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Mercury Content of Tobacco Products

by

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1971

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ABSTRACT

Mercury contamination of food products results from contact with soil, water, and air polluted with mercury from industrial sources, as well as from the use of mercury-containing pesticides and fungicides on plants. A method was developed for extracting mercury from tobacco products. The mercury content of various tobacco products was determined, using an atomic absorption spectrophotometer.

INTRODUCTION

The purpose of the project was, initially, to prepare and study the properties of carbonyl cyanide. This was abandoned in late January as a result of experimental difficulties encountered. The background, experimental details, and discussion of that project are given in Appendix C of this paper.

In recent months, much public attention has been focused on the problem of mercury pollution contaminating food products. Studies have been conducted to determine the mercury levels in fish,[1] milk,[2,3] poultry,[4] and water.[5] Mercury can be ingested, inhaled,[6] or absorbed through the skin,[7] and finds its way into various organs, particularly the brain,[6] kidneys,[5] and liver.[8]

Once in the body, ionic mercury precipitates all proteins with which it comes into contact. A large quantity of an active mercury compound ingested at one time will cause rapid death. Small quantities of mercury inhaled or otherwise incorporated into the body over a long period of time will result in chronic mercury poisoning. The early symptoms of this chronic poisoning include fatigue, loss of appetite, headache, irritability, nervousness, inflammation of the eyes, toothache, and soreness of the gums.[9] Removal of the victim from the source of mercury usually results in a slow reversal of the ill effects, and eventually, full recovery. Continued exposure will intensify the symptoms, adding tremors, numbness in the arms and legs, loss of muscular coordination, loss of memory, loss of auditory and olfactory senses, and emotional disturbance.[10] The use of mercury compounds in the haberdashery industry, long unrecognized as a serious problem, led to the mass poisoning of the "mad hatters" of Minemata.[11]

The relative toxicity of the mercury compound depends on the relative ease of formation of the mercuric ion. Thus mercuric chloride is highly toxic, while some organic mercurials, such as those used in antiseptics, are quite harmless in reasonable quantities.[7]

Industrial pollution has been cited as a major source of mercury contamination. Less well known as a possible source is the use of mercury-containing pesticides and fungicides on a variety of crops, including tobacco.[12, 13, 14, 15]

A recent Japanese study[16] determined the mercury content of cigarettes by neutron activation analysis. These researchers found the mercury content to vary from 0.09-1.3 parts per million (ppm). The tests did not include any American brands.

During the past year, the mercury problem has received what may be a disproportionate amount of public anxiety. True, mercury contamination may represent a serious health hazard. But as yet, authorities cannot even agree on what the "safe" amount of mercury in food products is. The United States government has set an arbitrary value at 0.5 ppm, ten times the amount allowed by the World Health Organization, the medical branch of the United Nations.[17] This in itself emphasizes the need for further investigation before any meaningful standards can be established. While this is being investigated, it is well to consider the possibility that there have always been relatively high concentrations of mercury in food products, and that only recently have technological advances enabled easy detection of such quantities as are present.

One such advance is the atomic absorption spectrophotometer. This instrument is capable of detecting trace amounts of various elements rapidly and accurately. The basic principles of atomic absorption spectrophotometry can be simply stated. Light of wavelength equivalent to the energy required to raise an atom from its low energy level to higher levels will be absorbed by the atom. A sample is aspirated into a flame, where it is atomized. Light of a preselected wavelength is focused through the vapor. A detector on the other side of the flame, opposite the light source, monitors the absorption of the light. The absorbance of a particular sample is proportional to the amount of the element being determined in the sample. By testing a series of samples of known concentration of the element in question, it is possible to arrive at a concentration/absorbance calibration curve.[18, 19] The absorbance of the unknown sample is plotted on this curve to obtain its mercury concentration. Once the unknown samples and calibration standards are prepared, the testing takes only minutes, and the method is extremely sensitive. The Colby instrument (Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer) is capable of detecting mercury in concentrations as low as 0.5 ppm.

The availability of this technique, and the intriguing results of the Japanese study, suggested the idea of testing American tobacco products for relative mercury content.

EXPERIMENTAL

Several of the pesticides and fungicides containing mercury are soluble in benzene. For the first attempt at extracting the mercury, tobacco was refluxed with benzene, the resulting mixture filtered and tested with the spectrophotometer. This proved impracticable. The benzene mixture burned with too hot a flame. The flame temperature quickly rose so high that there was some danger of melting the ventilation hood of the spectrophotometer. Readjusting the aspiration rate to compensate for the effect of the burning benzene could not be accomplished without disassembling and readjusting the entire aspirator-nebulizer mechanism. Since other members of the department were using the instrument intermittantly, this was impossible. The benzene extraction was subsequently eliminated.

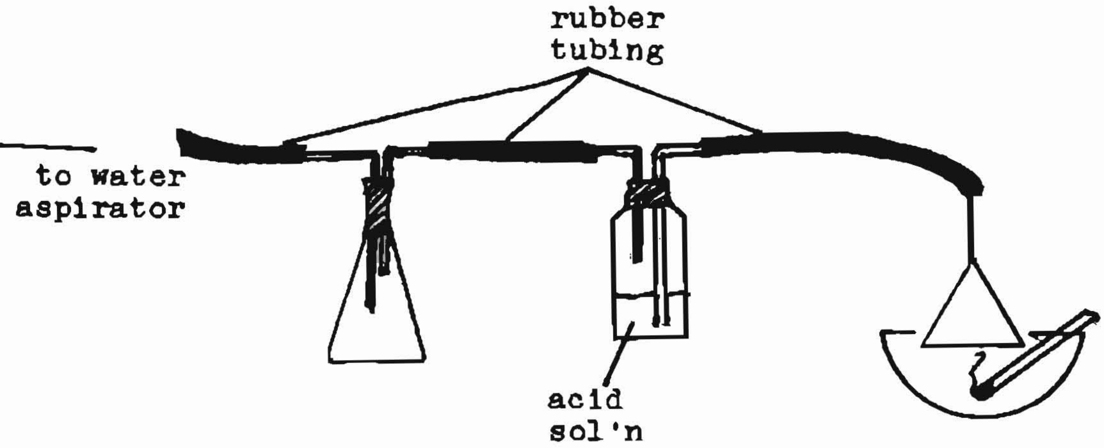
In the next procedure attempted, the tobacco was boiled with concentrated nitric acid, approximately 30 ml for two cigarettes. The acid solution was neutralized with sodium hydroxide, and this solution filtered and tested on the spectrophotometer. On the first attempt at analysis, the salts quickly clogged the burner head; the flame temperature was not sufficiently high to vaporize the sodium nitrate.

Attempts were made to remove the interfering salts by selective dissolution. According to the Handbook,[20] sodium nitrate, but not the mercury salts, should be soluble in alcohol. In practice, the solubility was insufficient to effect the desired separation. About this time we began to suspect that the water soluble residues from the decomposition of the tobacco would clog the burner as much as had the sodium salt. Consequently, attention was switched to trying to extract the mercury salt while leaving the sodium salt and residue in water solution.

Shaking the solution of water, sodium nitrate, and mercuric nitrate with diethyl ether caused the white mercury salt to turn yellow, while leaving the sodium nitrate unaffected. The yellow salt was found to be insoluble in water and only slightly soluble in ether. This salt resembled mercurous nitrate in color and solubility, and was assumed to be the reduced salt of the original mercury compound. The yellow salt was combined with hydrogen peroxide in an attempt to oxidize it to the water soluble compound. The mixture was gently refluxed. Some reaction appeared to be taking place, generating gas bubbles. This reaction proved extremely temperamental and quickly built up sufficient pressure to blow off the top of the condenser if overheated slightly. Even when the temperature was maintained at a level sufficient to permit a reaction without exploding, several hours' reaction time did not alter the properties of the salt; it remained insoluble in water.

In the third attempt, the cigarettes were burned. The smoke was drawn off through an aspirator and dissolved in water. The ash was refluxed with dilute (2%) nitric acid, and diluted to twice its initial volume. Both solutions were tested with the spectrophotometer. The results of this test constitute Sample Set A. Appreciable mercury was found in the ash solution (B), and measurable mercury was found in the smoke solution (C). The combined total exceeded the amount of mercury found when two cigarettes of the same brand were refluxed with dilute nitric acid, filtered, and this solution tested. Apparently, the method of burning the cigarettes was more efficient in extracting mercury than was decomposing the unburned tobacco. Further, the ashing method was much more rapid. In accordance with these results, the following method was established for further mercury extractions:

The tobacco product was burned, the smoke drawn off through an aspirator and bubbled through 25 ml of 2% nitric acid solution. The aspirator apparatus consisted of a funnel inverted over the burning tobacco; the funnel was connected via a short piece of rubber tubing to a glass tube which led below the surface of the acid solution. The flask containing the acid solution was connected through a trap to a water aspirator (see diagram).



When combustion was complete, the ash was combined with the smoke/acid solution. The aspirator apparatus was rinsed with two 5-ml portions of deionized water, and this water was added to the nitric acid solution. The solution was refluxed gently on a steam bath for two hours, cooled to room temperature, and filtered. The reaction flask and residue were rinsed with three 5-ml portions of deionized water. This brought the total volume of the solution to 50 ml. This solution was tested with the spectrophotometer. The standard solutions used to calibrate the instrument were prepared daily from a 1000 microgram (ug) solution. The wash water and solutions used were prepared from deionized distilled water. All glassware and sample bottles were cleaned daily by washing with detergent and with boiling nitric acid, rinsing with distilled water and deionized water, and drying in air. The aspirator apparatus was cleaned between determinations by washing with detergent solution and rinsing with acetone, which removed all visible traces of smoke residue.

As the smoke was bubbled through the nitric acid solution, the solution invariably turned red in color. Addition of the ash and refluxing caused the solution to turn brown. Filtration and dilution lightened the color to tan. The solution of ash without smoke (Sample Set A, Sample B) was colorless. Upon aspiration in the spectrophotometer, all samples (including B, above) caused the flame to burn bright orange, a color change generally associated with the presence of carbon in the sample.

RESULTS

Three sets of samples were run in this manner. The results of the tests appear in tabular form in Appendix A and in graphical form in Appendix B. To obtain the graphs in Appendix B, the % absorption, as read on the spectrophotometer, was converted to absorbance using the tables that accompany the instrument. The absorbance was plotted against amount of mercury present in the sample. Since this was difficult to read for the unknowns in the first set of graphs, the region 0-10 ug mercury was expanded on the second set, and the mercury content of the unknowns read from this set.

Except as noted, two cigarettes were used for each test. The volume of the test solution was twice that of the calibration standard. Therefore, the amount of mercury per cigarette can be read directly from the graphs. The mercury content of the cigar tested is computed in ppm relative to the cigar weight. The pipe tobacco samples (Sample Set D, Samples C and D) consisted of pipe tobacco rolled into cigarettes. The mercury content in ppm is computed on the basis of the weight of tobacco used, weighed as received.

DISCUSSION

The results obtained may be considered to be correct relative to each other, but only approximately objectively "true" values, since there are several sources of possible experimental error. The aspirator apparatus was not as efficient as it ideally might have been. Despite the rinsing with water, some of the smoke (and presumably the mercury) was retained by the walls of the rubber and glass tubing. This could be dislodged only by washing with detergent solution and acetone. In view of the limited time available to make the tests (the method of extraction was resolved late in the semester), excessive rinsing with water and subsequent evaporation of the excess water did not seem a practical means of increasing the accuracy of the experiment. Had more time been available, a more suitable aspirator apparatus might have been devised. Shortening the tubing between funnel and acid bath, and thereby decreasing the surface area for the smoke to adhere to, would improve the accuracy. Not all of the smoke dissolved in the acid solution. This might be corrected by bubbling the smoke through a long, narrow tube filled with the acid solution, rather than through a shallow solution in a flask.

The testing method was designed to determine the total mercury content of the tobacco product, within the limits being discussed. The nature of the mercury compound present would have to be taken into account to determine the amount likely to be volatilized; some compounds would be more volatile at the temperature of burning tobacco than others, and consequently, would be more likely to add mercury to the smoke. As pointed out in the introduction[7] some mercury compounds are relatively harmless, while others are highly toxic. The nature of the mercury compound present would vary from one field of tobacco to another, with the source of contamination-- pesticides, fungicides, industrial pollution of water or air.

No attempt was made to duplicate human smoking habits. The smoke was not drawn through the filter, which introduced another error: some filters would be more effective in stopping mercury than others. In actual smoking, not all of the smoke would be inhaled, and not all of the mercury inhaled would necessarily be retained in the body. Tests incorporating a smoking machine that closely approximates human smoking habits, combined with test animals to inhale the smoke would give a more accurate estimate of the real danger, if any, from mercury poisoning through smoking.

Obviously a wider range of samples and more tests on each brand would vastly improve the reliability of the data. Reproducibility of results might be expected, judging from the results of the Marlboro tests (Sample Set C, Sample A, and Sample Set D, Samples A, B, and E). Each of these four tests was run on two cigarettes taken from the same pack, but no two tests were on cigarettes from the same pack. The results agree, within experimental error. This is, admittedly, a small sample, and no guarantee that all the results would be reproducible. However, the prognosis for reproducibility is guardedly optimistic.

The efficiency of performing the tests would be greatly improved by the addition of more people in the sample preparation stage. Each set of 4-5 samples required approximately six hours' preparation time, not including preparation of standards. Since mercury has a tendency to become reduced on standing and to plate out on the walls of the containing vessel, all unknown samples and calibration standards had to be prepared and used on the same day; otherwise a significant decrease in the mercury content in solution might have occurred. Considering the preparation time, few samples could be run on any given day. Could more samples be prepared to run with the same set of standards, efficiency and accuracy would both be improved.

The figures obtained are considerably higher than those of the Japanese study. This would seem to indicate a higher level of contamination in American tobacco, from the pesticides and fungicides used, the industrial contamination, or both. A comprehensive study of the mercury in tobacco problem would require a comparison of tobacco farming methods and locations.

For the reasons discussed, the figures given in the appendices do not necessarily reflect the relative danger to the human user from the various products tested. However, the mercury content is quite high, and it is reasonable to expect that some percentage of the mercury is inhaled in normal smoking. Extensive further tests are indicated to determine how high this percentage is, and what its effect on the human body might be.

Calibration Data: Sample Set A

Sample	% Absorption	Absorbance	ug Hg
5	49.70	0.2484	50
6	26.80	0.1355	25
7	10.10	0.0462	10
8	5.17	0.0323	5
9	3.14	0.0230	2
10	2.80	0.0146	1
11	2.28	0.0123	0.5

Sample Set A

Sample	Weight (g) tobacco	Weight/2	% Absorption	Absorbance	ug Hg	ppm Hg
A	1.5046		2.22	0.0097	----	----
B	1.512	0.756	4.20	0.0186	1.50	1.98+
C			1.35	0.0057	----	----

A: Winston (acid sample)
B: Winston (Burned sample)
C: Winston (smoke only)

Calibration Data: Sample Set B

Sample	% Absorption	Absorbance	ug Hg
5	49.60	0.2976	50
6	27.81	0.1416	25
7	11.57	0.0580	10
8	6.53	0.0292	5
9	2.71	0.0120	2
10	1.85	0.0081	1
11	0.72	0.0031	0.5

Sample Set B

Sample	Weight (g) tobacco	Weight/2	% Absorption	Absorbance	ug Hg	ppm Hg
A	1.518	0.759	3.85	0.0170	3.00	3.95
B	1.558	0.774	3.31	0.0146	2.43	3.14
C	1.520	0.760	3.87	0.0172	3.05	3.79
D	1.432	0.716	3.25	0.0143	2.41	3.38

A: Tareyton
B: Kool Filter King
C: Salem
D: Winston

Calibration Data: Sample Set C

Sample	% Absorption	Absorbance	ug Hg
5	55.15	0.3468	50
6	30.56	0.1582	25
7	12.55	0.0583	10
8	7.15	0.0322	5
9	3.58	0.0158	2
10	1.69	0.0074	1
11	1.10	0.0048	0.5

Sample Set C

Sample	Weight (g) tobacco	Weight/2	% Absorption	Absorbance	ug Hg	ppm Hg
A	1.510	0.755	4.50	0.200	2.9	3.85
B	1.450	0.740	3.10	0.0138	2.33	3.15
C	1.513	0.756	3.00	0.0136	2.28	3.02
D	3.46	1.73	4.15	0.0182	2.52	1.46
E	1.493	0.747	4.54	0.0202	2.93	3.92

A: Marlboro
B: Lark
C: Chesterfield
D: Philly Cheroot (cigar)
E: Marlboro Menthol

Calibration Data: Sample Set D

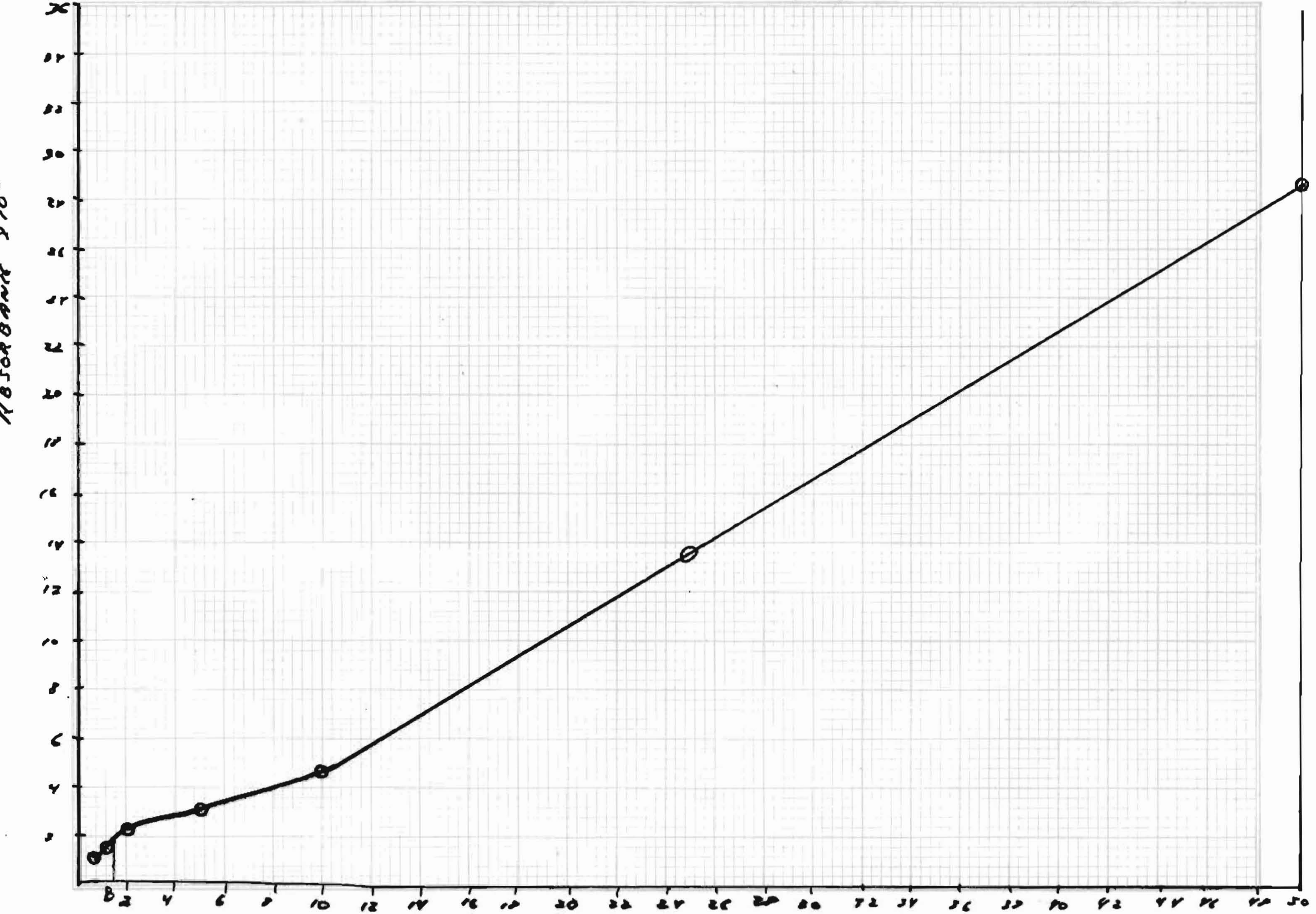
Sample	% Absorption	Absorbance	ug Hg
5	51.44	0.3139	50
6	28.72	0.1471	25
7	12.99	0.0604	10
8	6.89	0.0310	5
9	2.90	0.0128	2
10	1.00	0.0044	1
11	0.69	0.0030	0.5

Sample Set D

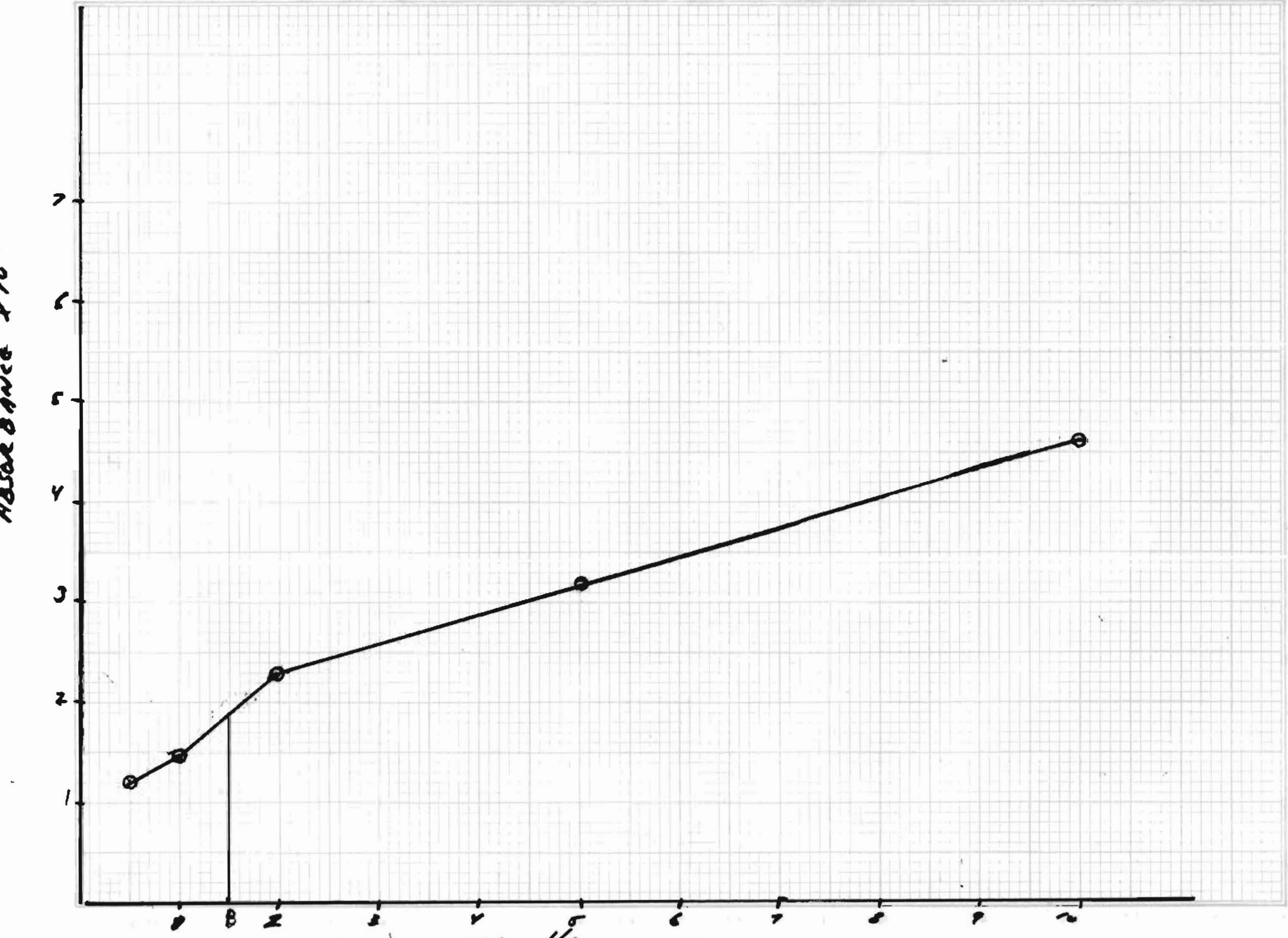
Sample	Weight (g) tobacco	Weight/2	% Absorption	Absorbance	ug Hg	ppm Hg
A	1.489	0.745	4.00	0.0177	2.83	3.81
B	1.488	0.744	4.00	0.177	2.83	3.81
C	1.795	0.898	2.67	0.0118	1.89	2.10
D	1.5797	0.7899	3.79	0.0168	2.65	3.23
E	1.490	0.745	3.98	0.0176	2.82	3.79

A: Marlboro
B: Marlboro
C: Middleton Cherry (pipe tobacco)
D: Borkum Riff (pipe tobacco)
E: Marlboro

SAMPLE SET R GRAPH 1



SAMPLE SET A GRAPH 2



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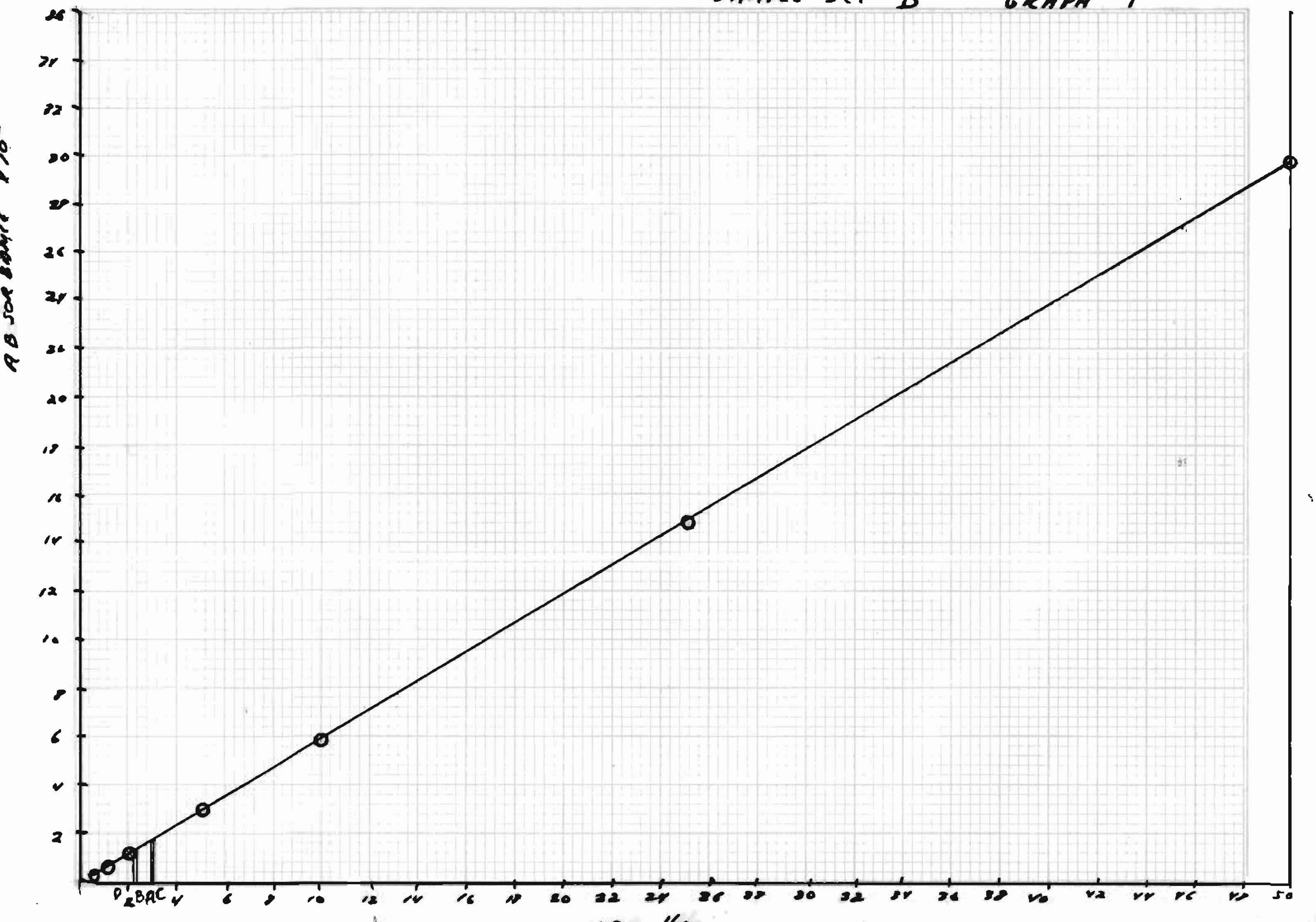

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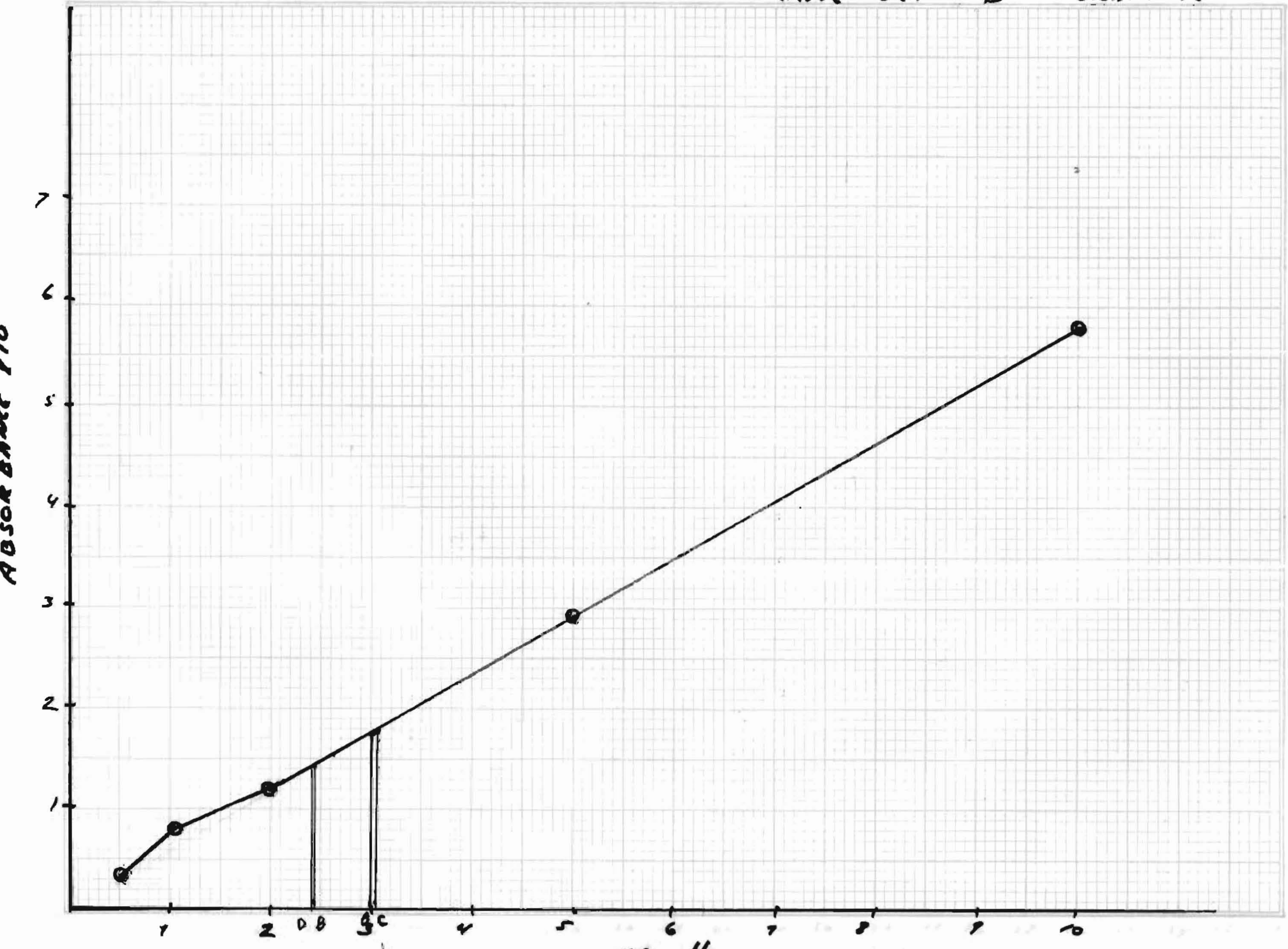

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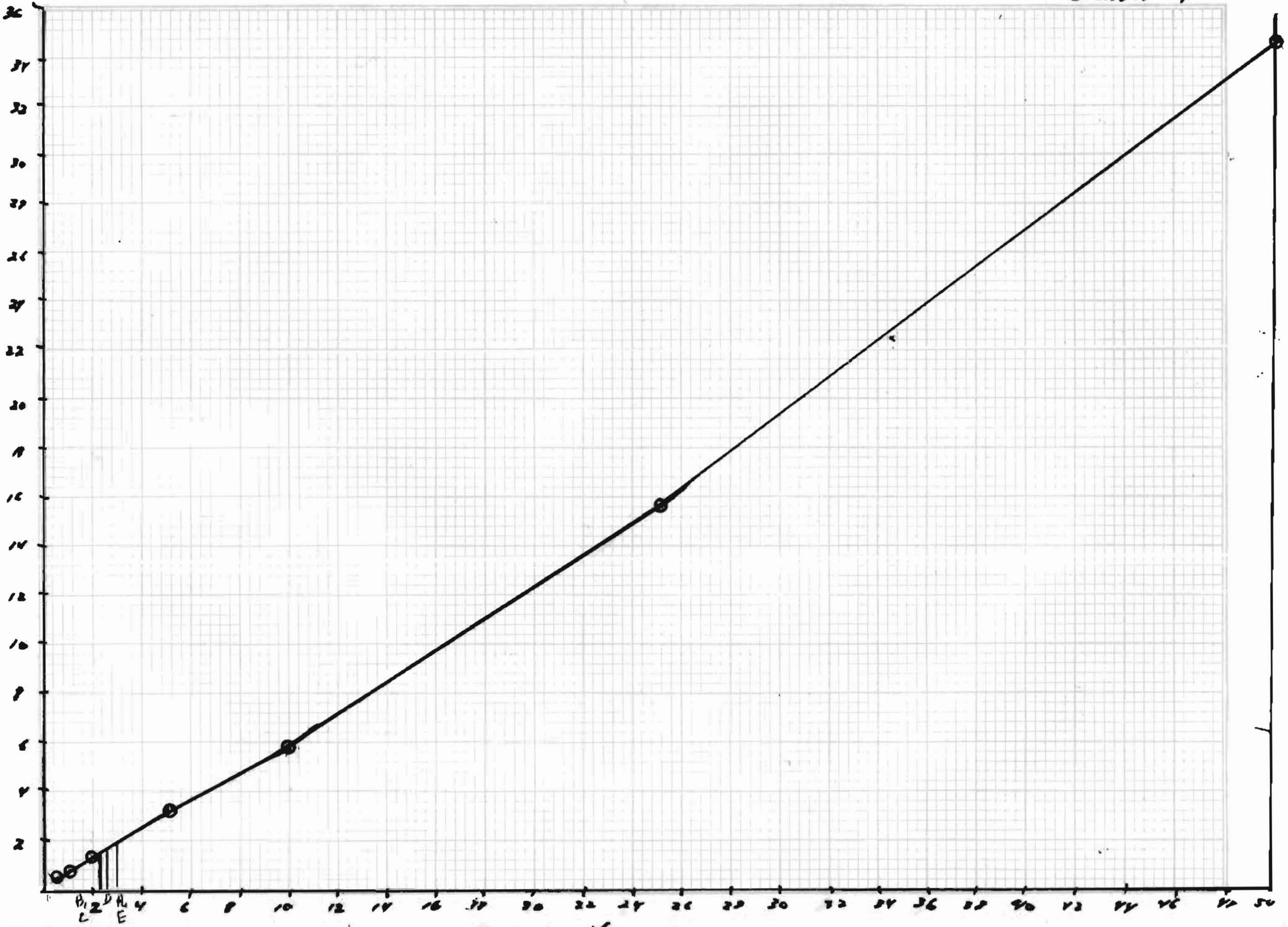
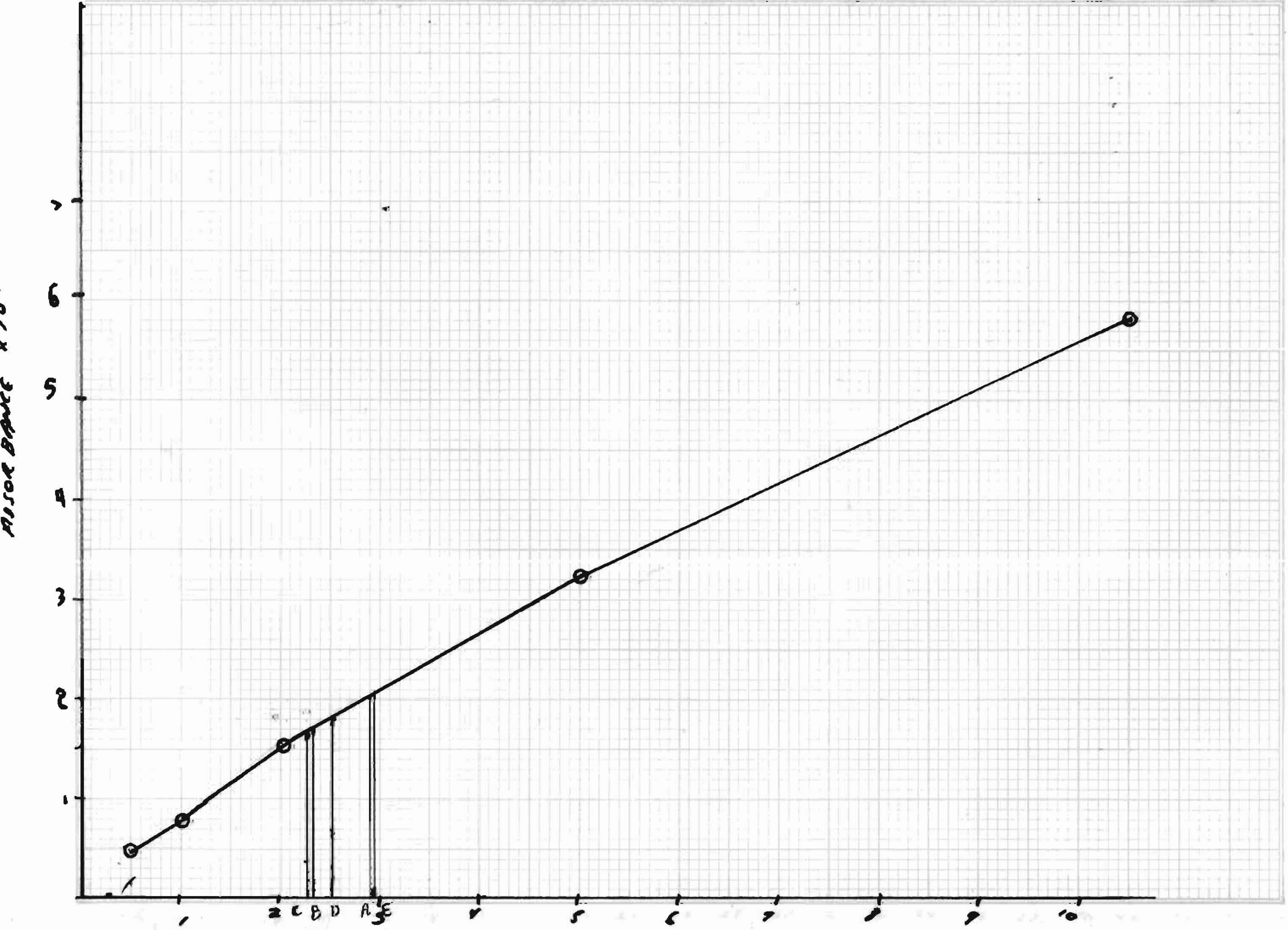


SAMPLE SET C   GRAPH 2



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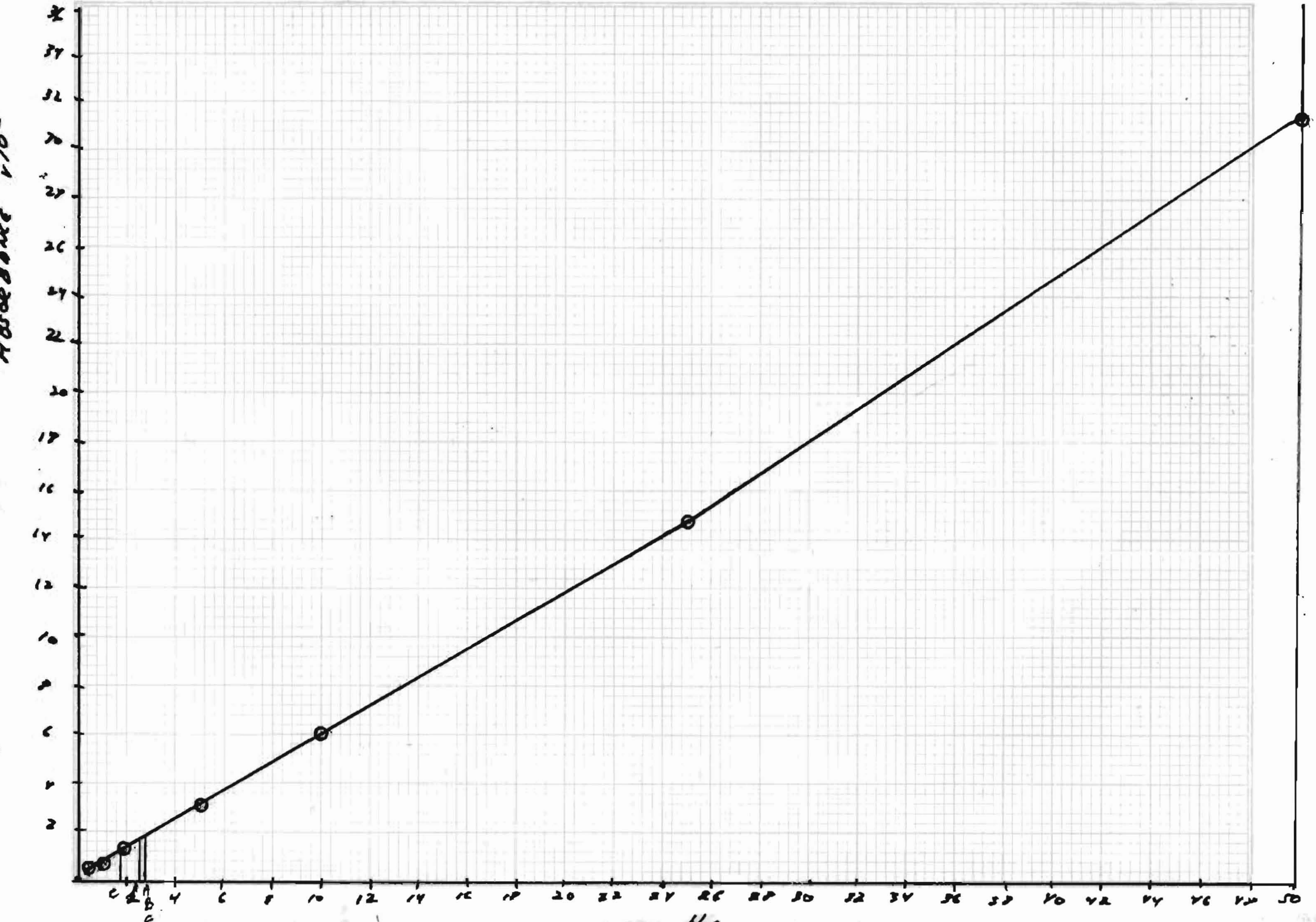

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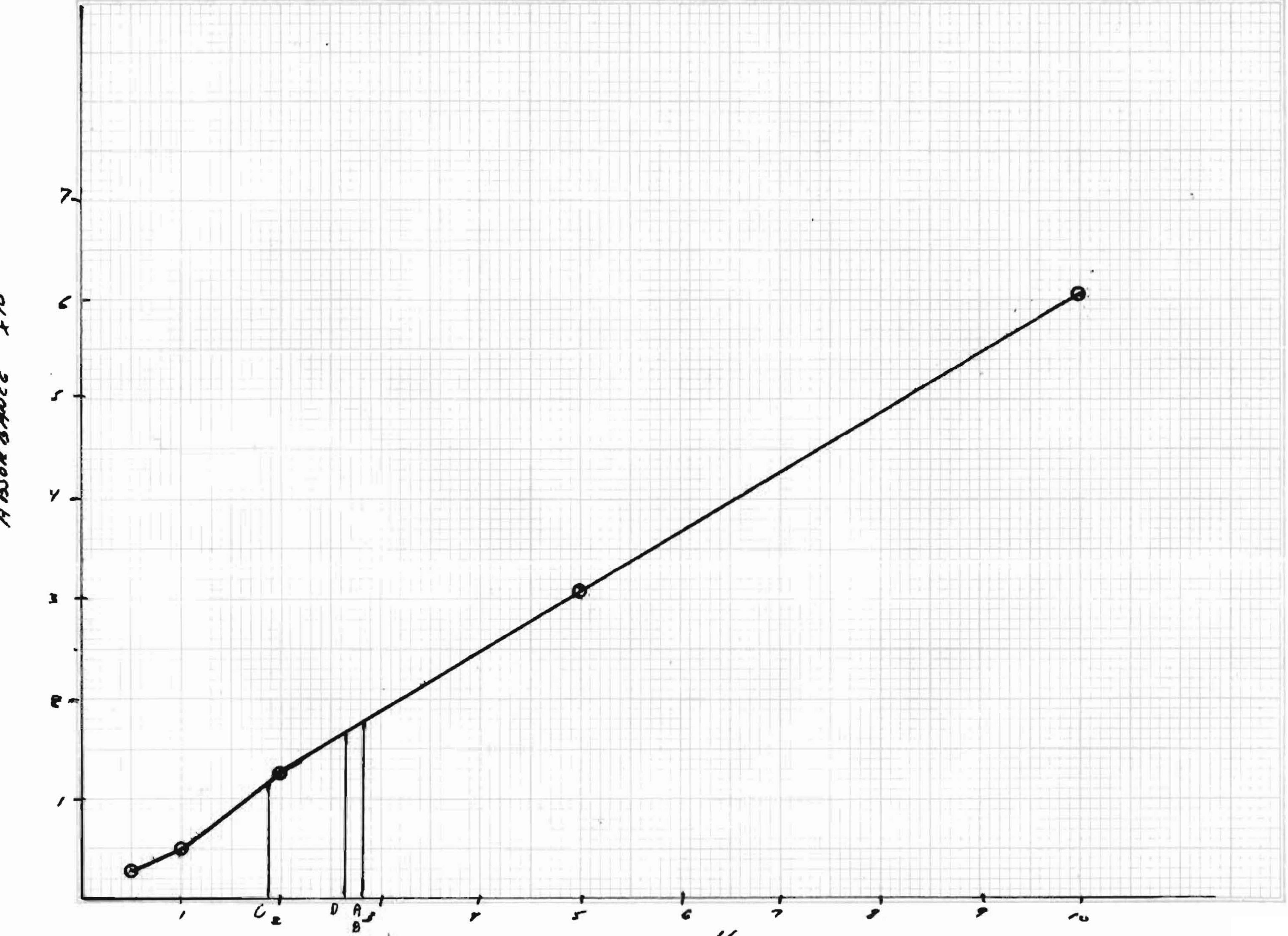


APPENDIX C

INTRODUCTION

Comparatively little work has been done with carbonyl cyanide. The first recorded preparation was by Malachowski,[21] who reported a synthesis from a diacyl derivative of a diisonitrosoacetone. This preparation was modified by Achmatowicz and Leplawy[22] by increasing the pressure under which the reaction occured. Reportedly, this reduced the risk of explosion and improved the yield.

Recently, Linn[23] found this method unsatisfactory for preparing carbonyl cyanide and developed an alternative synthesis from tetracyano ethylene (TCNE). In the Linn method, TCNE is oxidized to tetracyano ethylene oxide (TCNEO). TCNEO is treated with n-butyl sulfide in diethyl phthalate to give carbonyl cyanide.

Glemson and Haŭser[24] investigated the properties of carbonyl cyanide and found: boiling point, 65.6°; ΔH_{vap}, 8969 cal/mole; dipole moment, 1.35×10^{-18} esu cm^{-1}. However, they also reported the substance to be stable to light, which Linn did not find to be true.

Malachowski and Jurkewicz[25] found carbonyl cyanide to be noticeably more reactive than its analog, phosgene. Particularly, carbonyl cyanide was found to react explosively with water.

In addition, $CO(CN)_2$ was found[25] to react only with olefins which have a hydrogen atom in the α-position to the double bond. The rate of such reactions vary with the hydrocarbon studied, being high for compounds of the RR'C=CRR' type, and low for compounds of the CHR:CHR' or CH_2:CHR types. Color changes varying from intense red to colorless accompany the reactions when at least one carbon of the C=C has no hydrogen attached, or when both carbon atoms carry hydrogen atoms with other compounds. The color fades when the reaction is complete.

The reaction of $CO(CN)_2$ with $(RMe_2:)_2$ produces a crystalline product, probably 2-cyano-2,3-dimethyl-1,3-butanedicarbonylcyanide.[25] A similar reaction with cyclohexane is exothermic and produces a crystalline substance, believed to be 2-cyanocyclohexane-1,3-dicarbonylcyanide.

Malachowski[26] reports further of the color changes that occur when treating aromatic hydrocarbons, their halogen derivatives, phenols, nitrophenols, aldehydes, ketones, and quinnones with carbonyl cyanide.

Further work in the same area[27] involved reactions with pyrrole, piperidine, o-toluidine, primary and secondary amines, and anhydrous N_2H_4.

Achmatowicz and Zwierzak[28] studied the reactivity of carbonyl cyanide with various pairs of compounds, such as styrene and chloroacetic acid, styrene and trichloroacetic acid, p-methylstyrene and acetic acid, and diphenylethylene and chloroacetic acid. The reactions were invariably exothermic with transient yellow to orange color effects. The organic acids, besides being incorporated into the structure of the final products, were believed to enhance the electrophilic reactivity of the carbonyl group of the $CO(CN)_2$. Further investigations were made of the reactions of $CO(CN)_2$ with compounds with electron-releasing substituents in the para-position. The reactions were invariably exothermic, with a characteristic color change.

In another paper, Achmatowicz[29] reported that $CO(CN)_2$ reacted readily at 0° with aromatic (Ar) compounds in the presence of aluminum chloride in diethyl ether or carbon disulfide to form ArCOCN. No reaction was noticed in the absences of $AlCl_3$. In a monosubstituted benzene derivative, only the para-isomers were formed. The absorption maximum of the C=O group in the ArCOCN was notably shifted toward a lower frequency as compared with that for ArCN. Attempts to replace both cyanide groups with aromatics were unsuccessful.

Kemula and Wierzchowski[30,31] observed the absorption spectrum of carbonyl cyanide in the gaseous state, and found that the absorption band appeared at 2570-3980 Å, and around 2300 Å. They ascribed this absorption to two electronic transitions in the C=O and C≡N groups. The absorption spectrum in ultraviolet consists of two bands, one from 2300 Å towards the shorter wavelengths, and one from 2700-3500Å. Both regions are active photochemically. The primary photochemical process splits the carbonyl cyanide molecule to carbon monoxide and two cyanide radicals, which polymerize.

The Raman spectrum of carbonyl cyanide in a solution of diethyl ether was also studied by Kemula,[32] using the mercury 4358 Å line as excitation. Among twelve theoretically possible frequencies, five lines of high intensity and two very weak lines were observed. Tramer and Wierzchowski[33, 34] studied the infrared spectrum of the pure liquid and of the ether solution, and determined the absorption coefficients. Analysis of the vibrational spectrum,[34] assuming the C=O and C-C bond lengths equal to those in acetone, was used to determine the force constants for the valence force model.

Prochorow[35, 36] studied the spectra of $CO(CN)_2$ in various solvents, including ethyl ether, dioxane, benzene, toluene, and p-xylene by the photoelectric method. All mixtures showed an "extra" absorption in the near u.v. region, partially superimposed on the weak absorption of the $n-\pi$ transition in carbonyl cyanide.

Westerkamp[37] determined the microwave spectrum of carbonyl cyanide. Puchalik[38] calculated that the molecular polarization at infinite dilution is equal to 64 cm^3, and the dipole moment equal to 1.5 ± 5% Debye units.

TRIPHENYL PHOSPHINE

While waiting for the arrival of the TCNE, it was decided to attempt a reaction with phosgene and triphenyl phosphine, for use in later comparison with a reaction of carbonyl cyanide.

Triphenyl phosphine was dissolved in dry toluene, cooled to 0°, and phosgene bubbled through. After several minutes, there was an apparent reaction; the solution became cloudy. Some long white needles were observed around the neck of the reaction flask. The colloidal suspension was allowed to stand overnight. By morning the cloudiness and all traces of white crystals had disappeared, leaving a clear, colorless solution with a small deposit of a yellow oil on the bottom of the flask.

The mixture was distilled, most of the clear liquid coming off at about 110°, the boiling point of pure toluene. During distillation, the oil became increasingly darker brown. Heating was discontinued after all of the clear liquid had distilled off. The oil thickened considerably on standing a short time. After approximately six hours, colorless, rod-like crystals appeared, mingled with a brown solid.

Many attempts were made to separate the crystals and determine their identity, by dissolving the mixture in benzene, chloroform, xylene, water, and benzene-water mixtures, at various temperatures, all without success. Fractional crystallization from benzene and from benzene-water mixtures also proved unsuccessful in separating the products. Solvents containing oxygen were avoided, since triphenyl phosphine can readily take an oxygen from many organic molecules, and we wished to avoid possible oxidation of the crystals. Finally, sublimation was attempted. Even maintaining the temperature of the outside jacket of the condenser at 80° for several days produced no effect. Raising the temperature above this caused the substance to decompose.

A quantity of triphenyl phosphine was dissolved in dry toluene and allowed to stand overnight. By morning, a combination of colorless liquid and yellow oil, similar to that of the phosgene "reaction", appeared in the flask. The toluene was distilled off, and the oil allowed to solidify, producing a mixture of brown solid and colorless crystals. Attempts to separate these products by the means already described proved ineffective, as did sublimation. On strong heating, the product decomposed.

It was tentatively concluded that there was no reaction with the phosgene, since the apparent "products" of the reaction were probably identical to those obtained without addition of phosgene.

A sample of triphenyl phosphine crystals was sublimed, producing colorless needles and a yellow oil. After standing several weeks in a capped bottle, the crystals had turned yellow. Conclusion: the initial oil was probably the result of impurities in the starting material; triphenyl phosphine is unstable, and should be purified immediately before use.

EXPERIMENTAL -- TCNEO

Preparation of TCNEO from TCNE, the first step in synthesizing carbonyl cyanide by the Linn method, proved unexpectedly difficult.

Three attempts were made with very small samples of TCNE (1-2g). The TCNE was dissolved in acetonitrile, cooled, oxidized with H_2O_2, and the mixture diluted with water. The crystals obtained were brown in color. After drying several hours in air, the crystals were dissolved in warm dichloroethane to be recrystallized. On all three attempts, despite prolonged refrigeration, the crystals did not come out of solution. Evaporating part of the solvent produced a yellow solution, which did not give crystals on refrigeration. Evaporation to dryness produced a black residue and white crystals that decomposed rapidly, crackling and jumping about in the flask. Strong heating of the solution caused it to decompose. Some crystals were finally recovered from the third sample after concentration of the solution, but these decomposed well below the melting point of TCNEO.

The procedure was repeated, using a 5 g sample of TCNE. In this and subsequent attempts at synthesis, the dilution of the mixture of hydrogen peroxide, acetonitrile, and TCNEO had to be carried out in several large flasks, due to the large amount of water required. TCNEO was eventually recovered, but several recrystallizations were necessary to purify the crystals.

to obtain pure crystals. A total of 6.34 g of pure TCNEO was eventually prepared in this manner.

The TCNEO was dissolved in 15 ml diethyl phthalate and stirred, surrounded by a 50° water bath. Eight ml di-n-butyl sulfide was added dropwise over 20 minutes, so as to keep the temperature approximately 50°. During the addition, the color of the solution changed from light orange to deep red-orange. After addition was complete, the temperature was raised to 80° for 15 minutes. The flask containing the mixture was attached to a vaccuum line.

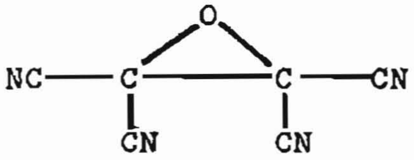
Traps were prepared at -23°, -83°, and -196°. The reaction flask was opened to the evacuated line and transfer allowed to take place. Repeated fractionation over a two day period separated a small amount of red liquid into the -83° trap. The vapor pressure of this liquid was 33 mm mercury at room temperature. The infrared spectrum was obtained in both the gas phase and in the liquid phase in carbon tetrachloride. This spectrum, compared with that previously obtained,[39] proved conclusively that the substance was not carbonyl cyanide.

The tentative conclusion drawn was that the carbonyl cyanide had probably polymerized while still in the reaction vessel. Since this occured at the end of January, no further attempt was made to determine the identity of the red substance.

DISCUSSION

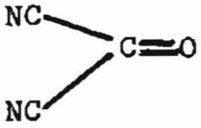
After consultation with the adviser, it was decided that nothing further could be gained from pursuing this project; nothing more of any practical value could be learned by repeated attempts at the same procedures. Consequently, this project was terminated at the end of January.

The instability of TCNEO is readily explained by an examination of its structure. It is a three membered ring with electron-attracting nitrile groups attached to the carbons:



For best results, this should be prepared immediately before use. Difficulties in purifying the TCNEO might be minimized if an effective means of purifying the starting material, TCNE, could be developed.

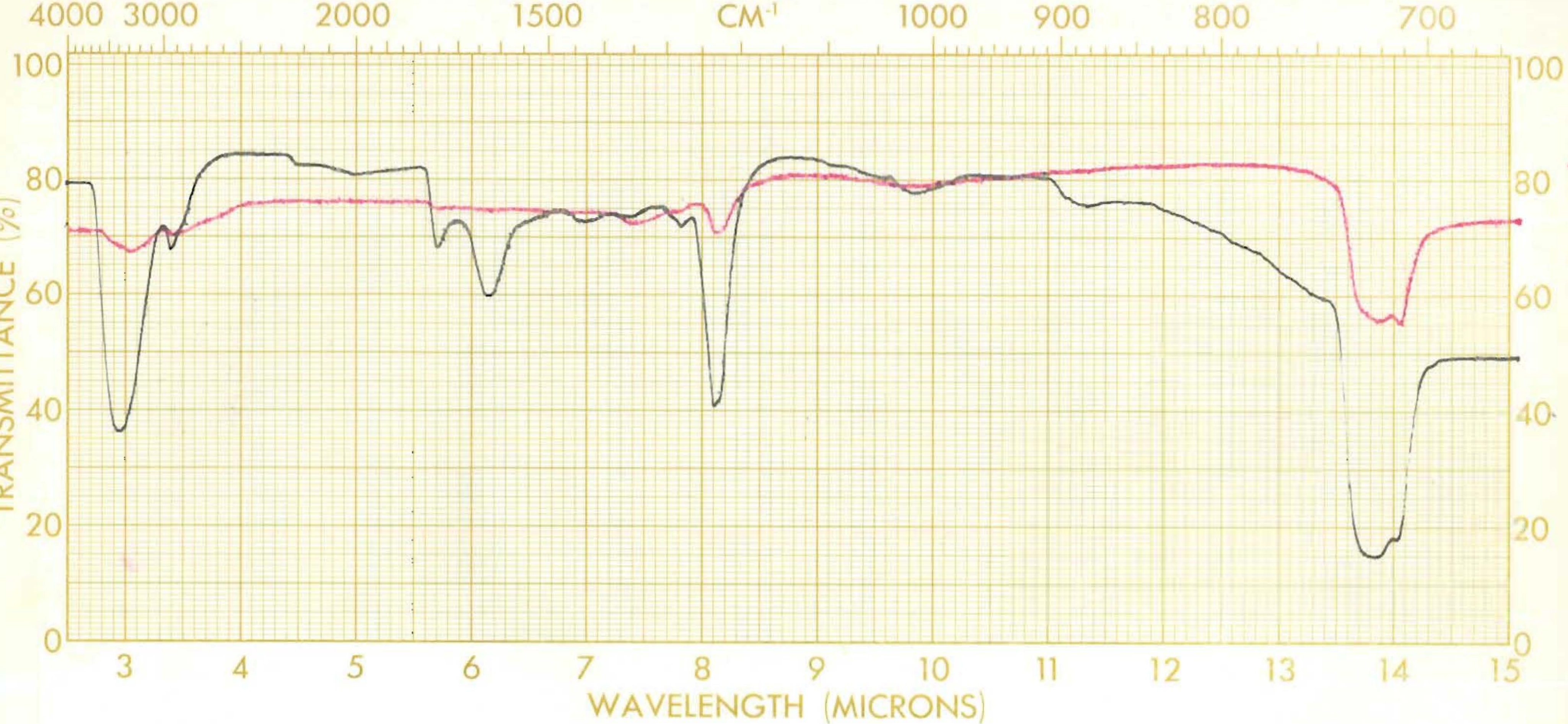
The last stage of the preparation is apparently the most temperamental. The carbonyl cyanide is also an unstable structure:



and tends to polymerize if left in the reaction flask beyond the necessary reaction time. It should be isolated as quickly as possible, even at the risk of losing some of the product. The alternative, as we found, is loss of all of the product.

As previously mentioned, the water wash solution of the crude TCNEO darkened on standing. Evaporation of the water produced an interesting product: a dark brown powder which seemed to expand to three or four times its initial volume on gentle heating. When placed in a capillary tube and gently warmed, the powder darkened to black and "climbed" the walls of the tube. Breaking of one such tube revealed that the solid had not really expanded in volume, but had spread itself out in a thin, even black layer. On strong heating in a sealed tube, the substance exploded violently. This may have been due to the presence of some crude, unstable TCNEO. On heating in air, the substance glowed bright red-orange and ramained iridescent for several seconds after it had been removed from the heat. By the time it had cooled, all of the solid had been vaporized. On heating in a limited amount of air, the substance gave off a white smoke and turned bright, metallic silver in color.

The powder was found to be insoluble in diethyl ether, benzene, carbon tetrachloride, chloroform, acetone, ethyl acetate, nitrobenzene, petroleum ether, dichloroethane, diethyl phthalate, and isopropyl alcohol. It was slightly soluble in warm acids, such as hydrochloric acid, phosphoric acid, acetic acid, and sulfuric acid. In strongly basic substances (NaOH and H_2O_2), the substance was extremely soluble. Evaporation of these alkaline solvents left no trace of the original dark material, only a small amount of white powder. Due to time considerations, the identity of this substance was not investigated further.



SPECTRUM NO.

SAMPLE — 83 FRACTION

RED [illegible] 55 [illegible]

BETA [illegible] CONDENSED LIQUID [illegible]

RED [illegible] IR [illegible]

ORIGIN

PURITY

PHASE [illegible]

THICKNESS

LEGEND

1. Red 13 mm

2. [illegible] condensed

DATE 1/28/7[illegible]

OPERATOR [illegible]

REMARKS

[illegible]

[illegible]

SPECTRUM NO.

SAMPLE

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Note: Unnumbered references are for methods of preparing mercury compounds for analysis, all found to be inappropriate to the problem at hand.