NATIONAL BUREAU OF STANDARDS REPORT

4047

STABLE CARBON ISOTOPE ANALYSIS

BY OPTICAL SPECTROSCOPY

by

R. E. Ferguson and H. P. Broida

Progress Report
to
Atomic Energy Commission

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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FOREWORD

This report covers the initial phases of the project on extending the optical spectroscopic method of stable isotope determinations to analysis of C^{13}/C^{12} mixtures.

Later, it is intended to publish this report in Analytical Chemistry.

F. G. Brickwedde

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STABLE CARBON ISOTOPE ANALYSIS BY OPTICAL SPECTROSCOPY

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ABSTRACT

An optical spectroscopic technique for measuring relative concentrations of the stable carbon isotopes, C^{12} and C^{13}, has been investigated. Acetylene prepared from the sample to be analyzed is burned in a premixed flame with air, and the relative intensities of Swan bands due to isotopic C_2 radicals are measured photoelectrically. The adaptability and accuracy of the method are discussed.

I. INTRODUCTION

Previous successful applications of optical spectroscopy to routine precision analysis of hydrogen isotope concentrations [1,2] have encouraged the study of such determinations for other stable isotopes. This note describes a technique for the measurement of relative concentrations of the carbon isotopes, C^{12} and C^{13}, utilizing C_2 radiation from a flame.

The C_2 bands have been used previously for the rough estimation of carbon isotope ratios [6,7]. The method to be described differs from previous ones in that a flame is the light source, measurements are made photoelectrically rather than photographically, and a calibration curve obtained with standard samples is used. These changes result in increased accuracy and a considerable decrease in the time required for analysis.

The carbon compound to be analyzed is converted by a generally applicable method to acetylene which is burned with air on a small burner, and the emission spectrum of the inner cone is observed photoelectrically. The relative intensities of the 1,0 band heads of the $^3\pi - {}^3\pi$ (Swan) system due to $C^{12}C^{12}$, $C^{12}C^{13}$, and $C^{13}C^{13}$ in the region of 4735 to 4755A are measured. The relative concentrations of the isotopes are then determined from a calibration curve constructed from intensity data obtained with acetylene samples of known C^{13} content. By the use of a calibration curve, possible difficulties caused by small isotope effects on reaction rates and differences in spectral characteristics of the isotopic C_2 radicals are avoided.

The 1,0 band was selected because of its relatively high intensity in a flame, the low intensity of background radiation at the head of the band, the relatively large separation of the band heads of the isotopic C_2 radicals (of the order of 7A), and because in this band the $C^{12}C^{13}$ head is clear of overlapping lines of the $C^{12}C^{12}$ spectrum.

An acetylene flame was chosen because of the relatively high intensity of C_2 emission from the inner cone. Air rather than oxygen was used to facilitate adjustment of flow rates at low total flow through the burner. With oxygen, it is difficult to avoid flashback and at low flow rates the flame is inconveniently sensitive to adjustments.

II. EXPERIMENTAL

Acetylene - C^{13} was prepared by the carbide method [3] from enriched $BaCO_3$ (Eastman Kodak Company). It was purified by three vacuum

distillations from a trap at dry ice temperature into a trap at liquid nitrogen temperature. Ordinary tank acetylene, freed of acetone by vacuum distillation, was used to dilute samples of the acetylene-C^{13} for the preparation of mixtures for analysis. The mixtures were prepared volumetrically on the vacuum line by first measuring acetylene-C^{13} and ordinary acetylene separately and then condensing them together into a storage bulb. Volume measurements were made at the same pressure to avoid the necessity of compressibility corrections.

The starting sample (66.6 atom per cent C^{13}) and one diluted sample (22.9 atom per cent C^{13}) were analyzed mass spectrometrically. The other mixture compositions, 11.9, 6.3, and 3.6 atom per cent C^{13}, were calculated from the results of these analyses and the volumetric dilution measurements. The mass spectrometric analyses showed a maximum of 1 per cent impurity, most of which was ethylene.

The isotopic acetylene mixtures prepared by dilution of C^{13} enriched acetylene with ordinary acetylene do not have the carbon isotopes distributed randomly among the acetylene molecules. For example, in the mixture containing 22.9 atom per cent C^{13}, the isotopic acetylenes $HC^{12}\equiv C^{12}H$, $HC^{12}\equiv C^{13}H$, and $HC^{13}\equiv C^{13}H$ are present in the concentrations 69: 16: 15, respectively. If the acetylene sample had been prepared from homogeneous $BaCO_3$ containing 22.9 atom per cent C^{13}, the respective concentrations would be approximately 59: 35: 5. The slight effect of the isotope distribution in the acetylene upon that in the C_2 in the flame will be discussed below.

The acetylene mixtures were burned on a small welding torch with an orifice diameter of 0.5 mm, using the delivery apparatus shown in Figure 1. The acetylene and air were premixed in the torch in proportions (somewhat less than the stoichiometric amount of air) which gave the greatest intensity of the C_2 bands. Control valves were set using tank acetylene and were left in the same position for all mixtures burned. The sample was delivered from a rubber gas expansion bag filled on the vacuum line; constant delivery was achieved by surrounding the bag with nitrogen at 5 psig from a pressure - regulated tank. The three-way stopcock shown in Figure 1 was used for flushing or evacuating the upper part of the assembly between determinations. A stable and reproducible flame of sufficient intensity was obtained with an acetylene flow of 6 cc/min. The samples ranged from 50 to 100 cc N.T.P. Ten separate spectra could be obtained with a 100 cc sample in a burning time of about 16 minutes.

The inner cone of the flame was focussed on the slit of a monochromator with photomultiplier detection and pen recording [4]*. Recorded intensities are directly proportional to the emitted light intensities. A slit height of 2 mm and a slit width of about 0.02 mm were used; this permitted the clear resolution of lines 0.6A apart. For the purpose of analysis considerably lower resolution would be adequate.

* Constructed by the Research Department, Leeds and Northrup Company and loaned to the National Bureau of Standards on a field trial arrangement.

III. RESULTS

Figure 2 shows recordings of the 1,0 band heads of the isotopic C_2 radicals obtained with three acetylene samples of different C^{13} content. The scanning rate was 12A/min. The first recording, A, made with acetylene containing 22.9 atom per cent C^{13}, is shown to illustrate the reproducibility of the relative band head intensities. The dotted line indicates the point at which the direction of scanning the spectrum was reversed and the tracing repeated as a mirror image. Curve B is a recording of the same spectral region with a flame of acetylene containing 6.3 atom per cent C^{13}. At this C^{13} concentration the $C^{13}C^{13}$ band head intensity is too low to stand out above the noise level, although the $C^{12}C^{13}$ head can still be measured accurately. Recording C was made with a flame of ordinary tank acetylene; the $C^{12}C^{13}$ band head is due to the natural abundance of C^{13}, which is about 1.1 atom per cent.

It can be seen from Figure 2 that the band heads are well separated and that the intensities can be measured easily. Only the $C^{12}C^{12}$ and $C^{12}C^{13}$ band head intensities are needed for the determination of the relative abundance of C^{13}. A calibration curve using these two band heads is shown in Figure 3, where the observed intensity ratio $C^{12}C^{13}/C^{12}C^{12}$ is plotted against the C^{13} abundance, expressed in atom per cent, in the acetylene burned. Each ratio plotted is the average for three separate determinations. In all cases, the standard deviation of the mean of the three measurements was less than 3 per cent of the mean value.

The corresponding precision in the C^{13} abundance, expressed in the same way, did not exceed 3 per cent of the measured abundance.

With samples containing less than 15 atom per cent C^{13}, the $C^{12}C^{12}$ and $C^{12}C^{13}$ intensities were very nearly proportional to the expected isotopic C_2 concentrations calculated by assuming a random distribution of the isotopes in C_2; thus it is estimated that the measured intensity ratio alone could be used directly to determine the C^{13} abundance to the nearest 1 per cent in this range. For greater accuracy the use of calibration curve is desirable.

The non-equilibrium composition of the isotopic acetylene mixtures burned was referred to earlier. Another study [5] has shown that the emission from the isotopic C_2 radicals in the flame depends to a slight extent upon the isotopic composition of the acetylene. For example, if the acetylene has a deficiency (compared with the statistical equilibrium concentration) of $HC^{12}\equiv C^{13}H$, the $C^{12}C^{13}$ intensity will be lower than that calculated from the C^{13} abundance alone. The effect is as if about one tenth of the C_2 comes directly from the carbon-carbon pairs of the acetylene introduced into the flame. It is necessary to take this effect into account if it is desired to make accurate measurements in the range above 15 atom per cent C^{13} on samples prepared by dilution with ordinary acetylene. This can be done by using a calibration curve obtained with acetylene samples similar in composition to those to be analyzed. On the other hand, in undiluted acetylene prepared from diluted CO_2 or $BaCO_3$, the isotopic species will

be present in nearly equilibrium concentrations and the effect will be absent.

IV. DISCUSSION

These results show that optical spectroscopy can be used for rapid and reasonably accurate determinations of C^{13}/C^{12} ratios. The major disadvantages of this method are (1) that acetylene must be prepared from the carbon-containing sample and (2) that the sample of acetylene is destroyed by the analysis. These disadvantages can be lessened by the following modifications of the procedures described above.

In actual application of the method, the carbon in the compound to be analyzed can be oxidized to CO_2. The CO_2 can then be converted to acetylene by the method of Monat and Robbins [8] with 98 per cent yield. This is a simple procedure and can be used for the preparation of acetylene from any carbon-containing substance.

To reduce the size of sample required for burning, the acetylene-C^{13} can be diluted with ordinary acetylene, remembering that the natural abundance of C^{13} is 1.1 atom per cent. The extent of dilution possible will depend upon the optical instrumentation used and upon the accuracy desired. In addition, the dead space in the burner assembly can be reduced and the rate of burning might also be decreased. It should be possible, with care, to reduce the total sample to less than 10 cc of acetylene.

The results reported here do not give basis for a reliable estimate of the accuracy possible with this method. In the determination of

hydrogen isotope ratios, using the same instrument, a precision of 0.1 per cent in the ratio of two intensities was obtained [1]. This may be taken at present, with the instrument used, as a lower limit to the precision which can be acheived in such measurements under optimum conditions.

The technique described here does not compare favorably with the mass spectrometric method in regard to the time required for sample preparation (preparation of C_2H_2 instead of CO_2), size of sample used (10 cc as compared to 0.1 cc) and in the stage of development of the procedure. However, it may be found useful, especially in laboratories which do not have access to a mass spectrometer, but which are equipped with an optical spectrometer of moderate resolving power.

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Figure Lengend

Figure 1. Burner assembly

Figure 2. Recordings of the 1, 0 band heads ($^3\pi - {}^3\pi$ transition) of C_2 in an acetylene-air flame.
A, acetylene - C^{13}, 22.9 atom per cent C^{13}.
B, acetylene - C^{13}, 6.3 atom per cent C^{13}.
C, ordinary tank acetylene.

Figure 3. Plot of observed $C^{12}C^{13}/C^{12}C^{12}$ band head intensity ratios against C^{13} abundance in atom per cent.

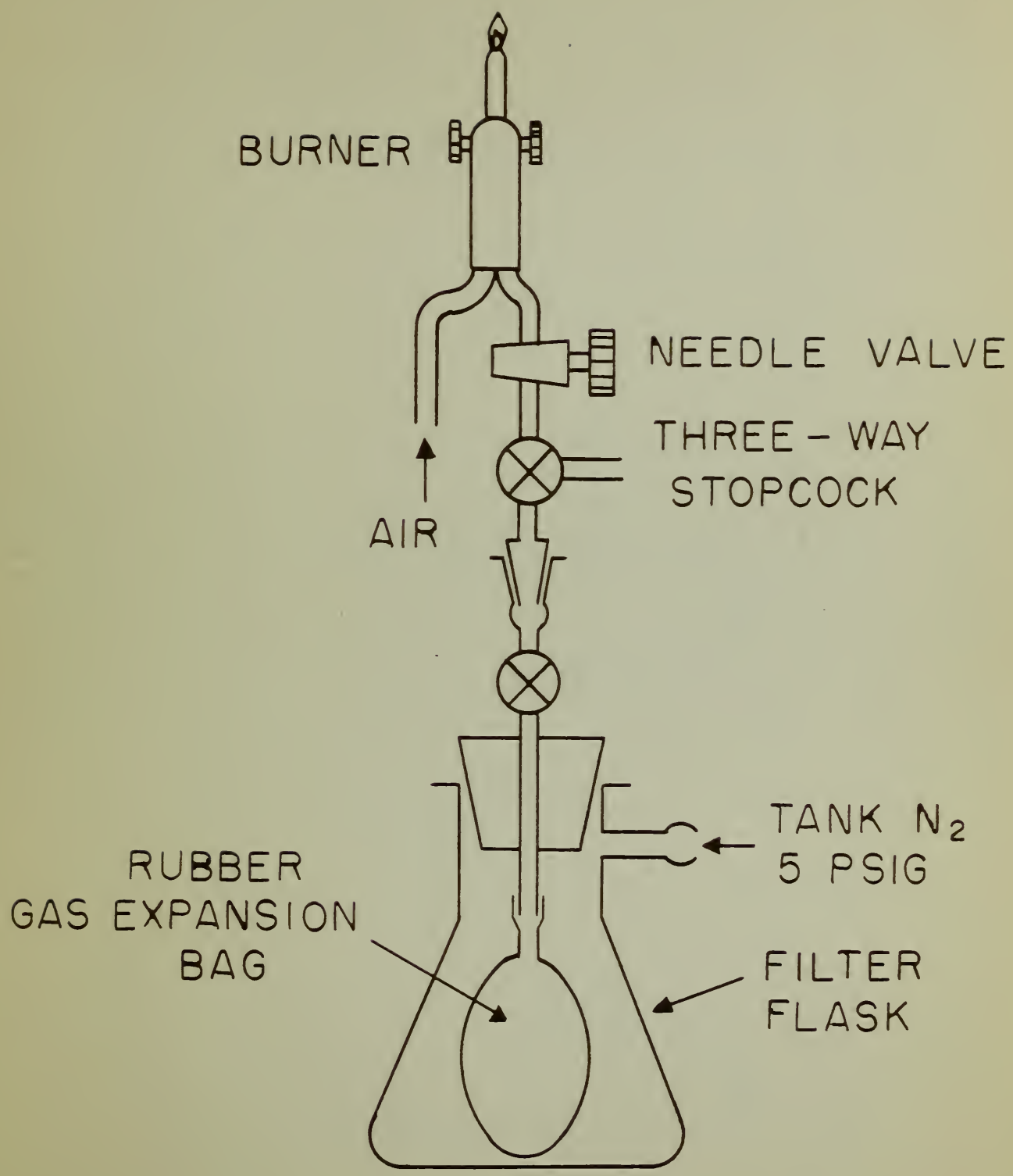
BURNER
NEEDLE VALVE
THREE - WAY
STOPCOCK
AIR
TANK N_2
5 PSIG
RUBBER
GAS EXPANSION
BAG
FILTER
FLASK

FIGURE 1

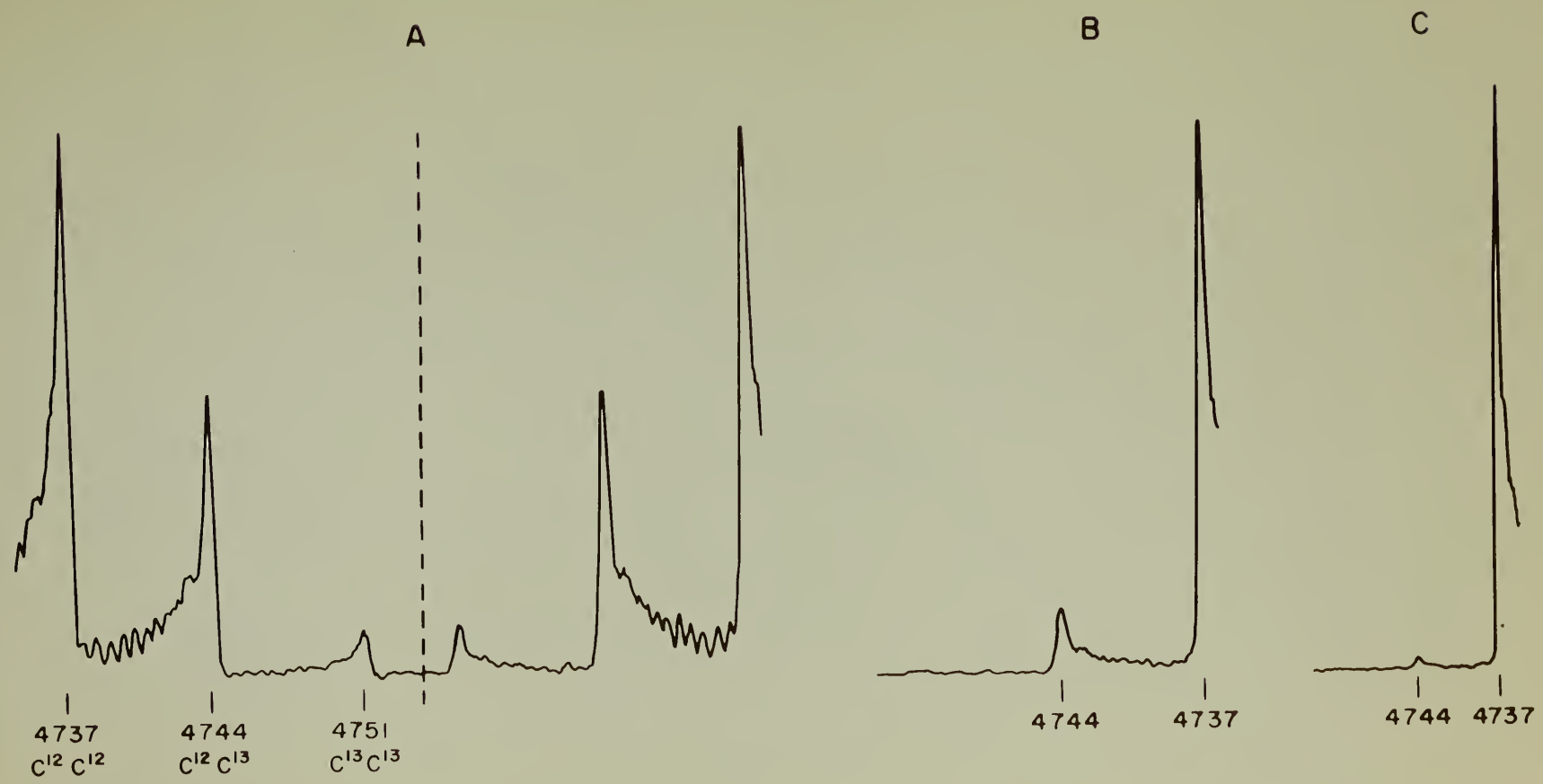

FIGURE 2

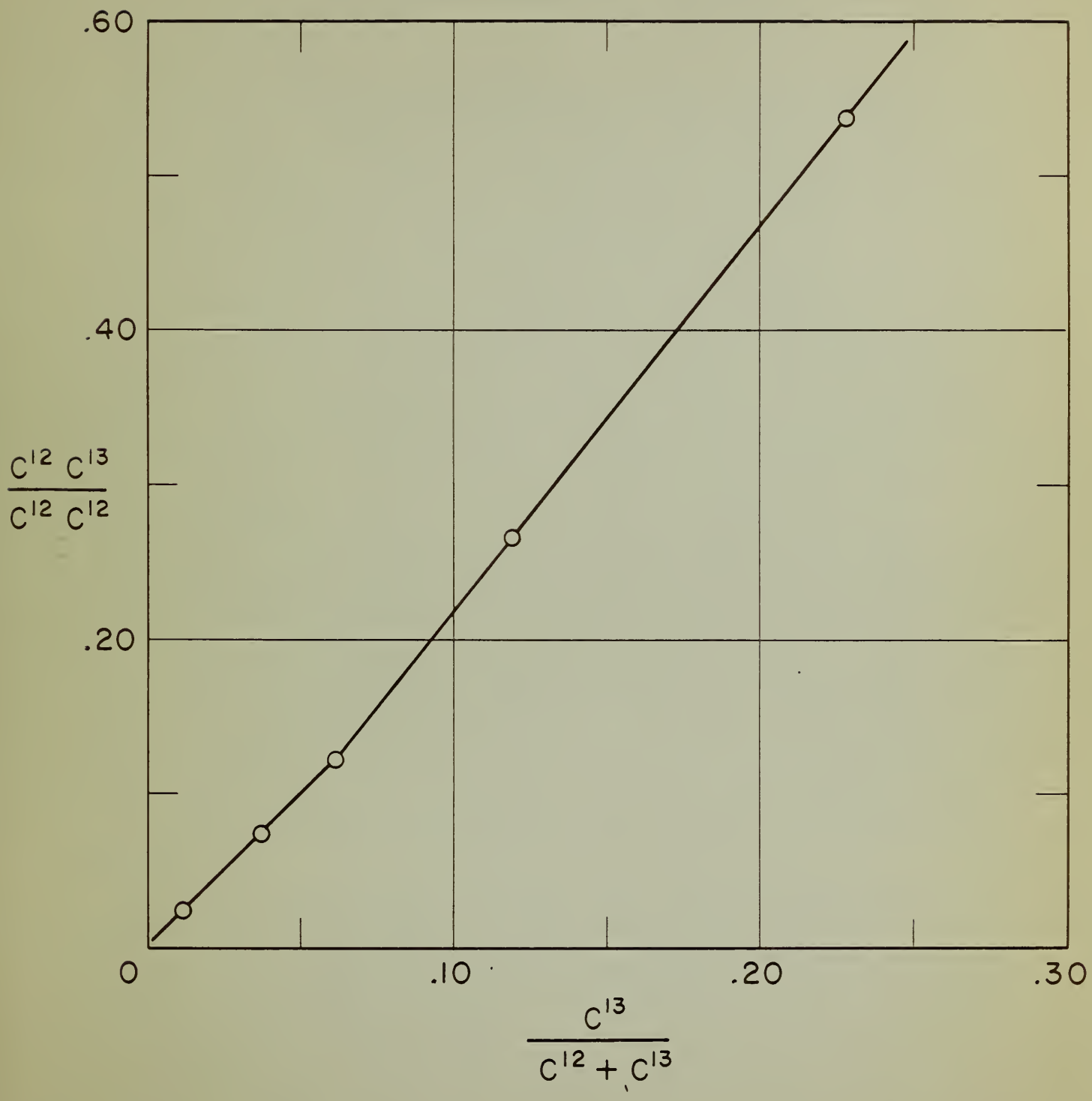

FIGURE 3

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