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Hydrogen Content Analysis

Short Title of Document or Addressee of Letter

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NUCLEAR PHYSICS INVESTIGATIONS

J. R. Dunning -- Director of Research

IMPROVED TECHNIQUE OF HYDROGEN CONTENT ANALYSIS BY SLOW NEUTRON SCATTERING

By

L. J. Rainwater
W. W. Havens, Jr.

Photostat Price $ 3.30
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ABSTRACT

The slow neutron transmission method of determining the hydrogen content of fluorocarbons depends on the fact that the slow neutron cross section of Hydrogen is much greater than the slow neutron cross section of Fluorine and Carbon. Replacing 1% of the F atoms by H atoms gives about a 10% change in neutron transmission for samples of the proper thickness. Improved accuracy and stability of the method has been achieved by using approximately monochromatic neutrons from the Columbia University Neutron Beam Spectrometer.

The neutron analysis method is simple, straightforward, requiring little time and no operations on the sample. The method is capable of giving answers to about 2 H atoms per 1000 (H + F) atoms for low H content samples. Controlled neutron energy is important because of the energy dependence of the hydrogen cross section.

A comparison of the results of this method with the results of McBee's pyrolytic method for 23 of the samples shows that the agreement of 14 of the 23 samples is within the experimental error. There seems to be a close correlation between the density and the specific refraction of a sample with its hydrogen content. There also seems to be some lesser correlation between the fluorescence, the sample and the hydrogen content.

INTRODUCTION

A previous paper (A-1212)[1] was issued October 1943, describing the results of the preliminary studies made at that time on the neutron analysis method for H content. This paper developed the theory of the method in detail and discussed the practical factors involved. Since then the procedure and apparatus used have been considerably modified and the effectiveness and reproducibility of the method improved. Routine analyses of fluorocarbon samples are now being made and it is the purpose of this paper to describe some of the changes in procedure and the more recent measurements.

THEORY

The principle employed may be explained briefly as follows: a collimated beam of slow neutrons is produced by using a cyclotron, suitable paraffin slabs and B_4C-Cd collimating tubes. Material placed in the beam will scatter the slow neutrons and reduce the intensity of the transmitted beam in an exponential fashion similar to the transmission of light or x-rays through an absorbing medium. If I_o represents the initial beam intensity and I represents the beam intensity after passing through the sample, then $I/I_o = e^{-A}$ where A is the absorption coefficient of the sample. If the sample is composed of several components (1, 2, 3, etc.), then the absorption coefficient is the sum of terms representing the effects of the separate components. If ρ_i represents the amount of material in the beam in gm/cm^2 of the ith component and K_i

(1) A-1212, Burger, L. L. and Rainwater, L. J., "Determination of ~~Hydrogen~~ 1R-392, 1.6-6, 10/21/43.

represents the mass absorption coefficient in cm^2/gm of the ith component, then $A = P_1K_1 + P_2K_2 + ---$, if the material is uniformly distributed over the area of the beam.

In practice measurements are made with the fluorocarbon materials in copper containers to give about 4 cm. thickness of oil in the beam. The transmission of a standard fluorocarbon sample is measured by alternating measurements with the standard in the beam and a blank holder in the beam. Considering only the ratio of the two intensities eliminates the effect of the holder and the value of K_{st} for the standard fluorocarbon oil is determined. By using a hydrocarbon material it is possible in a similar way to obtain a value of K_{CH_2} for a material of the type $(CH_2)_n$. An impure fluorocarbon may then, to a close approximation, be considered equivalent to a mixture of the standard material and a hydrocarbon oil.

In order to express the magnitude of the effect we have considered the pure fluorocarbon oil to be of the form $(CF_2)_n$. If n is arbitrarily set equal to 500, this becomes $C_{500}F_{1000}$. Replacing a certain number, α, of the 1000 F atoms by H atoms changes this to $C_{500}F_{(1000-\alpha)}H_{\alpha}$. The results of these measurements are usually expressed by giving the value of α which is equal to the H atoms per 1000 (H + F) atoms.

Since the cross section of a CH_2 molecule for slow neutrons is about ten times the cross section of a CF_2 molecule (the exact factor depends on the neutron energy), replacing 1% of the F atoms by H atoms gives about a 10% change in the cross section. If the total transmission of the standard oil is about e^{-1}, then the ratio of the intensity with

sample in the beam to the intensity with the standard in the beam (corrected to the basis of equal gm/cm^2) will be about 0.90 or a 10% effect in transmission.

METHOD OF CALCULATING THE HYDORGEN CONTENT OF AN UNKNOWN FLUOROCARBON OIL

1. The densities of the standard and of unknown samples of fluorocarbon oils are measured and the cell thickness determined to give the values of ρ for the standard and the samples.

2. Transmission measurements are made alternating the standard and a blank holder in the beam to obtain the value T_{st} = transmission of the standard material. From this $K_{st} = \left(\frac{-\log T}{\rho}\right)_{st}$ is calculated.

3. Transmission measurements are made alternating the standard and a sample in the beam to obtain $\left(\frac{T_{sa}}{T_{st}}\right)$. Multiplying by T_{st} gives T_{sa} and the values of $K_{sa} = \left(\frac{-\log T}{\rho}\right)$ is calculated.

4. With the standard always in the beam a thickness of hydrocarbon material is alternated in and out of the beam. The value

$$K_{CH_2} = \left(\frac{-\log T}{\rho}\right)_{CH_2}$$

is calculated from the transmission measurement.

5. From K_{st}, K_{CH_2}, and K_{sa} the value of α, which gives the number of CH_2 molecules present for $(1000 - \alpha)$ CF_2 molecules, can be computed for

$$\left[M_{CF_2}(1000 - \alpha) + M_{CH_2}\alpha\right]K_{sa} = M_{CF_2}(1000 - \alpha)K_{st} + M_{CH_2}\alpha K_{CH_2}$$

where the M's are the molecular weights of the substances.

In practice it has been found more convenient to introduce the experimentally determined quantity $R = (K_{sa} - K_{st})/K_{st}$ and solve for α in terms of R and the other experimentally determined parameters. After carrying through the algebra the final result is given by

$$\alpha = \frac{1000\ R\ K_{st}}{\left[0.28\ (K_{CH_2} - K_{st}) + 0.72\ R\ K_{st}\right]}$$

Since K_{CH_2} and K_{st} have been found to be constant when using monochromatic neutrons, a plot of α vs R has been made and the value of α is determined for a specified value of R from the graph (See Figure 1).

It should be emphasized that α is a value determined relative to the standard oil used. If the standard oil contains hydrogen, the difference between the standard and the sample is what is measured.

NEUTRON ENERGY DISTRIBUTION AND NEUTRON DETECTION

The neutrons used for these measurements are produced in the cyclotron by bombarding a Be target with deuterons. This produces fast neutrons which are slowed in a paraffin "source" slab to give an effective source energy distribution containing all energies from the thermal region (average 0.04 e.v.) to the fast neutron energies. When a BF_3 proportional counter is used as detector about 90% of the counting rate is due to neutrons removed by Cd (energies below about 0.5 e.v.) while 10% is due to slow neutrons of higher energies. The shape of the distribution in the region of thermal energies, as well as the ratio of counts with and without Cd, depends on the thickness of the paraffin, the direction of the incident fast neutron radiation, and several other factors. In the early

measurements (see report A-1212) the entire distribution of neutrons was used to minimize the number of measurements and the time required to obtain a given statistical accuracy of counting. Measurements using just that portion of the neutron distribution removed by Cd (below 0.5 e.v.) were usually not made as twice as many separate measurements are required to obtain a given answer and the length of each count for a given overall statistical accuracy is increased.

In order to account for fluctuation and changes in the cyclotron intensity a second slow neutron counter is used as a monitor. This is placed in a position where the counting rate is proportional to the cyclotron intensity but will not be affected by the presence of samples placed in the collimated slow neutron beam. The ratio of detector to monitor counts then corresponds to detector counts per unit time for a source of constant intensity.

Using the entire neutron distribution from the source slab has the following disadvantages:

1. The hydrogen cross section is dependent on the neutron energy and increases with decreasing energy. Since the shape of this distribution is not easily reproducible and is not stable over a period of time, the values of K_{st} and K_{CH_2} are not very reproducible.

2. In passing through a sample, the "soft" (low energy) radiation is more rapidly removed than the "hard" components so the quality of the radiation reaching the detector is dependent on the absorber. This means that the effective K values will depend strongly on the nature and thickness of the material in the beam.

3. The ratio (K_{CH_2}/K_{st}) will be much smaller for the complete distribution than for thermal energy neutrons alone.

VELOCITY SELECTOR METHOD

It is evident from the above discussion that the ideal method of measurement would use monochromatic neutrons of low energy to obtain reproducible values for the K_s and as large a value as possible for the ratio (K_{CH_2}/K_{st}). Since a slow neutron velocity spectrometer system has been developed at Columbia in connection with other work it has seemed desirable to use it for these measurements.

The principle of operation of this device is as follows: The cyclotron arc is normally kept off but is turned on for an interval of T_1 microseconds once in every cycle of T microseconds. Within a few microseconds of this burst the deuterons are accelerated to strike the Be target and the fast neutrons given off, reach the paraffin slab, are slowed down and leave the front of the paraffin slab with the energy distribution discussed above for continuous operation. Thus a burst of slow neutrons emerges from the paraffin slab almost simultaneous with the arc pulse. The slow neutron detector, situated at a distance (5.8 meters) from the paraffin slab, is made normally insensitive over most of the cycle except for an interval of duration, T_2, at a time, t, after the arc pulse. The slow neutrons detected must have the velocity $v = l/t$ and will thus be of known energy. For the purpose of these measurements, a value of $T_1 = 200$ microseconds, $T_2 = 800$ microseconds and $T = 3000$ microseconds has been chosen. Measurements were made using widely different timings, t, to see if the same results could be obtained using widely different

neutron energies. It was found that the agreement between measurements using different energy monochromatic neutrons always gave the same results within the accuracy of the measurement even though K_{CH_2} differed by a factor of 3 in the extreme measurements.

Since K_{st} is almost independent of the energy over a wide range, the sensitivity of the method will be proportional to K_{CH_2} and it is much better to use low energy neutrons. The measurements have now been standardized to use a timing of 2300 microseconds between the centers of the arc and the detector modulation intervals. Although the distribution obtained is not strictly monochromatic, it is nearly enough so to be quite reproducible and the quality of the beam remains essentially unchanged in passing through the sample.

EFFECT OF A DIFFERENT C-F RATIO

Since the cross section of F is smaller than that for C and its atomic weight is greater, there is a change in K_{sa} produced by changing the C-F ratio as well as by changing the H content. This effect should be unimportant for oils made by similar processes but should be mentioned for completeness. For an increase in the F/C ratio of 0.10 the effect is the same as for a decrease in H content of one H atom per 1000 (H + F) atoms. Thus the results are a factor of 50 less sensitive to a change in the F ratio than to the H ratio.

SAMPLE MATERIALS

The material tested was largely regular C-2144 production by both liquid phase and vapor phase methods. Measurements on these samples were made as part of a testing program for The Kellex Corporation and for U.S.E.D. In addition, several special samples were tested including some for Dr. Burford in connection with the retreatment studies made at Johns Hopkins University.

GD-1336 and GD-1337 were prepared from GD-1335 (Lot 39) by treatment with AgF_2.

JHL-M, -N, -A2, -B2 were prepared from Lot 45. The former two by treatment with 20% F_2, while A2 and B2 were reacted with F_2 in the presence of CoF_3.

JHL-C2 was prepared in the same manner except that the starting material was Lot 44.

Lot 3-1, Drum 9, was a C-816 sample which had been found to react with C-616 causing plugging of barrier. Subsequent chemical analysis showed sufficient water present (0.011% by wt.) to account for the plugging. This quantity would not contribute significantly to the observed hydrogen content.

The reference material for the samples in the latter part of the table was GD-903. This was an early vapor phase product which had been retreated with CoF_3. This was known to be low in hydrogen content and for these measurements it was assumed that this material was pure $(CF_2)_n$. The earlier standard contained some GD-902 which was shown to be nearly identical. As the results given by the neutron method indicate

only a difference in hydrogen content, it should be emphasized that values reported are relative to GD-903. If GD-903 contains hydrogen, then the values reported will be low by this amount.

Density measurements were required for calculation of hydrogen values. These measurements were made by Division III of SAM using a 25 cc. pycnometer at 25.0° C. and should be accurate to about 0.1%. Division III of SAM also cooperated in this work by taking care of the samples and changing samples in the holders. The neutron measurements were made by the Columbia University group using the cyclotron and the associated Neutron Velocity Selector equipment.

RESULTS

The results are summarized in the Table. Column I lists the oil sample and the method of preparation. (V = vapor phase, L = liquid phase.) Column 3 gives $\mathcal{L}$ = H atoms per 1000 (H + F) atoms. (On this scale a pure fluorocarbon has $\mathcal{L}$ = 0 while a pure hydrocarbon has $\mathcal{L}$ = 1000.) This number times 0.044 would be the average number of H atoms per molecule if the molecular size is taken as $C_{22}F_{44}$. Negative values indicate less hydrogen than the standard, GD-903. If there is a greatly different C-F ratio, a small effect may be due to this. Column 4 is calculated directly from $\mathcal{L}$ on the assumption that the atom ratio is of the form $(C_{500}F_{(1000-\mathcal{L})}H_{\mathcal{L}})$.

The remaining columns list other significant analytical constants for the oils. Columns 5 and 6 list the specific refraction and the relative fluorescence of the oils as determined[2] by SAM Division

(2) D-R40, Burger, L. L., "Rapid Determination of Hydrogen," 4/9/45.

III. Column 6 gives the % H by weight obtained by Dr. McBee's pyrolytic method. Values followed by p were reported by Purdue and those followed by d by duPont using the Purdue apparatus. Samples of the other oils tested were sent to duPont but the results were not available here at this writing.

For the measurement of most of the samples a standardized technique has been used and a single calibration curve has been found to be suitable. The following values have been determined for these conditions:

$$K_{st} = 0.1492 \text{ cm}^2/\text{gm}$$

$$K_{CH_2} = 4.80 \text{ cm}^2/\text{gm}$$

$$\mathcal{L} = \frac{1389 \text{ R}}{(12.13 + \text{R})}$$

For the value $\mathcal{L} = 80$ which is the order of magnitude of most of the liquid phase samples, the slow neutron transmission of the sample is less than half that for the standard. The changes observed were thus changes of a <u>factor</u> of 2 or 3 rather than a few per cent. For $\mathcal{L} = 10$ (average for the vapor phase production) the effect is about 10%.

In Figure 2 the density is plotted against the value of the H content from these measurements. Figures 3 and 4 similarly plot the specific refractivity and fluorescence as functions of the H content. These curves are given for comparison. A more complete description of this work is given in reference 2.

DISCUSSION

Data on viscosity, vapor pressure, and H_2O content were obtained from The Kellex Corporation Laboratories for a number of the samples. Plots of these quantities vs. H content showed no correlation, however, and were discontinued. The C-616 residue test likewise showed no correlation. Actual residue tests show $<$ 0.001 gm. TF_4 per gm. of oil whereas the value, for $\alpha = 110$, would be 1.6 gm. TF_4 per gm. of oil for a complete reaction.

From Figure 2 it can be seen that, for oils produced by a standard process, density is a fairly reliable indication of the H content. Those oils manufactured by the vapor phase method have a somewhat higher density as well as consistently lower values for the H content. To show the magnitude of the density change to be expected from simple considerations a calculation was made assuming a simple mixture of $(1000 - \alpha)$ molecules of $(CF_2)_n$ for α molecules of $(CH_2)_n$. The separate densities are taken as 2.05 gm/cm^2 and 0.80 gm/cm^2, respectively. The dotted line gives the predicted slope which agrees reasonably well with the effective slope of the points. The extreme disagreement between the standard, GD-903, and the retreated sample, JHL-B2, indicates the degree to which materials receiving widely different treatments with about the same H content can vary in density.

In Figure 3 specific refraction is plotted against H content. Theoretically this should give good correlation and it is seen that the points in this plot come closest to falling along a straight line. The dashed lines are theoretical lines showing the agreement of the measured

and predicted slopes. The results for the vapor phase oils fall nearly into line in this plot. JHL-M, JHL-N and JHL-A2 appear to have allow specific refraction. This might be explained by the presence of HF which was detected in these samples but not measured quantitatively.

The per cent H by weight determined by McBee's method agrees in most cases with our values. In general our values are slightly higher for those samples containing large amounts of H and slightly lower for material of low H content. On the basis of the assigned error, the agreement is within the experimental error for 14 of 23 samples for which we have data. The time required for analysis of a sample by the neutron method is of course very much less.

dm

TABLE OF RESULTS AND COMPARISONS

Sample	Density 25°C.	$1000\frac{\alpha_H}{H+F}$	% H by Wt.	Specific Refraction	Fluorescence Lot 47 = 100	% H by Wt. Analysis
Std (GD-902 (GD-903	2.075	0.00	0.00	--	--	--
Lot 3-1, Drum 9	1.838	5 ± 4	0.020	--	1	--
GD-1274 L	1.980	55 ± 6	0.23	--	--	0.21
Lot 13 L	1.970	66 ± 6	0.28	--	--	--
22 L	1.970	82 ± 6	0.35	0.1062	86	.315
30 V	2.050	5.5 ± 3	0.022	.1016	27.5	.052
39 L	1.974	82 ± 6	0.35	.1061	93	.35
42 L	1.985	57 ± 6	0.24	.1045	72	.22
44 V	2.045	5 ± 3	0.02	.1018	38	.04
45 L	1.965	85 ± 6	0.36	.1065	98	.36
47 L	1.963	84 ± 6	0.36	.1066	100	.36
49 L	1.999	43 ± 6	0.18	.1033	52.5	.18
50 L	1.987	62 ± 6	0.26	.1049	65	.25
51 L	1.988	60 ± 6	0.25	.1048	69	.25
Std GD-903	2.077	0.00	0.00	0.1025	1	--
Lot 34 V	2.047	4	0.016	.1019	27	--
43 V	2.047	6.1	0.025	.1019	60	0.04 d
46 V	2.038	24	0.10	.1028	46	0.08 d
60 V	2.037	23	0.10	.1032	65	0.11 d, 0.10 d
68 V	2.041	18	0.075	.1025	43.5	--
72 L	1.977	80	0.34	.1057	95	--
74 L	1.971	101	0.44	.1079	112	--
75 L	1.974	88	0.38	.1059	93	--
76 L	1.974	84	0.36	.1059	92	--
77 L	1.983	69	0.29	.1047	80	--
78 L	1.983	67	0.28	.1047	57	0.26 d
79 L	1.973	94	0.41	.1078	112	--
80 L	1.965	97	0.42	.1075	112	0.38 d
81 V	2.040	11	0.046	.1022	54	0.065 d
82 V	2.031	24	0.10	.1024	45	0.07 d
83 L	1.964	104	0.45	.1078	113	0.39 d
84 L	1.961	109	0.48	.1078	124	--
85 L	1.965	99	0.43	.1071	125	--
86 L	1.968	91	0.39	.1069	125	--
89 V	2.039	8	0.032	.1020	--	--
90 V	2.041	10	0.042	.1021	--	--
91 V	2.041	12	0.050	.1022	--	--
92 V	2.046	7	0.030	.1018	--	--
GD 1335 L	1.974	90	0.39	.1061	93.5	--
1336	2.002	33	0.14	.1030	39	0.15
1337	2.002	32	0.13	.1032	29.5	0.12
JHL-M L	1.969	95	0.41	.1062	69	0.34 d
JHL-N L	1.977	78	0.33	.1053	47	0.23 d
JHL-A2 L	1.995	47	0.20	.1030	13.5	--
JHL-B2 L	2.029	-4	-0.014	.1001	3	--
JHL-C2 V	2.054	-3	-0.012	.1010	1	--

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10 × 10 to the ½ inch, 5th lines accented
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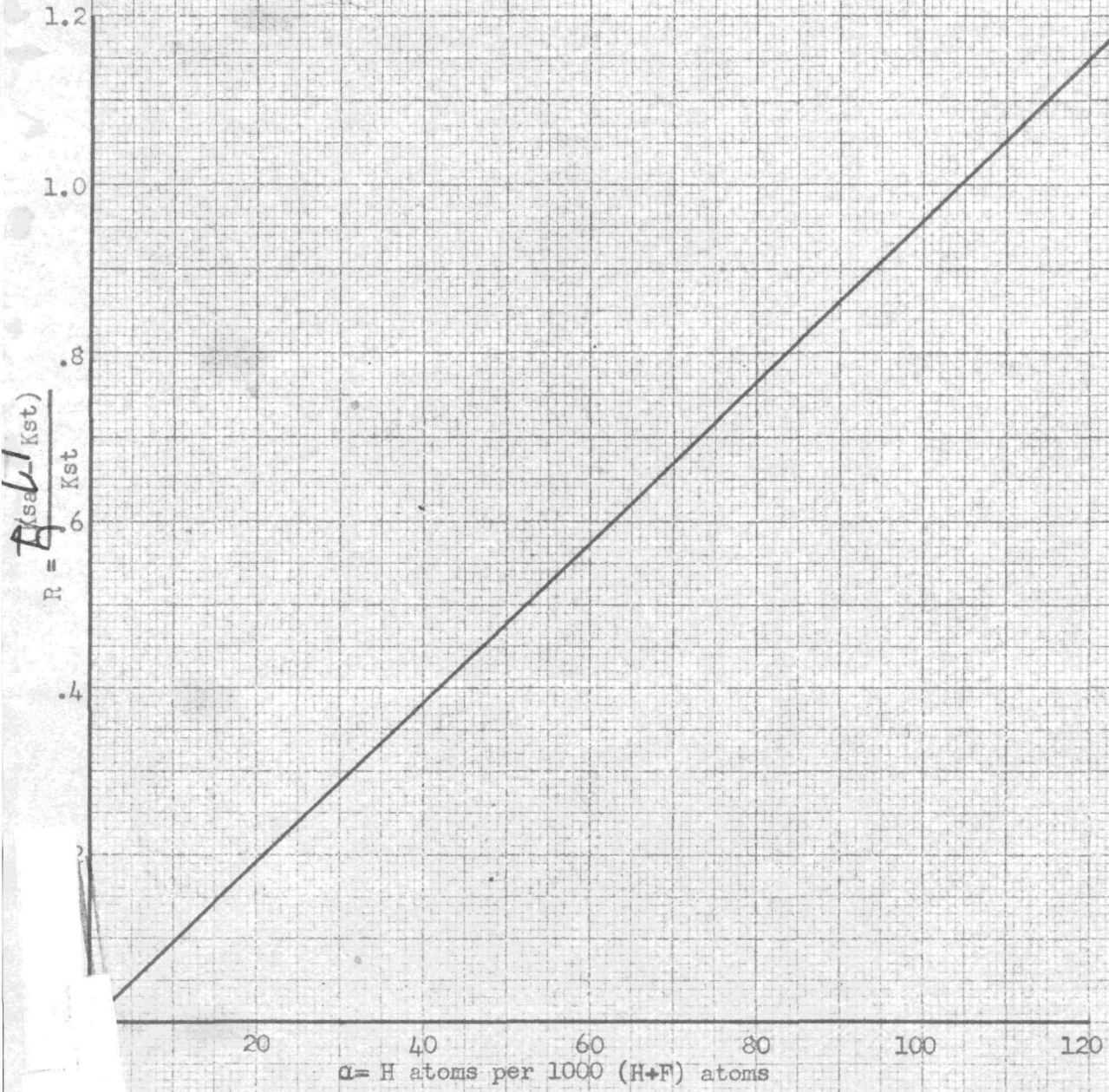
Fig. 1
Flourocarbon Analysis Calibration Curve

α= H atoms per 1000 (H+F) atoms



$$\alpha = \frac{1389R}{(12.13+R)}$$ is formula for the curve

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Fig. 2

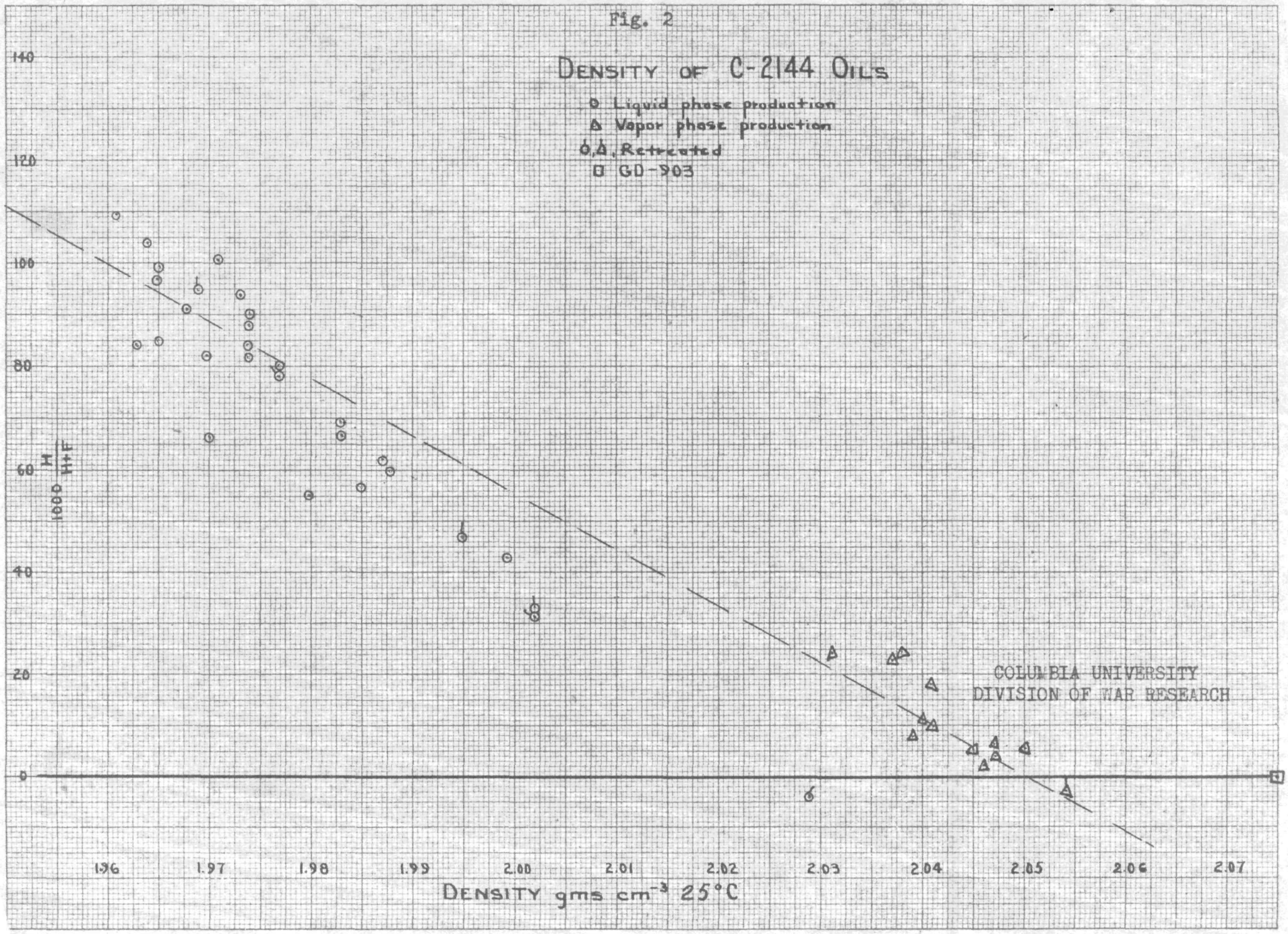

Fig 81

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Fig. 3

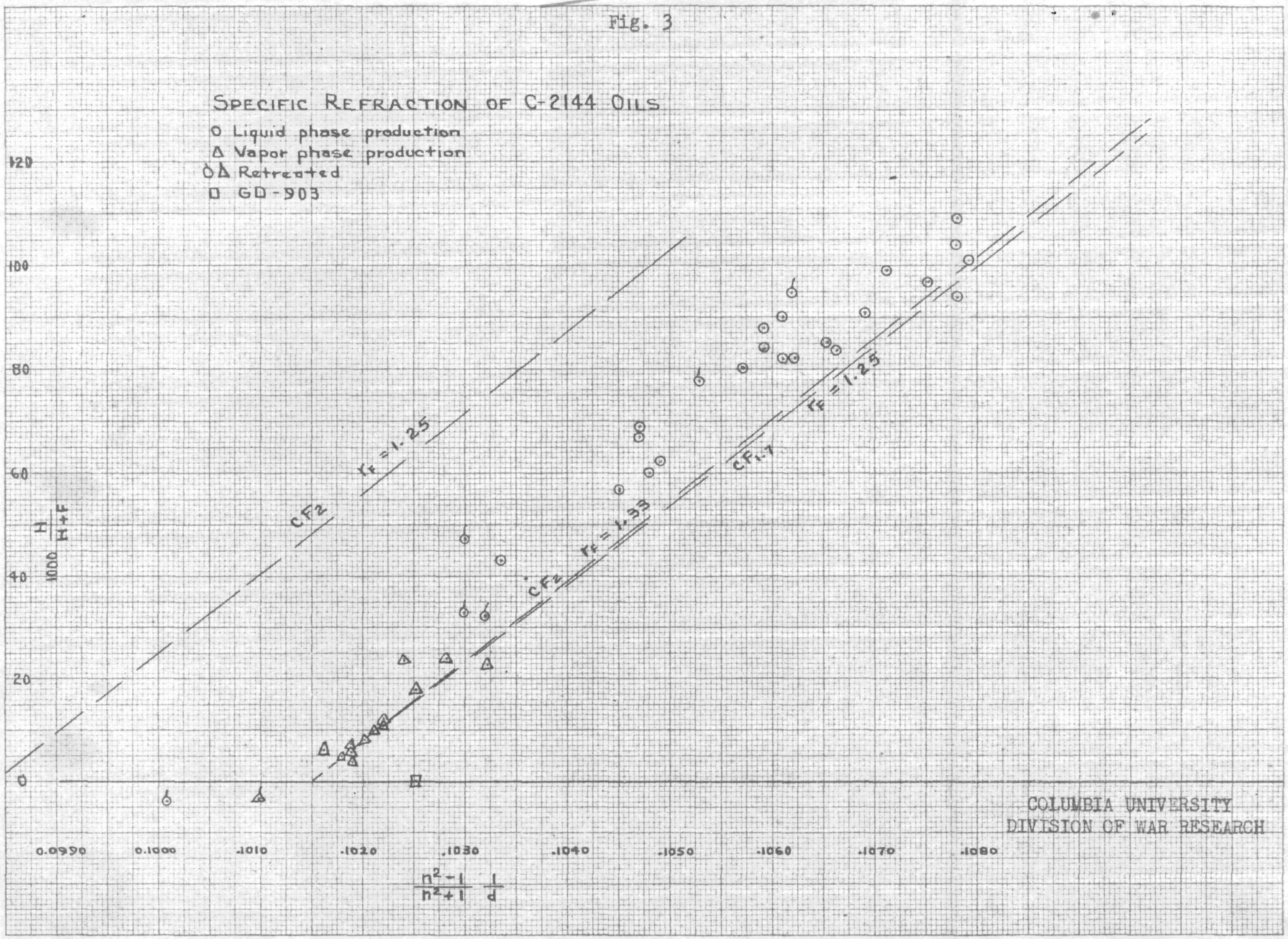

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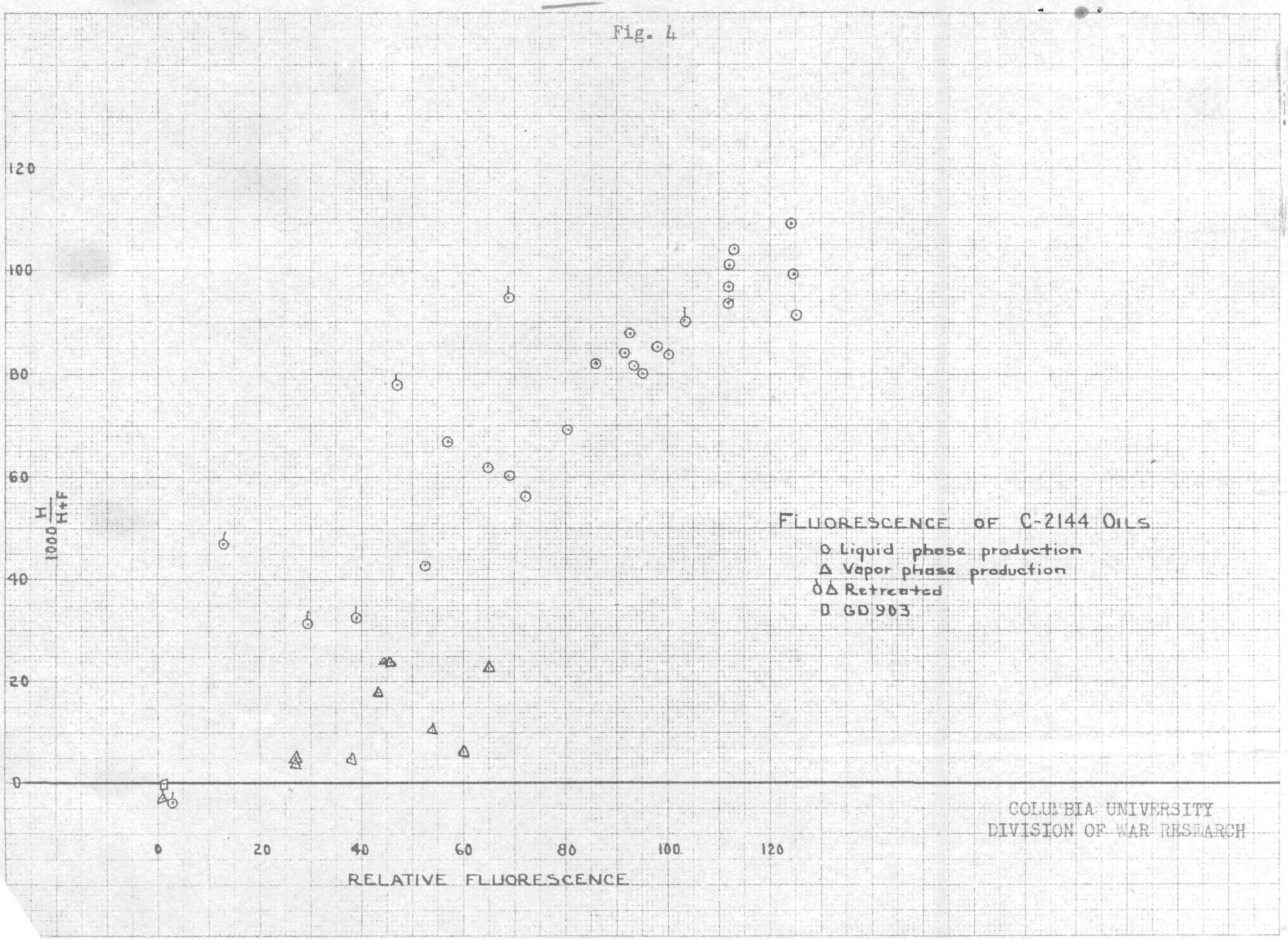
Fig. 4



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