where M_1, M_2, M_3, M_4 are the masses of the incident; target, light and heavy reaction products, respectively. If $M_1 = M_3$ and $Q=0$ we have elastic scattering, if $Q<0$ inelastic scattering, and for $M_1 \neq M_3$ a reaction.

The energy of the light product particle is the quantity which is measured and for elastic scattering it is given by:

$$\frac{E_1}{E_0} = \frac{M_1^2}{(M_1 + M_2)^2} \{ \cos \psi \pm [(M_2/M_1)^2 - \sin^2 \psi]^{1/2} \}^2 \quad 2)$$

where E_0 is the incident energy, E_1 the final energy, and ψ the angle of observation relative to the incident beam. Note that the value of E_1/E_0 , called the scattering ratio, is independent of the incident energy. The energy of the light particle from a reaction is given by:

$$E_1 = E_0/M^2 \{ (M_1 M_3)^{1/2} \cos \psi \pm (M M_4/E_0 + M_2 M_4 - M_1 M_3 \sin^2 \psi)^{1/2} \}^2 \quad 3)$$

where $M \equiv M_1 + M_2 \approx M_3 + M_4$ and the energies are defined above. The measurement of the final energy of the light particle at an angle ψ thus allows the determination of the mass of the heavy target particle, and, in particular, for the case of isotopes of C, N, and O it uniquely identifies the element and isotope.

The number of atoms of a particular target species present is proportional to the number of scattered particles and is found by the following relation:

$$T \propto N(E_1, \psi) / (N_B \cdot c(\theta) \cdot d\Omega) \quad 4)$$

where T is the number of target atoms per cm^2 , $N(E_1, \psi)$ is the number of detected particles with energy E_1 at an angle ψ , N_B is the number of incident particles, $c(\theta)$ is the differential cross section in cm^2/sr , that is, the probability for the reaction or scattering of interest, and $d\Omega$ is the solid angle subtended by the detector at the target. The absolute accuracy of the determination of T is mainly limited by our knowledge of $c(\theta)$ which at energies and angles of interest for C, N, and O measurements will be typically a few per cent. This means that absolute determinations of abundances will be limited to that accuracy. However, if we consider the measurement of changes in the abundance of an isotope relative to the composition of

a standard sample, the accuracy can be much better; with a practical limit of $\sim 0.1\%$.

Abundance ratios can be found most accurately by using a single detector to measure the energies of particles emitted at a given angle. In that case the isotope is identified by the energy and type of particle and the abundance ratio is just:

$$R = T_1/T_2 = [N_1(E_1, \psi)/N_2(E_1, \psi)] \cdot [c_2(\theta)\sigma_1(\theta)] \quad 5)$$

If two detectors are used, for example to measure two different types of particles, then a ratio of solid angles must also be included as well as possible differences in counter efficiencies. If a standard sample is used for calibration T_1/T_2 is known and R can be used to determine the cross section ratio.

$$c_2(\theta)/c_1(\theta) = R \cdot N_2(E_1, \psi)/N_1(E_1, \psi). \quad 6)$$

The ratio of the absolute abundances of the two isotopes in the unknown is then found by substituting the ratio of cross sections given in equation 6 into equation 5. The fractional abundance of each isotope is then found by remembering that the sum of the fractional abundances is equal to unity.

Conceptually, to this point, the determination is trivial. In practice care in choosing detectors and obtaining good energy resolution will be required. The most demanding task is the use of target techniques to make thin targets able to withstand high beam currents and the use of good vacuum techniques to prevent contaminants from pump oil or other vapors in the chambers from depositing on the target and introducing errors. Such techniques are well known to the nuclear physicist; however

the degree of ultimate application may well hinge on the ease and reliability with which targets can be obtained. One suggested method to obtain oxygen targets will be discussed in a following section. One experimental point that should also be mentioned specifically is the question of target heating. Most organic materials cannot withstand the heating effects of several microampere currents of heavy charged particles. Special care must be given to the preparation of thin targets and to the use of techniques, such as target wobblers, which permit the use of reasonable beam currents. The details will depend on the compound of interest. We will not discuss here types of particle detectors appropriate for these experiments or details of experimental hardware, but refer the reader to the paper of Amsel et al. ⁽³⁾ which gives an introductory survey.

The application of these nuclear techniques to qualitative analysis is by no means new, but the main emphasis has been on its use for trace element identification. A rather general discussion of the applications of elastic scattering techniques has been given by Cohen and Moyer ⁽⁴⁾ and Jolly, Gruhn, and Maggiore. ⁽⁵⁾ A detailed discussion of the use of nuclear reactions in measurement of light element concentrations is given by Amsel et al. ⁽³⁾

The interaction of the standard beams of ^1H , ^2H , ^3H , ^3He , and ^4He with C, N, and O isotopes in the energy region below 4 MeV have been studied intensively for many years and a large literature exists on the Q-value and cross sections for the reactions. The Q-values are tabulated in Table I and were taken from the NAS-NRC 1960 Nuclear Data Tables and 1971 mass tables of Wapstra and Gove. ⁽⁶⁾ While later and

and more accurate mass tables exist, these Q-values are given in a convenient form in the 1960 Nuclear Data Tables and are more than adequate for the present discussion.

Summaries of experimental cross section results have been given by Jarmie and Seagrave⁽⁷⁾ and Kim, Milner, and McGowan.⁽⁸⁾

A very general survey of all experimental results is given by Ajzenberg-Selove and Lauritsen⁽⁹⁾ on $A = 11$ and 12 nuclei and by Ajzenberg-Selove⁽¹⁰⁾ for $A = 13-15$, and $A = 16, 17$.

The rare isotopes of C, N, and O are ^{13}C , ^{15}N , ^{17}O , and ^{18}O with normal abundances of 1.11, 0.37, 0.037, and 0.204%, respectively.

Presumably in most cases the uptake of the enriched tracer compound will not change the isotope ratios by a very large amount and it will be necessary to measure the changes with modest precision.

The precision of the determination will be limited by the counting statistics and ultimately the cross section for the process that identifies the rare isotope. For example, in the case of ^{12}C - ^{13}C , the uncertainty in the ratio, $R = ^{12}\text{C}/^{13}\text{C}$, is then given by $\pm R/\sqrt{N_{13}}$ where N_{13} is the total number of particles detected for the process which identifies the presence of ^{13}C . For $N_{13} = 10^6$ the uncertainty in the ratio is then $\pm 0.1\%$. In practice the total number of detected particles will be limited by the cross section, maximum beam current which the target can withstand, the magnitude of the background, and the total time available for the measurement.

III. Determination of R by Elastic Scattering

As we have seen in equation 2, the elastic scattering process can be used to differentiate between different target nuclei by a simple

measurement of the energy of the outgoing particle. The mass discrimination is best for $\psi \approx 180^\circ$. Although the scattering cross sections will be largest at forward angles this advantage is negated by the smaller energy separations of the scattered particles. A rough upper limit to target thickness, t , that may be used without seriously degrading the system can be estimated by letting the maximum energy loss in the target, $dE/dx \cdot 2t$ for back angle scattering be equal to or of the order of the energy resolution of the detector used. Since scattering can occur at the front or rear surface of the target this energy loss is the energy spread of the scattered beam. For 4 MeV protons in polyethylene, for example, dE/dx is 100 keV/mg/cm^2 and the resolution of commonly used silicon detectors is $\sim 20 \text{ keV}$; thus the maximum organic target thickness is $\sim 0.2 \text{ mg/cm}^2$.

The scattering ratio for protons scattered by targets with atomic masses from 12 to 18 is shown in Figure 1. Figure 2 shows the range of values obtained for incident particles with atomic masses of 1, 2, 3, and 4.

Now, from reference to Table I, it can be seen that the nuclear reactions produced by beams of protons and alphas are minimal compared to those produced by deuterons, tritons, and ^3He . The latter particles produce many unwanted reaction particles which complicate the detection of the elastically scattered particles and hence are not as useful as protons and alphas. It is not so easy to choose between protons and alphas, however. Alphas produce a bigger kinematic shift, but dissipate more energy in the target and are somewhat harder to detect with good resolution in semiconductor particle detectors.

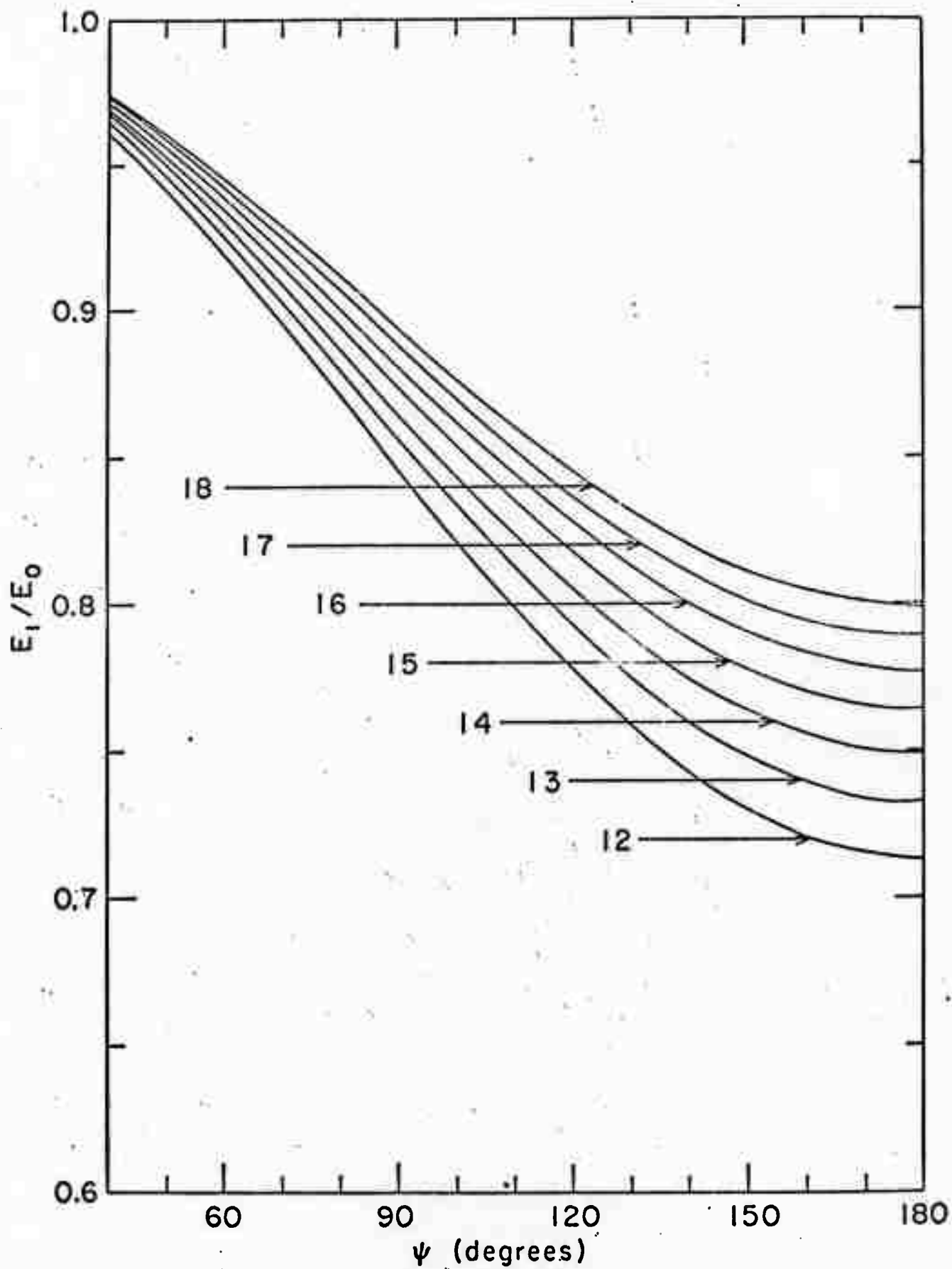


Figure 1

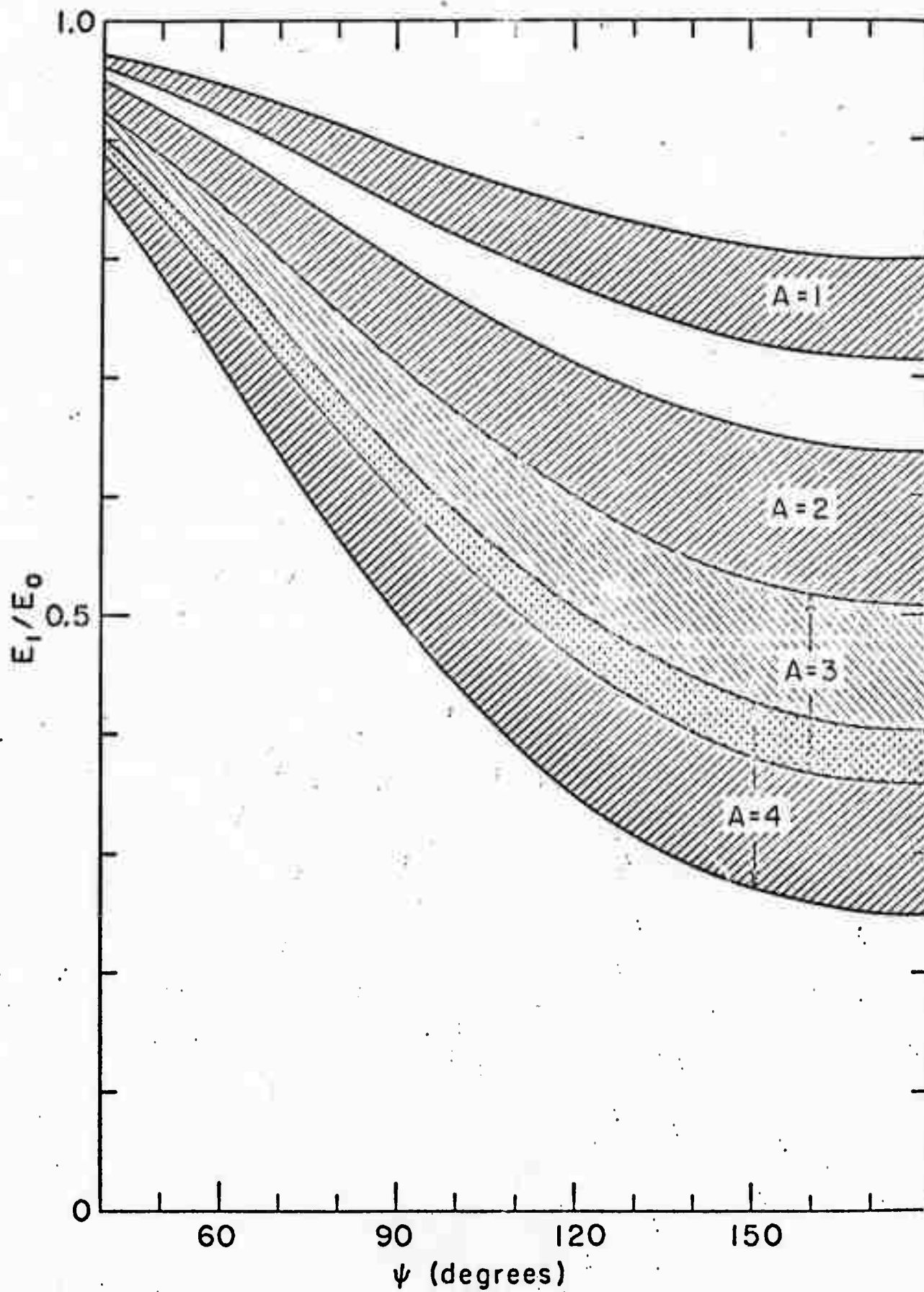


Figure 2

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For a particular example we will take the case of the measurement of ^{12}C - ^{13}C ratios. A sample with the composition of polyethylene and a proton beam current of $1.0\ \mu\text{A}$ are assumed. The first approach might be to use a reasonably high bombarding energy $\sim 3.0\ \text{MeV}$ for example, in order to get as large as possible difference in energies between the particles scattered from the two isotopes. Target thickness has been adjusted so that the total rate is 50,000 counts/sec which is a reasonable limit imposed by commonly available electronics. An annular detector with an acceptance angle of $\pm 1^\circ$ was assumed with an angle of observation of 160° . The energy separation between protons scattered from the two isotopes is then 55 keV. The experimental conditions with a target thickness of $75\ \mu\text{g}/\text{cm}^2$ are such that it should be feasible to resolve the peaks corresponding to the two isotopes. A rate for ^{13}C of 500 to 1000 counts/sec can be achieved and hence the abundance ratio, R , can be determined to $\pm 1\%$ in 10 to 20 sec and to $\pm 0.1\%$ in 1000 to 2000 sec.

The large difference in the counting rates for scattering from ^{12}C and ^{13}C also illustrates a possible limitation; namely, the counting equipment can be rate limited by particles scattered by the abundant isotope. In order to reduce this rate it is possible only to search for an energy where the cross section for the abundant isotope is a minimum relative to the other cross section. Some advantage can be had from this, i.e. where non-Rutherford nuclear effects are operative at low energies, but it is not generally applicable. However, for the ^{12}C - ^{13}C case there is a resonance in $^{12}\text{C}(p,p)^{12}\text{C}$ scattering at $E_p \sim 1.7\ \text{MeV}$ and a rather narrow minimum occurs there. If an estimate is done for this energy the rate for ^{13}C scattering can be increased from the above by a factor of 3 to 5 and R can be measured to $\pm 0.1\%$ in a time of perhaps 500 sec.

For alpha particle scattering by ^{12}C examination of the excitation curves shows a deep minimum at about $E_{\alpha} = 3.2 \text{ MeV}$ and an angle of $\sim 105^{\circ}$ in the laboratory system. Choosing this energy and a target thickness of $10 \mu\text{g}/\text{cm}^2$ and again a $1 \mu\text{A}$ current of He^+ gives a rate of 470/sec. Here the dynamic range for scattering from ^{12}C and ^{13}C is very good; but it is probably difficult to increase the rate very much by increasing the beam current because of the increased specific ionization and energy loss to the target. It again appears that a determination of R to $\pm 0.1\%$ in $\sim 2000 \text{ sec}$ is feasible.

It is concluded that it should be feasible to measure the isotopic abundance of ^{12}C - ^{13}C to $\sim \pm 0.1\%$ in a time of $\sim 2000 \text{ sec}$ by elastic scattering techniques. Better precision is possible with longer counting periods, but it improves only as $t^{1/2}$.

Similar considerations will apply to the determination of ^{14}N - ^{15}N and ^{16}O - ^{17}O - ^{18}O abundances. In these cases the overall composition of the target will be important since the total counting rates will probably be determined by scattering from carbon. If nitrogen and oxygen are present in small amounts the determination will be relatively inaccurate, perhaps $\pm 1\%$ in the ratio, for counting periods of 2000 sec. If a more sophisticated magnetic spectrometer was used it would be possible to eliminate the unwanted particles, but on the other hand it will be at the expense of solid angle so that the final result may be similar.

IV. Determination of R by Nuclear Reactions

The advantage of determining R by the use of a suitable nuclear reaction is that one need not be limited by the rate from the abundant

isotope, but can choose a reaction which will optimize the detection of the rare isotope. While many of the charged particle reactions give reaction products which can be identified uniquely the cross sections are in general quite low. Neutron producing reactions in several cases present very attractive features. The cross sections can be quite large and are often substantially bigger than the cross sections for reactions producing charged particles. The neutrons can, by choice of suitable detection systems, be detected with high efficiency large solid angle detectors. The neutrons produced by reactions in other constituents of the target can again be rejected by proper choice of type of detector and bombarding energy. For these reasons only reactions which produce neutrons will be considered.

The neutron producing reaction is used to indicate the abundance of the rare isotope and the elastic scattering technique can be used to give either the amount of the abundant isotope or the total amount of the element present. Equation 5 must now be multiplied by the ratio of the solid angle-efficiency product for the two detectors. For a particular experimental arrangement relative values of R can be measured accurately, but absolute values will be rather imprecise. This emphasizes the need to use a standard sample for calibration.

For the ^{12}C - ^{13}C measurement, inspection of Table I shows that the $^{13}\text{C}(\alpha, n)^{16}\text{O}$ reaction is attractive since neutrons produced by the alpha particle bombardment of the other light nuclei can be easily discriminated against with a simple hydrogenous proton recoil type neutron detector. Making the rather conservative assumption that the neutrons are detected with 5% efficiency in a solid angle of .09 sr and that a 100 keV thick

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target can be used at an alpha energy of 3.65 MeV where the cross section is 30 mb/sr, then 10^6 neutrons can be detected in a time of about 300 sec. The time required to measure R to $\pm 0.1\%$ is thus less than the time for the same determination by elastic scattering by a factor of about 5.

For the ^{14}N - ^{15}N pair a similar technique can be used with the (d,n) reaction. The cross section is not very large, about 5 mb/sr at 2 MeV which, however, can be compensated for by a thicker target. The use of a thicker target would spoil the energy resolution, but the $^{14}\text{N}(d,p_0)^{15}\text{N}$ reaction rather than elastic scattering could be used to measure the amount of ^{14}N present. Since the (d,p₀) reaction has a Q-value much more positive than the other possible deuteron induced charged particle reactions no great resolution in the charged particle detector is needed and adequate rates can be obtained. The counting time required to make a determination of the ratio would depend on the amount of nitrogen present in the sample of interest.

The case of the ^{16}O - ^{18}O pair can be handled by use of the (p,n) reaction. ^{18}O is the only light isotope which produces neutrons if the proton energy is kept below 3 MeV. A target thickness and angle of observation are chosen which permit a semiconductor detector to resolve protons elastically scattered by ^{16}O from protons scattered by other elements. The determination can then be made at a proton energy of 2.650 MeV where there is a maximum in the $^{18}\text{O}(p,n)^{18}\text{F}$ cross section. The average total cross section is 25 mb.⁽¹¹⁾ The neutrons have low energy and can be detected in a properly designed neutron counter with essentially 100% efficiency and a solid angle close to 4π sr. If a

target of LiOH $17 \mu\text{g}/\text{cm}^2$ thick is assumed, which results in a proton energy loss of 10 keV, the resulting rate is $8 \times 10^5/\text{sec}$ and the determination can be made accurately. The actual counting rate would be at least a factor of 10 less because of rate problems in the detection system.

The measurement of ^{17}O by the reaction technique does not look as promising as for the other isotopes. The (d,t) reaction might be of use but would require the use of particle identification techniques which are cumbersome. The (α,n) reaction is perhaps the most hopeful, but here since the $^{13}\text{C}(\alpha,n)^{17}\text{F}$ reaction has a more positive Q-value, time-of-flight techniques would be needed for a rather precise neutron energy measurement.

V. Examples of ^{16}O - ^{18}O and ^{12}C - ^{13}C Isotopic Abundance Ratios Determined by Elastic Scattering

In order to illustrate the application of the elastic scattering technique several spectra were obtained for the energy distribution of protons elastically scattered by targets containing C and O. The angle of observation was about 160° and the counter solid angle was 1.65×10^{-4} steradians. The equipment that was used was designed for other experiments and no attempt was made to minimize data collection times for this particular use.

The first target that was used represents one possible technique whereby thin oxygen targets can be prepared in an easy way for the determination of ^{16}O - ^{18}O ratios in water samples. A thin Li target, $\sim 100 \mu\text{g}/\text{cm}^2$, was vacuum evaporated onto a $20 \mu\text{g}/\text{cm}^2$ carbon foil. The target was then removed from the evaporator and the lithium

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allowed to either oxidize or form the hydroxide by reacting with the oxygen and water vapor present in the atmosphere. This technique gave a stable target with oxygen as the heaviest constituent.

This method could be used in general to prepare thin oxygen targets from samples of oxygen gas or water. The fresh Li target would be exposed directly to the oxygen or over the water sample of interest without exposure to atmospheric oxygen. Bubbling of a noble or non-reacting carrier gas through the water could hasten the reaction. The targets should be totally converted from the metallic form and should be stable enough to be transferred after preparation to the scattering chamber with minimal precautions.

In Fig. 3 data is shown for proton bombardment of a Li-C-O target with a beam current of about 0.5 μ A for two hours. In this case the statistical accuracy for the ^{13}C peak is $\sim \pm 4\%$. The ^{18}O peak is not as strong and the statistical accuracy is $\sim \pm 10\%$. The determination of the ^{18}O abundance is more difficult than for ^{13}C because the relative isotopic abundance is less.

Figure 4 shows two pulse height spectra obtained for proton bombardment of two carbon foils. The target used for the spectrum shown in Fig. 4a was a 20 $\mu\text{g}/\text{cm}^2$ foil of natural carbon. For Fig. 4b a 15 $\mu\text{g}/\text{cm}^2$ foil enriched in ^{13}C was used. Analysis of this data gives the composition of the enriched foil as $(84 \pm 8\%)$ ^{13}C relative to an assumed natural value of 1.11%. It should again be emphasized that the data shown here was taken to illustrate the technique and no effort was made to minimize data collection times or to attain high precision.

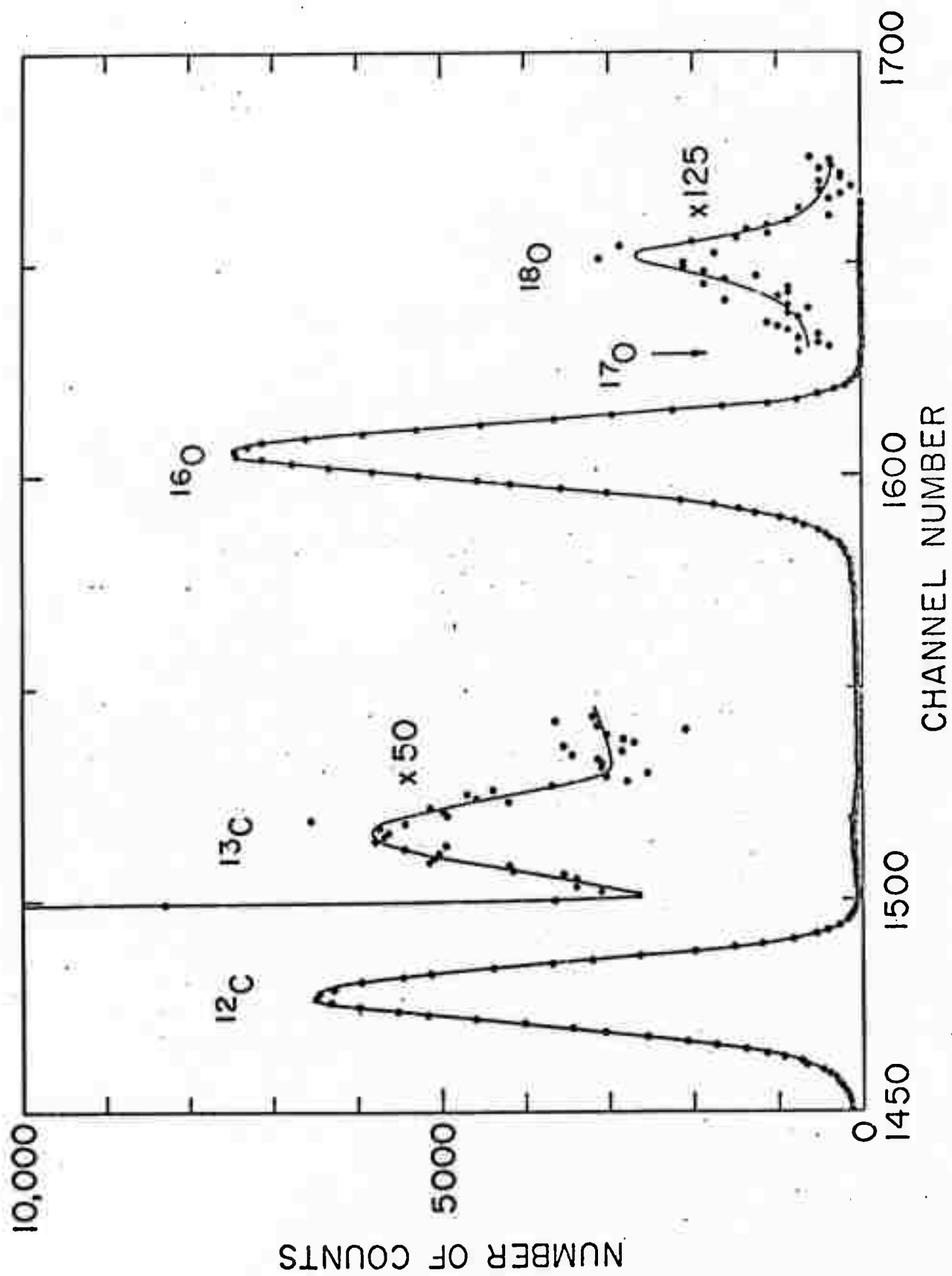


Figure 3

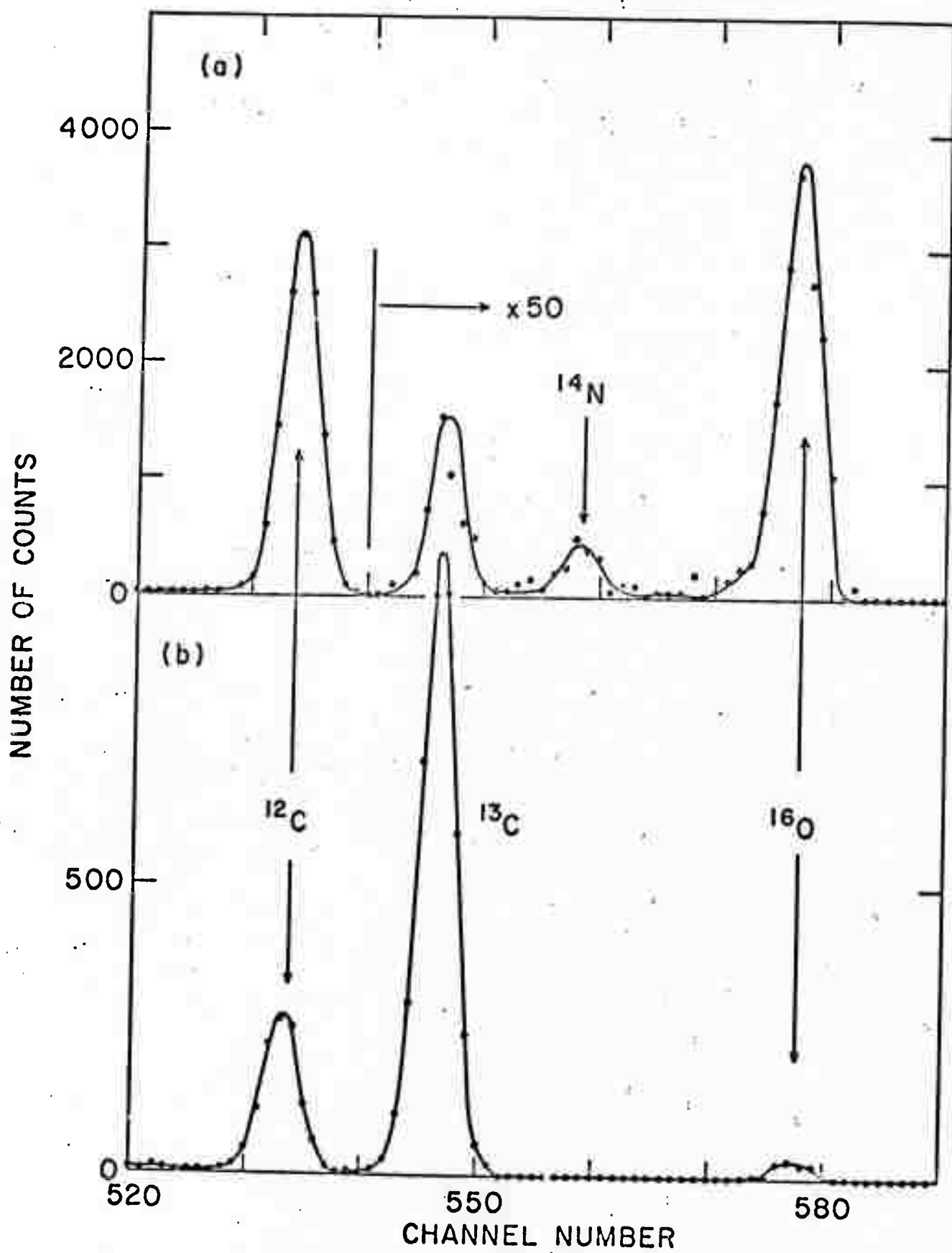


Figure 4

VI. Conclusions

We have examined the possibility of determining isotopic abundances of the C, N, and O isotopes in organic samples largely free of heavy elements. Very simple elastic scattering measurements should be capable of determining the ratios to about $\pm 0.1\%$ where the element of interest is a major constituent of the sample. In some cases the use of a nuclear reaction to tag the rare isotope of interest may give somewhat improved results. Determination should be possible with running times of 5-30 min so that the analysis of many samples should be convenient.

This method, while it may not have the ultimate sensitivity of mass spectrometric methods, does have several advantages. It does not depend on the cleanliness of an ion source and therefore may be more suitable for processing large batches of samples. Possible preferential extraction of one isotope by the ion source is not a problem. Targets can be prepared from small amounts of material, perhaps 1 to 10 mg.

It appears that the use of small Van de Graaff accelerators for routine analysis of C, N, O isotopic concentrations shows promise of convenience, ease of determination and fair accuracy and could be a valuable tool for isotopic analysis. Even though some progress has been made in such applications, it appears that the field has not yet been well explored. Close cooperation between biologists and chemists and others who are interested in the results of specific measurements with the experimental nuclear physicist who is knowledgeable about the experimental equipment will be necessary to most fruitfully exploit these basically nuclear techniques.

Acknowledgments

We wish to thank Drs. Leona Libby, Martin Posner, and Harvey Wegner for helpful discussions and suggestions.

Table I. Q-values in keV for reactions induced by p, α , t, ^3He , and ^4He bombardment of stable isotopes of C, N, O. The values are taken from ref. 6.

Reaction/Target	^{12}C	^{13}C	^{14}N	^{15}N	^{16}O	^{17}O	^{18}O
p, n	-18390	- 3004	- 5931	- 3543	-16212	- 3544	- 2450
p, d	-16496	- 2722	- 8329	- 8610	-13444	- 1917	- 5822
p, t	-23330	-15186	-22400	-12905	-20408	-11329	- 3706
p, ^3He	-19694	-13185	- 4779	-10666	-15242	- 8550	-14097
p, ^4He	- 7557	- 4064	- 2922	4964	- 5218	1193	3980
d, n	- 281	5325	5066	9901	- 1627	3372	5768
d, p	2722	5951	8610	275	1917	5822	1732
d, t	-12463	1311	- 4296	- 4577	- 9411	2116	- 1789
d, ^3He	-10463	-12040	- 2056	- 4715	- 6633	- 8275	-10570
d, ^4He	- 1342	5167	13574	7687	3110	9802	4256
t, n	4014	9901	14478	7786	1257	7557	6109
t, p	4641	911	4852	- 230	3706	3521	3133
t, d	- 1311	1918	4577	- 3758	- 2116	1789	- 2301
t, ^3He	-13351	-13410	- 138	- 9755	-10390	- 8780	13984
t, ^4He	3857	2279	12263	9605	7687	6045	3750
^3He , n	- 1152	7123	969	5006	- 2980	4290	13118
^3He , p	4779	10666	15242	8550	2021	8321	6873
^3He , d	- 3550	2056	1798	6633	- 4895	104	2499
^3He , t	-17620	- 2239	- 5166	- 2779	-15448	- 2780	- 1686
^3He , ^4He	1856	15630	10024	9743	4908	16435	12530
^4He , n	- 8508	2214	- 4737	- 6430	-12145	588	- 700
^4He , p	- 4964	- 7411	- 1193	- 3980	- 8114	- 5657	- 5620
^4He , d	-13574	- 7687	- 3110	- 9802	-16332	-10031	-11479
^4He , ^3He	-17869	-12263	-12522	- 7687	-19215	-14216	-11820
^4He , ^4He	-15630	-12401	- 9743	-18077	-16435	-12530	-16621

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FIGURE CAPTIONS

- Fig. 1 Scattering ratios for protons scattered by target nuclei with masses between 12 and 18 as a function of laboratory scattering angle. E_0 is the energy of the incident particle and E_1 is the energy of the scattered particle.
- Fig. 2 Scattering ratios for mass 1, 2, 3, and 4 bombarding particles scattered by target nuclei with masses between 12 and 18 as a function of laboratory scattering angle. Target nuclei with intermediate masses have scattering ratios which fall in the cross hatched areas. E_0 is the energy of the incident particle and E_1 is the energy of the scattered particle.
- Fig. 3 Portion of a pulse height spectrum showing the scattering of 3.0 MeV protons by a target of Li, C, and O. The laboratory angle of observation is 160° .
- Fig. 4 The spectrum shown in 4a shows the elastic scattering of 3.0 MeV protons at an angle of 156° by a $20 \mu\text{g}/\text{cm}^2$ natural carbon foil. In 4b the spectrum obtained under identical conditions with a $15 \mu\text{g}/\text{cm}^2$ ^{13}C enriched foil is shown. The ^{13}C abundance in the enriched foil was found to be $(84 \pm 8)\%$ from this data.