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The purification, analysis and growth of single crystals of organic semiconductors

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THE PURIFICATION, ANALYSIS AND GROWTH OF SINGLE CRYSTALS OF ORGANIC SEMICONDUCTORS

BY

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ABSTRACT

The purpose of this investigation was to design and construct a furnace for growing large single crystals of organic compounds by slow crystallization from the melt by the Bridgman technique. The crystals obtained by this furnace will be used in a later investigation of the intrinsic electrical and optical properties of organic semiconductors.

The methods described have been used with success to produce large single crystals of anthracene and ethyl-p-aminobenzoate with diameters of 1/2 inch.

The most promising methods of purification of anthracene, which were chemical synthesis, washing, recrystallization from solvents, sublimation, dimerization, co-distallation and zone refining have been investigated. The relative merits of each method were explored and discussed with particular attention to co-distillation which is considered to be the most applicable. Anthracene of higher purity than commercial zone refined anthracene was prepared and is believed to be adequate for crystal growth and subsequent electrical measurements.

A very simple fluorescence technique for quantitative analysis of traces of naphthacene in anthracene was developed which employs a colloidal suspension of the sample. Sensitivity approaching 0.1 ppm naphthacene in anthracene is readily obtainable. The method is convenient to use, involving only small samples and uncomplicated manipulative techniques. For rapid semiquantitative analysis, it provides a visible fluorescence color correlation with the level of impurity.

APPROVAL OF THESIS

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INTRODUCTION

Organic Semiconductors

Organic semiconductors can be defined as structures containing an appreciable number of carbon-carbon bonds and which have, in general, an electrical conductivity which is intermediate between that of metals and insulators (typically 10^{-20} to 10^{2} ohm^{-1} cm^{-1}). The conductivity increases, usually exponentially, with temperature. Four types of organic systems have exhibited semiconductor properties (4):

(a) Simple molecules such as anthracene
(b) Free radicals or free radical ions
(c) Charge-transfer complexes (iodine-perylene)
(d) Polymers (irradiation or pyrolysis)

Conductivity. The electrical conductivity, σ, of a pure organic semiconductor varies with temperature T in the following manner:

$$\sigma = \sigma_o \exp \left[-Eg/2kT \right] \tag{1}$$

where σ_o = constant of the material (conductivity at T approaching infinity)
Eg = apparent energy gap or activation energy for conductance)
k = Boltzman's constant
T = absolute temperature

Measurements of conductivity at various temperatures are used with equation (1) to determine the energy gap, Eg. The energy gap is the difference in energy between the highest level in the valance band and the lowest level in the conduction band and is considered the activation energy for conductance. Generally Eg is of the order of one electron-volt (ev), although experimental values range from 0.1 ev for cyanthrone to 1.85 ev for naphthalene (16).

One of the objectives of this study is to obtain a better understanding of the mechanism of electronic conduction and to find the characteristic functions in molecular structures that contribute to the electrical conductance.

Purity. The first problem in the investigation of conduction in organic semiconductors is the preparation of the samples. A criterion for purity in anthracene, for example, is that the material should possess the fluorescence proper to itself and not, which can arise from traces of other aromatic compounds. Garrett (16) discusses four methods of purification: crystallization from a solvent, sublimation, chromatography and zone refining. Little is known of the relative merits of each technique and Garrett (16) writes, "Clearly it is going to be necessary, sooner or later, to undertake a critical comparison of these purification methods with a degree of vigor that has not yet been attempted."

Pure material is required to permit intrinsic measurements free of the effects of contamination. Trace impurities present even below the parts per million level, have a significant effect on the electrical and optical properties.

Polycrstalline and Single Crystal Samples. Measurements on compressed powders (16) and evaporated films (27) should be viewed with suspicion. The main reasons for doubt are interfacial effects, the role of surface conduction and anisotropy. Anisotropy in electrical properties involves changes in property with different crystallographic directions. From the point of view of the history of research with the better known organic semiconductors, the usefulness of polycrstalline samples is considerably less than that of single crystals. The growing of single crystals of organic materials is made easier by the use of highly purified materials as spurious nucleation on insolubles is then absent.

Purpose of Investigation

The author intends to study the intrinsic electrical and optical properties of organic semiconductors. This investigation, The Purification, Analysis and Growth of Single Crystals of Organic Semiconductors, includes the first three steps of the complete project. In order to determine the part played by impurities in the organic semiconductors a quantitative analytical method must first be determined, sensitive to levels below one part per million. Secondly, a critical comparison of the many purification techniques must be conducted. Finally the highly purified samples must be grown into single crystals.

Conductivity Studies of Anthracene

Anthracene is found in very small amounts in coal tar. It has a melting point of 217°C, a boiling point of 354°C (15) and exhibits a blue-violet fluorescence in both the crystalline and dissolved states. The crystal structure is a monoclinic one and belongs to the C_{2h}^{5} space group (34). Most of the materials studied in detail as organic semiconductors are monoclinic and belong to the space group C_{2h}^{5}. Anthracene exhibits some conduction (considered to be electronic) and it has been the most extensively studied organic semiconductor, probably because of its availability and simplicity of structure. Considerable published information on anthracene exists for corroboration. For these reasons this investigation is concerned primarily with anthracene. When the techniques have been refined with anthracene other organic materials can be studied.

Mette and Pick (24), Ionkuchi (19) and Riehl (33) carried out conductivity measurements on single crystals of anthracene. No test of purity was applied, but they stress that it is desirable that investigations be done on the purest available compounds.

Anthracene exhibits anisotropy in electrical characteristics and both measurements of the temperature-dependence of the conductivity and energy gap are reported to vary with different crystal directions (16). Measurements on polycrystalline materials such as compressed powder samples and evaporated films are not considered very reliable for this reason, as well as interfacial effects and the role of surface conduction.

ANALYSIS OF ANTHRACENE-NAPHTHACENE MIXTURES BY FLUORESCENCE MEASUREMENTS

The assay of trace impurities in anthracene prepared for growth of large single crystals offers considerable difficulty. The analysis of anthracene purified by zone refining or other techniques requires analytical methods sensitive to less than 1 ppm of impurity content.

The fluorescence of anthracene and of the anthracene-naphthacene system has been studied widely. As little as one part per million (ppm) of naphthacene is reported (32) to influence the system fluorescence. The fluorescence of anthracene has been studied using single crystals (12,23,36), microcrystalline suspensions (3), potassium bromide pellets (43), and in dilute solution (12,32,37). Naphthacene fluorescence in the presence of anthracene has been investigated in solid solution (13,27,32), in dilute solution (12,13,32) and with anthracene-coated screens (7).

Pure crystalline naphthacene exhibits very weak fluorescence (32). However, in dilute solid solution in anthracene, the normal blue-violet fluorescence of anthracene is almost completely quenched by the green naphthacene fluorescence. When mixed crystals are heated to the melting point, the green fluorescene vanishes at the instant the mixture is liquified. The same phenomenon occurs when crystals are dissolved in benzene. Naphthacene fluorescence does not result from the direct excitation of the low concentration of naphthacene present, nor does it arise from absorption of energy from the emission of the anthracene (27,32). In solid solution it is postulated that the anthracene host absorbs the exciting energy and transfers it to the naphthacene solute by means of sensitized fluoresence (32,42), or by excitation migration (11,12,13,27). When naphthacene-anthracene molecules are separated beyond crystal lattice distances either by fusion or by a liquid solvent, the energy transfer cannot occur as readily as in solid solution.

The present investigation presents a very simple fluorescence technique for quantitative analysis of traces of naphthacene in anthracene, employing a collidal suspension. Sensitivity approaching 0.1 parts per million (mole basis) naphthacene in anthracene is readily obtainable. The method is convenient to use: sample preparation is simple, the sample size is small and manipulative techniques are uncomplicated. For rapid semiquantitative analysis, it provides a visible fluorescence-color correlation with the level of impurity.

EXPERIMENTAL

Apparatus

A Farrand Optical Co. Spectrofluorometer equipped with a 150-watt Xenon arc lamp, an R.C.A. 1P28 photomultiplier tube, two grating monochromators and a one centimeter fused-quartz sample cuvette was employed for all fluorometric measurements. The phototube was connected by an R.C.A. microammeter to a Varian strip recorder, type G-10.

Reagents

Pure anthracene was prepared by synthesis from anthraquinone using the method described by Fieser (10) followed by zone refining (7).

Naphthacene (melting point 340-342°C) was purchased from Matheson, Coleman and Bell Co. (Catalog No. 9082) and used without further purification.

Reagent grade isopropyl alcohol was obtained from Baker Chemical Co. (Catalog No. 9084).

Procedure

Preparation of Standard Samples. An accurately weighed sample of anthracene, 125 mg, was dissolved in 250.0 ml of isopropyl alcohol, producing a stock solution containing 0.5 mg of anthracene per ml. Naphthacene (35 mg) was similarly dissolved in 250.0 ml of isopropyl alcohol producing a stock solution containing 0.140 mg per ml. Successive dilutions of 2-ml aliquots of the naphthacene stock solution with isopropyl alcohol gave stock solutions containing 1.218 (10^{-8}), 2.44 (10^{-10}), 9.78 (10^{-12}) and 3.91 (10^{-13}) moles of naphthacene per ml. The standard solutions were mixed in proportion required to prepare 59 naphthacene-anthracene mixtures, with naphthacene content ranging from 0.6 to 4360 ppm in anthracene.

Colloidally Suspended Samples. A colloidal suspension of each sample was formed by rapidly adding 125 ml of distilled water to 4 ml of the standard alcohol sample. Colloidal suspensions prepared in this manner exhibit strong naphthacene fluorescence, indicating that the naphthacene co-precipitates with the anthracene. Fluorescence measurements were made with the exciting monochromator adjusted to produce peak fluorescence; Anthracene is excited maximally at 365 mu. The Tyndall and Rayleigh types of emission (28), which produce light of the same wavelength as the incident source, do not present a problem with the anthracene-naphthacene system. The exciting wavelength used, 365 mu, lies below the fluorescent emission of the system which is at 400 to 510 mu. Colloidally suspended samples remain stable (no settling out) for periods up to 1-2 hours.

Clear Solution Samples. Clear solutions in isopropanol were made by adding 125 ml of isopropanol to 4 ml of the standard alcohol samples. The fluorescence of these solutions was measured as described above.

RESULTS AND DISCUSSION

At the exciting wavelength of 365 mu, colloidal suspensions of naphthacene-anthracene exhibit six fluorescence emission peaks. Three fluorescence emission peaks can be resolved for anthracene, at 405 (maximum), 430 and 450 mu. Three fluorescence emission peaks can also be resolved for naphthacene at 510, 540 and 575 mu, the maximum being at 510 mu. These results are similar to those described for dilute solution spectra (3, 32, 37). Typical fluorescence emission spectra of naphthacene-anthracene colloidal suspensions are presented in Figure 1. Fluorescence spectra of clear alcohol solutions are shown in Figure 2.

Semiquantitative Evaluation of Results

As naphthacene content increases from 0.6 to about 300 ppm, the intensity of anthracene fluorescence at 405 mu decreases, and that of naphthacene at 510 mu increases. This is most readily followed by measurement of the emission peak height. Table 1 summarizes the results of the experimental data obtained.

Above 300 ppm naphthacene, the intensity of the naphthacene peak decreases. This is brought about by self-quenching of the fluorescence emission caused by marked interaction between naphthacene molecules at higher concentrations.

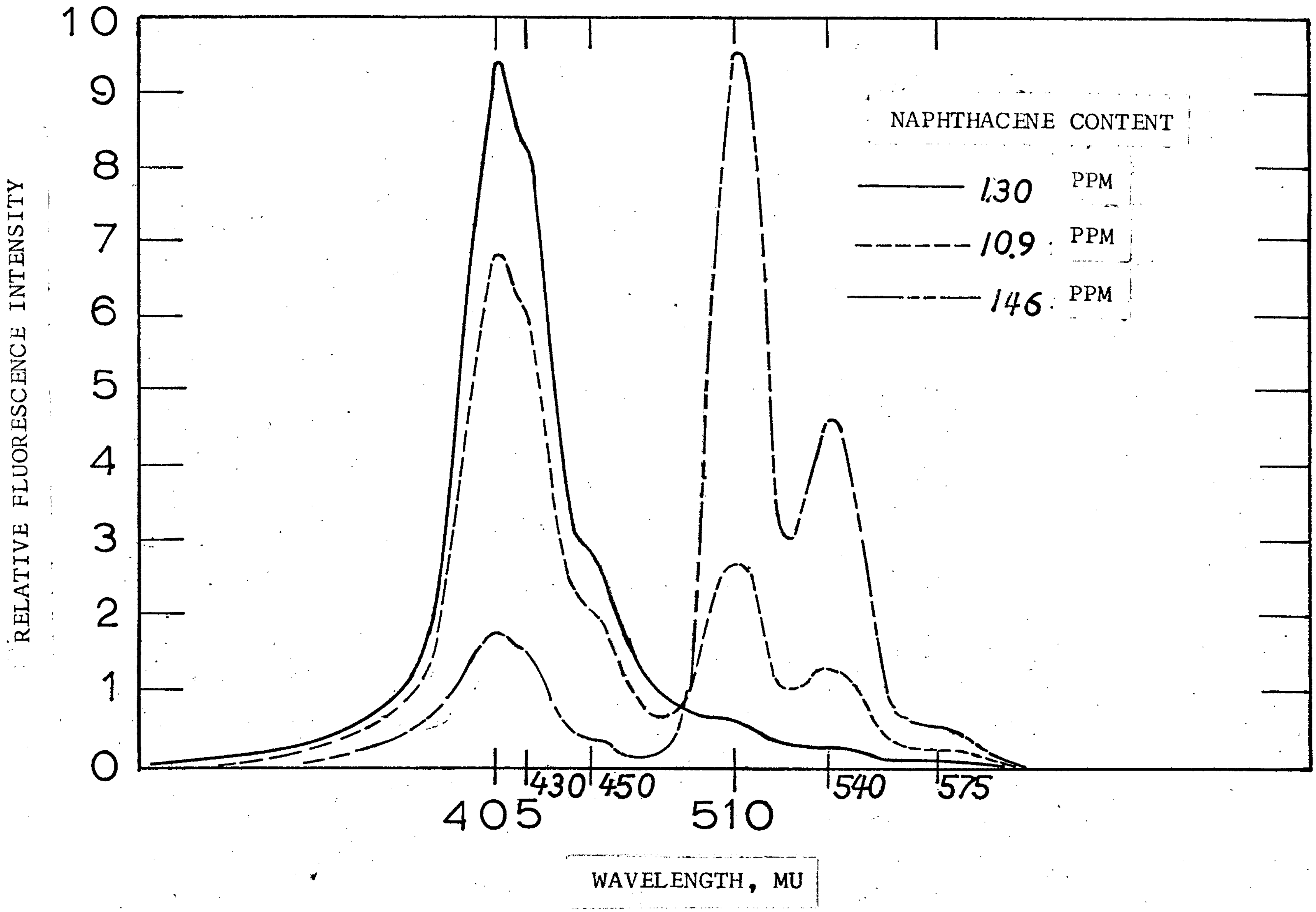


FIGURE 1, TYPICAL FLUORESCENCE RESPONSE SPECTRA OF ANTHRACENE NAPHTHACENE COLLOIDAL SUSPENSIONS

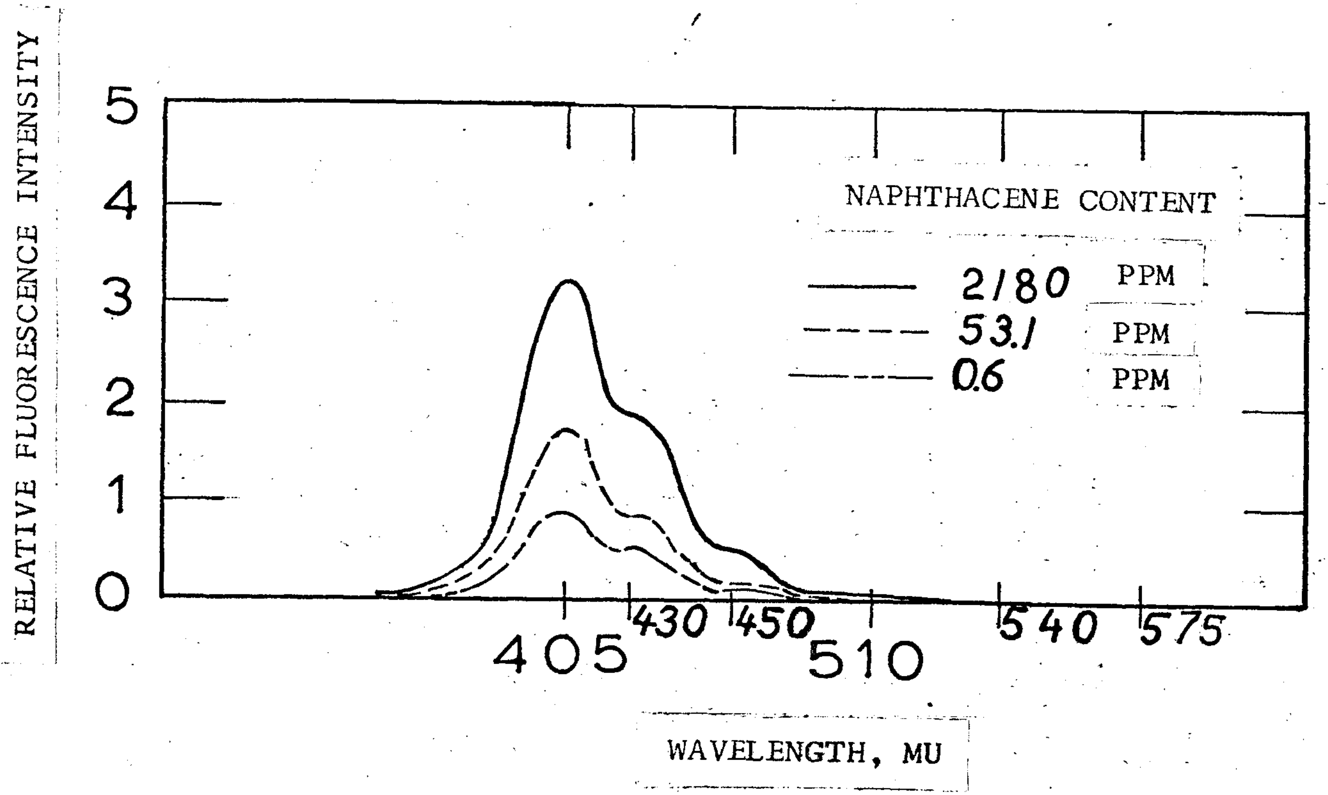


FIGURE 2, TYPICAL FLUORESCENCE RESPONSE SPECTRA OF ANTHRACENE NAPHTHACENE ISOPROPANOL SOLUTIONS

TABLE 1

FLUORESCENCE OF COLLOIDAL SUSPENSIONS OF NAPHTHACENE AND ANTHRACENE

NAPHTHACENE CONCENTRATION IN ANTHRACENE (PPM-MOLE BASIS)		FLUORESCENCE COLOR	FLUORESCENCE INTENSITY		INTENSITY RATIO R=(I 510/I 405)
Corrected	Uncorrected		NAPHTHACENE I 510 mu	ANTHRACENE I 405 mu	
.6	0	blue-violet	.187	7.20	.026
.775	.175	blue-violet	.28	7.1	.0394
.834	.234	blue-violet	.42	9.1	.046
1.07	.467	blue-violet	.40	7.7	.052
1.30	.701	blue-violet	.58	9.46	.0613
1.65	1.05	blue-violet	.63	8.5	.0740
2.0	1.40	blue-violet	.610	7.6	.0804
2.7	2.10	blue-violet	.58	5.2	.112
3.5	2.90	blue-violet	1.0	7.6	.132
5.0	4.36	blue-violet	1.29	6.55	.197
6.8	6.23	blue-violet	2.10	8.04	.262
9.1	8.51	blue	2.9	8.4	.345
10.9	10.3	blue	2.75	6.8	.405
13.1	12.5	blue	2.99	6.2	.482
16.5	15.9	blue-green	3.24	5.68	.571
22.4	21.8	blue-green	4.63	6.18	.749
31.1	30.5	blue-green	5.0	4.73	1.06
39.8	39.2	blue-green	5.27	4.09	1.30

TABLE 1 (CONTINUED)

NAPHTHACENE CONCENTRATION IN ANTHRACENE (PPM-MOLE BASIS)		FLUORESCENCE COLOR	FLUORESCENCE INTENSITY		INTENSITY RATIO R=(I 510/I 405)
Corrected	Uncorrected		NAPHTHACENE I 510 mu	ANTHRACENE I 405 mu	
53.1	52.5	green	5.69	4.0	1.42
74.7	74.1	green	5.8	2.58	2.25
87.9	87.3	green	4.52	1.8	2.52
146.	145.	green	9.79	1.98	4.94
175	174	green	10.5	1.62	6.43
199	198	green	10.7	1.82	5.88
199 repeat		green	10.4	1.47	7.02
219	218	green	12.2	1.79	6.8
291	290	green	11.3	1.24	9.11
437	436	green	8.56	1.23	6.95
727	726	green	9.9	.65	15.2
871	870	green	11.1	.70	15.88
1090	1090	green	10.18	.50	20.3
1452	1452	green	9.4	.498	18.8
2180	2180	green	9.42	.374	25.2
2420	2420	green	8.3	.37	22.4
2780	2780	green	8.2	.37	22.1
2780 repeat		green	8.7	.366	23.8
3050	3050	green	7.42	.33	22.5
3200	3200	green	8.33	.345	24.1
3780	3780	green	7.05	.342	20.6
4360	4360	green	6.88	.29	23.0
pure naphthacene		none	0	0	0

The visually observable fluorescence emission offers a rapid semiquantitative estimation of naphthacene content. The color of the colloidal suspensions changes much more markedly than does that of the solid anthracene in either single crystal or polycrystalline form.

Above 40 ppm naphthacene, the intensity of the 510 mu naphthacene emission peak is greater than that of the 405 mu anthracene peak, and samples of greater concentration all appear green upon excitation. However, with the colloidal suspension technique, the blue anthracene fluorescence at 405 mu is spectrometrically measurable up to 4360 ppm naphthacene, contrary to the statement by Sloan (38) that it is completely extinguished at 0.3 ppm naphthacene content.

Quantitative Evaluation of Colloidal Spectra

Figure 3 presents a log-log plot of peak intensity ratio of naphthacene to anthracene, $R = (I_{510mu}/I_{405mu})$ as a function of added naphthacene content. The realtionship is linear in the range of 10 to 300 ppm naphthacene, but shows curvature below 10 ppm. Observation of the fluorescence of the "pure" standard anthracene indicated the presence of naphthacene by an intensity ratio of 0.026. On the assumption that the linearity should hold even at low naphthacene content, the linear portion of the curve was extrapolated. This extrapolation suggested that naphthacene in the "pure"

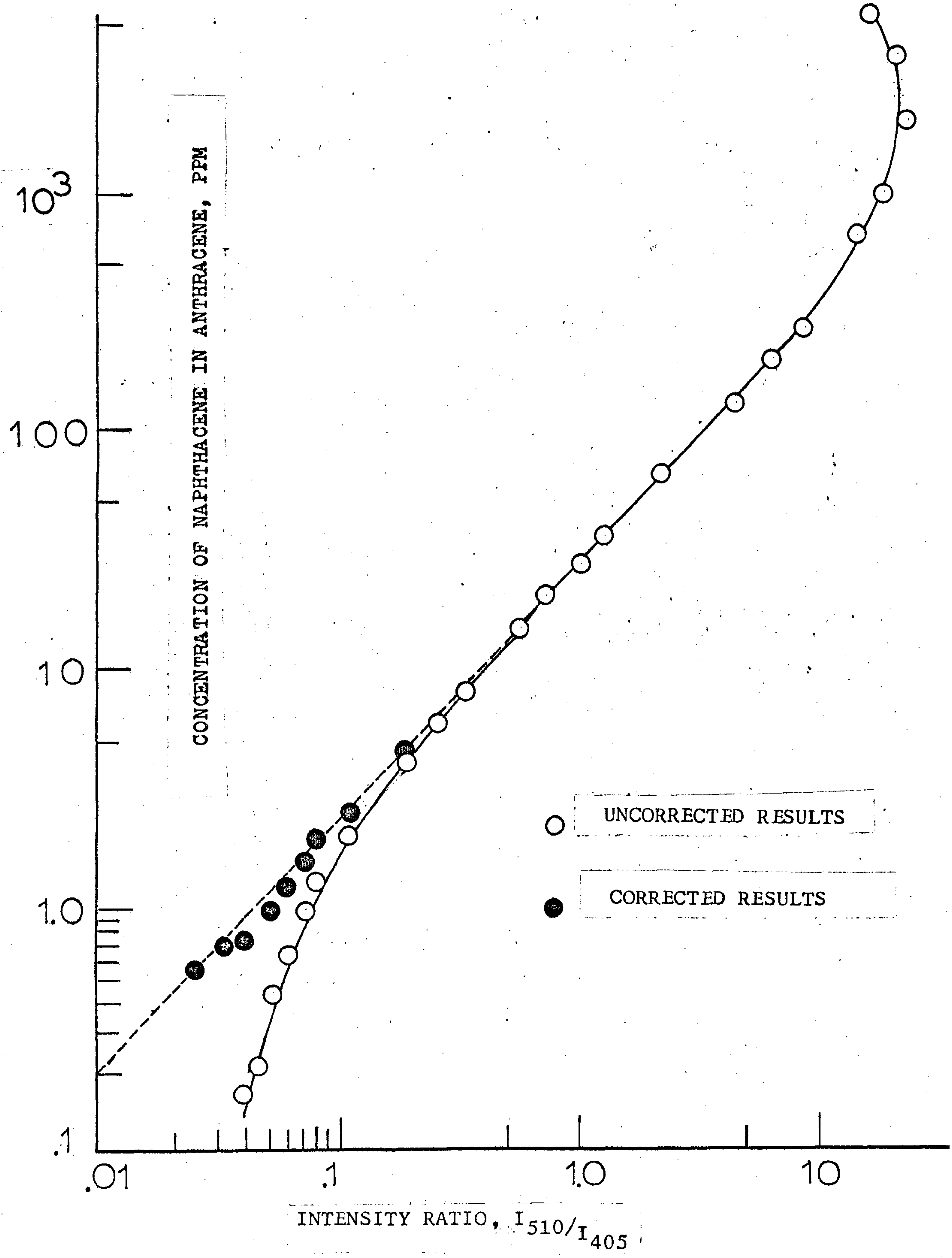


FIGURE 3, INTENSITY RATIO AS A FUNCTION OF NAPHTHACENE CONTENT IN ANTHRACENE FOR COLLOIDAL SUSPENSIONS standard amounted to 0.6 ppm. When all of the observations were rectified for this additional 0.6 ppm naphthacene content in the original, all of the experimental points coincided closely with the linear predicted curve. Hence, it may be concluded that the log naphthacene concentration is proportional to the log fluorescence intensity ratio up to a concentration of 300 ppm. The established realtionship may be represented by the straight line equation

$$\log C = 1.06 \log R + \log 28.1 \qquad (2)$$

or by the exponential equation

$$C = 28.1\ R^{1.06} \qquad (3)$$

where C is the naphthacene concentration, ppm, in anthracene and R is the intensity ratio. This relationship was used in the estimation of napthacene in unknowns assuming that the linearity is continuous to concentrations as low as 0.10 ppm.

Above the 300-600 ppm level, self-quenching of the fluorescence causes small deviations, and above 600 ppm increasing deviations from linearity.

Table 2 lists the differential naphthacene concentration and differential intensity ratio of naphthacene-anthracene mixtures in a colloidal suspension. The differential

Table 2

DIFFERENTIAL INTENSITY RATIO OF COLLOIDAL SUSPENSIONS OF NAPHTHACENE AND ANTHRACENE

DIFFERENTIAL NAPHTHACENE CONCENTRATION IN ANTHRACENE* (ppm-mole basis)	DIFFERENTIAL INTENSITY RATIO
0	0
.07	.0064
.175	.0134
.234	.0201
.467	.026
.701	.0353
1.05	.0480
1.4	.0544
2.10	.0858
2.9	.106
4.36	.171
6.23	.236
8.51	.319
10.3	.379
12.5	.456
15.9	.545
21.8	.723
30.5	1.03
39.2	1.27
52.5	1.39
74.1	2.22
87.3	2.49
145	4.91
174	6.40
198	5.85
198	6.99
218	4.47
218	6.77
290	9.08
436	6.92
726	15.2
870	15.85
1090	20.27
1452	18.8
2180	25.17
2420	22.4
2760	23.8
2780	22.1
3050	22.47
3200	24.1
3780	20.6
4360	23.0

*based on a standard having .6 ppm naphthacene and an intensity ratio of .026

naphthacene concentration in anthracene is the amount of naphthacene added to the "pure" standard anthracene which contained 0.6 ppm. The differential intensity ratio is the difference in intensity ratio between the "pure" standard and the prepared sample.

Figure 4 is a plot of the log differential peak intensity ratio versus the log differential naphthacene concentration. In the differential concentration range of 0.07 to 300 ppm the log differential concentration is proportional to the log differential fluorescence intensity ratio and can be represented by the straight line equation

$$\log dC = 1.06 \log dR + \log 27.6 \qquad (4)$$

or by the exponential equation

$$dC = 27.6\ dR^{1.06} \qquad (5)$$

where dC is the differential naphthacene concentration, ppm, in anthracene and dR is the differential intensity ratio. The above results indicate that were a "pure" standard of zero ppm available, equations 2 and 3 could be used in the extended naphthacene concentration range of 0.07 to 300 ppm.

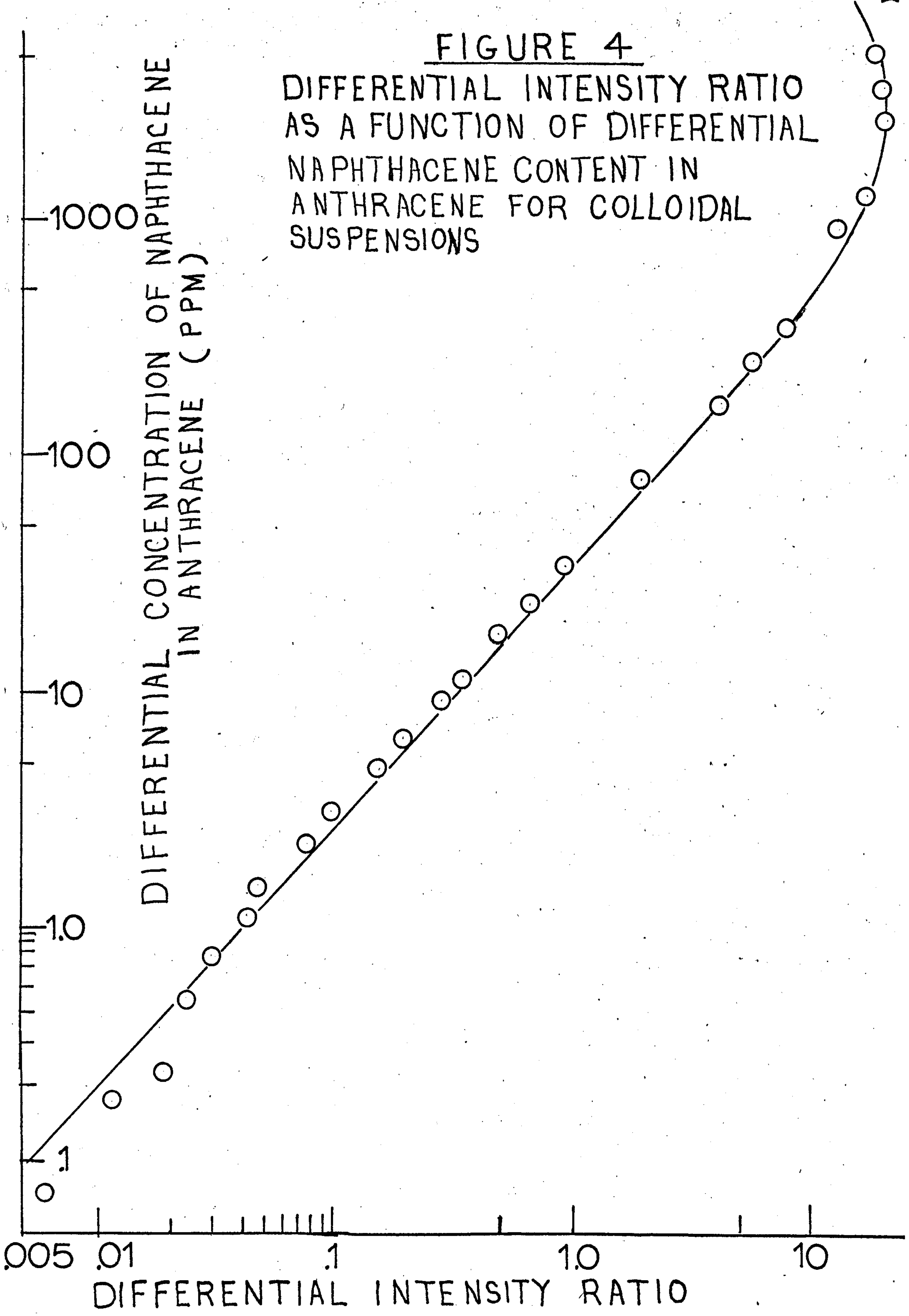


FIGURE 4

DIFFERENTIAL INTENSITY RATIO AS A FUNCTION OF DIFFERENTIAL NAPHTHACENE CONTENT IN ANTHRACENE FOR COLLOIDAL SUSPENSIONS

Comparison of Colloidal Suspension Spectra With Solution Spectra

The results of fluorescence measurements on dilute solutions of naphthacene-anthracene in isopropanol are summarized in Table 3. The results indicate that mixtures of naphthacene-anthracene in isopropanol solution are much more insensitive to fluorescence analysis than are the colloidal suspensions. The fluorescence intensity ratio of dilute naphthacene-anthracene solutions changes from zero to 0.0368 in the range of 0.6 to 2180 ppm naphthacene content, while the intensity ratio of colloidal suspensions varies from 0.026 to 25.2. At concentrations as high as 4360 ppm naphthacene in anthracene the observed fluorescence of dilute solutions is blue. Spectrometric measurement at higher naphthacene levels indicates some emission at 510 mu, but the intensity of this bears no significant relationship to the naphthacene content.

The strong fluorescence of colloidal suspensions when compared to dilute solutions indicates that the naphthacene co-precipitates with the anthracene allowing an energy transfer to occur by means of sensitized fluorescence or excitation migration.

Precision and Reproducibility

The fluorescence intensity versus concentration data of colloidal suspensions display considerable scatter, which is due primarily to colloidization techniques. Repeated runs at the same napthacene concentration in anthracene often exhibited different heights of the maximum anthracene

Table 3

FLUORESCENCE OF ISOPROPANOL SOLUTIONS OF NAPHTHACENE AND ANTHRACENE

NAPHTHACENE CONCENTRATION IN ANTHRACENE (ppm-mole basis)	FLUORESCENCE COLOR	FLUORESCENCE INTENSITY		INTENSITY RATIO
		NAPHTHACENE (I 510 mu)	ANTHRACENE (I 405 mu)	R=(I 510/I 405
.60	blue-violet	0	.93	0
53.1	blue	0	1.62	0
219	blue	0 - .03	.94	0 - .032
2180	blue	.13	3.26	.0368
pure naphthacene	none	0	0	0

and naphthacene peaks. This is demonstrated in the data of Tables 4,5,6, and 7 for naphthacene concentrations of 0.6, 22.4, 74.7 and 291 ppm respectively. This can probably be attributed to the mixing operation of the standard alcohol sample with the distilled water, which for each run can result in a different particle size in the colloidal phase. Bowen and Lawley (3) measured the fluorescence of microcrystalline suspensions of anthracene. They report that the intensity of the anthracene emission peak at 405 mu increased as the anthracene particle size decreases. They postulated that these results occur "because much of the fluorescence is unable to escape through the large flat surfaces (of the particles), and undergoes numerous reflexions within the thin layer, emerging at the narrow faces." Change in particle size would bring about changes in the surface-volume ratio of the fluorescing solids. Smaller particles with greater specific surface would show greater emission intensity if the fluorescence is wholly or almost wholly a surface phenomenon.

It is corollary that a decrease in particle size of naphthacene causes an increase in the maximum naphthacene emission peak. This effect of particle size is eliminated in part by use of the intensity ratio which remains relatively constant for a given naphthacene concentration in anthracene and a given colloidal concentration, as may

Table 4

COMPARISON OF FLUORESCENCE INTENSITIES AND RATIO VARIATIONS WITH CONSTANT NAPHTHACENE CONTENT IN A COLLOIDAL SUSPENSION

NAPHTHACENE CONCENTRATION IN ANTHRACENE (ppm-mole basis)	RUN NOS. (n)	FLUORESCENCE INTENSITY ANTHRACENE (I 405)	DEVIATION OF FLUORESCENCE INTENSITY FROM EXP. MEAN (d)	SQUARE OF DEVIATION OF FLUOR. INT. FROM EXP. MEAN (d^2)
.60	1	7.00	−.22	.0484
.60	2	6.98	−.24	.0576
.60	3	8.30	+1.08	1.17
.60	4	6.50	−.72	.519
.60	5	7.30	+.08	.0064
		mean = 7.22	Σ(d) = 2.34	$\Sigma(d)^2$ = 1.80
		FLUORESCENCE INTENSITY NAPH. (I 510)		
.60	1	.180	−.008	.64 (10^{-4})
.60	2	.180	−.008	.64 (10^{-4})
.60	3	.220	+.032	10.2 (10^{-4})
.60	4	.170	−.018	3.24 (10^{-4})
.60	5	.190	+.002	.04 (10^{-4})
		mean= .188	Σ(d) = .068	$\Sigma(d)^2$ = 14.1 (10^{-4})
		INTENSITY RATIO (R=I 510/I 405)		
.60	1	.0257	−.0003	9 (10^{-8})
.60	2	.0256	−.0004	16 (10^{-8})
.60	3	.0265	+.0005	25 (10^{-8})
.60	4	.0262	+.0002	4 (10^{-8})
.60	5	.0260	0	0
		mean = .0260	Σ(d) = .0014	$\Sigma(d)^2$ = 54 (10^{-8})

Table 5

COMPARISON OF FLUORESCENCE INTENSITIES AND RATIO VARIATIONS WITH CONSTANT NAPHTHACENE CONTENT IN A COLLOIDAL SUSPENSION

NAPHTHACENE CONCENTRATION IN ANTHRACENE (ppm-mole basis)	RUN NOS. (n)	FLUORESCENCE INTENSITY ANTHRACENE (I 405)	DEVIATION OF FLUORESCENCE INTENSITY FROM EXP. MEAN (d)	SQUARE OF DEVIATION OF FLJOR. INT. FROM EXP. MEAN (d^2)
22.4	1	5.51	+.05	25 (10^{-4})
22.4	2	4.82	-.64	.41
22.4	3	5.35	-.11	.0121
22.4	4	6.18	+.72	.519
		mean = 5.46	$\sum(d) = 1.52$	$\sum(d)^2 = .944$
		FLUORESCENCE INTENSITY NAPH. (I 510)		
22.4	1	3.01	-.35	.122
22.4	2	2.76	-.60	.256
22.4	3	3.02	-.34	.116
22.4	4	4.63	+1.27	1.61
		mean = 3.36	$\sum(d) = 2.56$	$\sum(d)^2 = 2.10$
		INTENSITY RATIO (R=I 510/I 405)		
22.4	1	.546	-.062	.00384
22.4	2	.573	-.035	.00122
22.4	3	.565	-.043	.00185
22.4	4	.749	+.141	.0199
		mean = .608	$\sum(d) = .281$	$\sum(d)^2 = .0267$

Table 6

COMPARISON OF FLUORESCENCE INTENSITIES AND RATIO VARIATIONS WITH CONSTANT NAPHTHACENE CONTENT IN A COLLOIDAL SUSPENSION

NAPHTHACENE CONCENTRATION IN ANTHRACENE (ppm-mole basis)	RUN NOS. (n)	FLUORESCENCE INTENSITY ANTHRACENE (I 405)	DEVIATION OF FLUORESCENCE INTENSITY FROM EXP. MEAN (d)	SQUARE OF DEVIATION OF FLUOR. INT. FROM EXP. MEAN (d^2)
74.7	1	2.69	+.24	.0576
74.7	2	2.55	+.10	.010
74.7	3	2.02	-.43	.185
74.7	4	2.40	-.05	.0025
74.7	5	2.58	+.13	.0169
		mean= 2.45	$\sum(d) = .95$	$\sum(d)^2 = .272$
		FLUORESCENCE INTENSITY NAPH. (I 510)		
74.7	1	5.09	+.32	.102
74.7	2	4.91	+.14	.0196
74.7	3	3.68	-1.09	1.19
74.7	4	4.36	-.41	.168
74.7	5	5.88	+1.11	1.23
		mean =4.77	$\sum(d) = 3.07$	$\sum(d)^2 = 2.71$
		INTENSITY RATIO (R=I 510/I 405)		
74.7	1	1.89	-.05	.0025
74.7	2	1.93	-.01	.0001
74.7	3	1.82	-.12	.0144
74.7	4	1.82	-.12	.0144
74.7	5	2.25	+.31	.096
		mean =1.94	$\sum(d) = .51$	$\sum(d)^2 = .127$

Table 7

COMPARISON OF FLUORESCENCE INTENSITIES AND RATIO VARIATIONS WITH CONSTANT NAPHTHACENE CONTENT IN A COLLOIDAL SUSPENSION

NAPHTHACENE CONCENTRATION IN ANTHRACENE (ppm-mole basis)	RUN NOS. (n)	FLUORESCENCE INTENSITY ANTHRACENE (I 405)	DEVIATION OF FLUORESCENCE INTENSITY FROM EXP. MEAN (d)	SQUARE OF DEVIATION OF FLUOR. INT. FROM EXP. MEAN (d^2)
291	1	1.37	+.06	.0036
291	2	1.25	-.06	.0036
291	3	1.49	+.18	.0324
291	4	1.21	-.10	.01
291	5	1.24	-.07	.0049
		mean = 1.31	$\Sigma(d) = .47$	$\Sigma(d)^2 = .0545$
		FLUORESCENCE INTENSITY NAPH. (I 510)		
291	1	9.53	-.87	.756
291	2	9.51	-.89	.793
291	3	10.9	+.50	.25
291	4	10.49	+.09	.0081
291	5	11.3	+.90	.81
		mean =10.4	$\Sigma(d) = 3.20$	$\Sigma(d)^2 = 2.62$
		INTENSITY RATIO (R=I 510/I 405)		
291	1	6.95	-.99	.980
291	2	7.61	-.33	.109
291	3	7.31	-.63	.397
291	4	8.66	+.72	.519
291	5	9.18	+1.24	1.54
		mean = 7.94	$\Sigma(d) = 3.91$	$\Sigma(d)^2 = 3.54$

be seen from the values listed in Table 8. The precision of the duplicate determinations of intensity ratio is ± 1.4, ± 15.5, ± 9.3 and ± 10.6 percent relative standard deviation for a collidal suspension containing 0.6, 22.4, 74.7 and 291 ppm naphthacene concentration in anthracene. These results indicate the superiority of the fluorescence intensity ratio, R, as a reliable measure of naphthacene content.

Concentrations as low as 0.1 ppm naphthacene in anthracene can be determined by fluorescence measurements using the colloidization technique. The sensitivity of this method can probably be extended to 0.01 ppm naphthacene content by further optimization of the technique, such as optimum colloidal concentrations, a purer standard and a more sensitive photomultiplier tube particularly in the 510 mu range. The R.C.A. 1P22 photomultiplier tube is suggested since it is twice as sensitive at this level as is the R.C.A. 1P28 which was used in all determinations. It should be noted that little amplification of the photomultiplier tube output was required with the colloidal suspensions tested. The spectrofluorometer was capable of amplification 100 fold beyond the range utilized. A more sensitive photomultiplier tube at the 510 mu level would, however, permit resolution of naphthacene at lower concentrations. Resolution at this point appears to limit the sensitivity of the method.

Table 8

DEVIATIONS OF FLUORESCENCE INTENSITIES AND RATIO FROM THE MEAN EXPERIMENTAL VALUE FOR COLLOIDAL SUSPENSIONS OF NAPHTHACENE AND ANTHRACENE

NAPH. CON. IN ANTH. (ppm)	AVERAGE DEVIATION FROM MEAN $(\Sigma(d)/n)$	STANDARD DEVIATION $S=\sqrt{\Sigma(d)^2/(n-1)}$	PERCENT RELATIVE STANDARD DEVIATION (S/mean)100	RANGE	CONFIDENCE INTERVAL (95%) (±)
FLUORESCENCE INTENSITY OF ANTHRACENE (I 405 mu)					
.60	.47	.67	9.3	1.80	.9
22.4	.38	.56	10.3	1.36	.9
74.7	.19	.26	10.7	.67	.3
291	.094	.116	8.74	.28	.1
FLUORESCENCE INTENSITY OF NAPHTHACENE (I 510 mu)					
.60	.014	.019	10.1	.05	.03
22.4	.64	.84	25	1.87	1
74.7	.614	.82	17.1	2.12	1
291	.64	.81	7.8	1.79	.9
INTENSITY RATIO (R = I 510/ I 405)					
.60	.00028	.00037	1.4	.0009	.0005
22.4	.07	.094	15.5	.263	.1
74.7	.122	.18	9.3	.13	.2
291	.78	.84	10.6	2.23	1

PURIFICATION TECHNIQUES OF ANTHRACENE

Synthesis of Anthracene

Experimental Technique. Anthracene was prepared by synthesis from anthraquinone using the method described by Fieser (10). Anthracene so produced should be free of the natural contaminates found in the coal tar anthracene.

Results. The prepared anthracene was analysed by the fluorescence technique and is listed as sample 6 in Table 9. The synthetically prepared anthracene contains 0.810 ppm of naphthacene. Although the solid crystal is slightly yellow in color, the colloidal suspension fluoresces a blue-violet. It is apparent that anthracene so prepared is surpassed in purity only by zone refined (sample 15) and multiple co-distilled (sample 13) anthracene.

Washing Anthracene

Experimental Technique. Crude anthracene, 90 - 95% practical grade anthracene, Baker Catalog number AX1600 was washed four times with small portions of cold acetone using the standard technique described by Adams and Johnson (1).

Results. Washed anthracene from crude coal tar anthracene does not appear to show any significant improvement over the untreated crude anthracene as shown in Figure 5. The analysis of washed (sample 2) and untreated crude anthracene (sample 1) is given in Table 9. Crude anthracene and washed anthracene

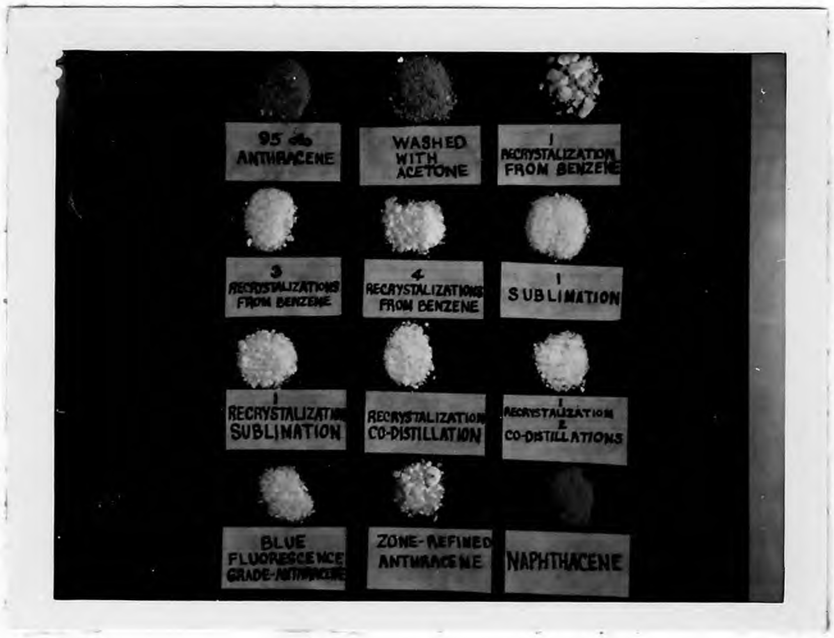


FIGURE 5, COMPARISON OF PURIFICATION TECHNIQUES OF ANTHRACENE

Table 9

ANALYTICAL RESULTS OF COLLOIDAL ANTHRACENE SAMPLES

SAMPLE NO.	SOURCE OF ANTHRACENE	DESCRIPTION		FLUORESCENCE INTENSITY		INTENSITY RATIO R	NAPHTHACENE CONTENT (PPM)
		COLOR OF SOLID	FLUORESCENCE COLOR IN COLLOIDAL SUSPENSION	ANTH. (I 405mu)	NAPHTH (I 510mu)		
1	95% Anthracene Eastman P480 (CRUDE)	Brown	Green	1.42	5.22	3.68	125
2	Crude, washed	Brown-yellow	Green	1.58	5.27	3.34	110
3	Crude, washed recrystallized	Green-white	Green	2.10	6.12	2.91	97
4	Crude, washed recrystallized 3 times	Pale yellow-green	Blue-green	4.00	2.50	0.625	18.0
5	Crude, washed recrystallized 4 times	white (slight pale green)	Blue	5.60	2.77	0.495	14.0
6	Crude, Sublimed	Yellow	Blue-green	4.20	3.70	0.881	26.0
7	Crude, sublimed recrystallized	Pale yellow	Blue-green	5.21	3.00	0.576	16.8

Table 9 (Continued)

SAMPLE NO.	SOURCE OF ANTHRACENE	DESCRIPTION		FLUORESCENCE INTENSITY		INTENSITY RATIO (R)	NAPHTH. CONTENT (PPM)
		COLOR OF SOLID	FLUORESCENCE COLOR IN COLLOIDAL SUSPENSION	ANTH (I 405mu)	NAPHTH (I 510mu)		
8	Prepared from anthraquinone	Slight yellow	Blue-violet	5.32	0.20	0.0376	0.810
9	Crude, *dimerized heated	Green	Green	1.43	5.12	3.58	119
10	Crude, co-distilled	White	Blue-violet	11.0	1.35	0.1228	3.00
11	Crude, washed, recrystallized, co-distilled	White	Blue-violet	6.00	0.600	0.100	2.50
12	Crude, washed, recrystallized, co-distilled twice	White	Blue-violet	6.8	0.37	0.0544	1.20
13	Crude, washed, recrystallized, co-distilled 3 times	White	Blue-violet	7.57	0.18	0.0237	0.47

* The dimer of anthracene (dianthracene) was analyzed as a colloidal suspension. The suspension did not show visible fluorescence and the fluorescence intensity at 405 mu and 510 mu was 0 and 0 respectively.

Table 9 (Continued)

SAMPLE NO.	SOURCE OF ANTHRACENE	DESCRIPTION		FLUORESCENCE INTENSITY		INTENSITY RATIO (R)	NAPHTH. CONTENT (PPM)
		COLOR OF SOLID	FLUORESCENCE COLOR IN COLLOIDAL SUSPENSION	ANTH (I 405mu)	NAPHTH (I 510mu)		
14	Blue-violet Fluorescent grade Matheson, Coleman	White	Blue-violet	7.10	0.50	0.0704	1.60
15	Fisher scientific zone refined	White	Blue-violet	8.0	0.23	0.0288	0.68
16	Prepared from Anthraquinone, zone refined	White	Blue-violet	7.21	0.187	0.0260	0.60

from crude contain 125 and 110 ppm naphthacene respectively. The fluorescence of colloidal suspensions of both materials is a deep green color.

Recrystallization

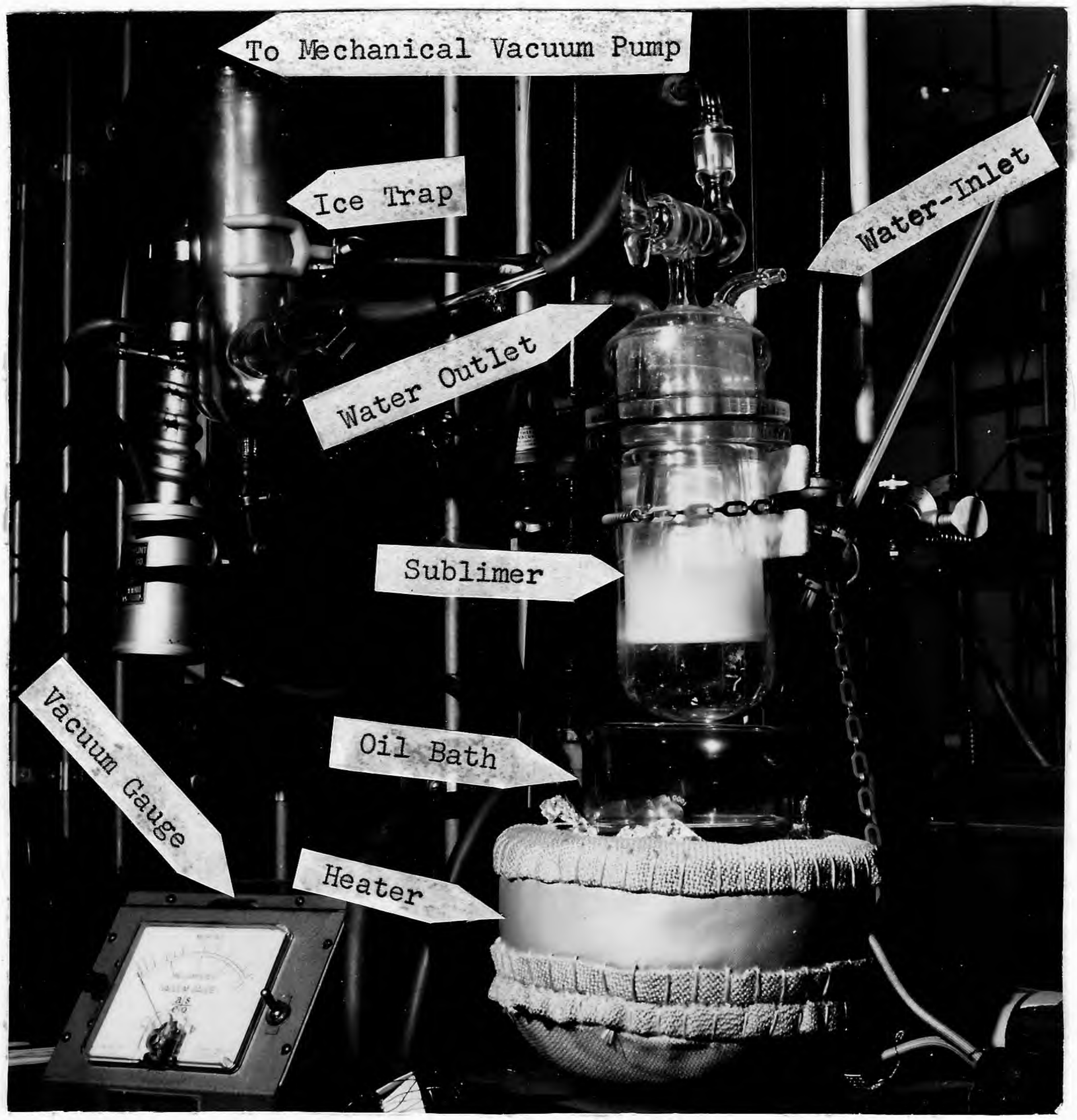
Experimental Technique. Crude washed anthracene was recrystallized from a benzene solution four times in succession using crystallization procedures described by Adams and Johnson (1).

Results. One crystallization from benzene visually improves the appearance of crude washed anthracene as shown in Figure 5, although the naphthacene content is only slightly changed (Table 9) from 110 ppm to 97 ppm. Three and four recrystallizations yield a material containing 18 and 14 ppm naphthacene respectively (samples 4,5). After four recrystallizations the anthracene sample appears white and in a colloidal suspension fluoresces blue.

Sublimation

Experimental Technique. Six to ten grams of crude anthracene were charged into the McCarter vacuum sublimation apparatus shown in Figure 6. The sublimer has a 70 mm O.D. lower section and the flat grind is 70 mm, and grooved for an O-ring. The jacket for the condenser is 57 mm O.D.

FIGURE 6, VACUUM SUBLIMATION APPARATUS



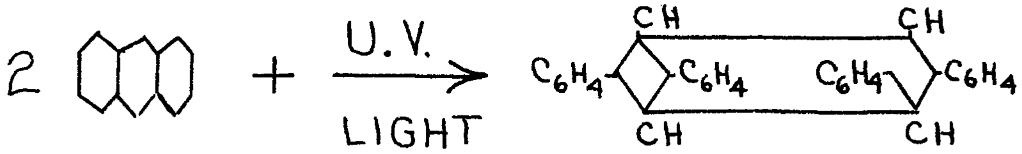
and the bottom of the cone opening is 45 mm in width. Sublimate forms on the inside surface of the cone and is easily removed by scraping. The system is evacuated to 8-20 microns of mercury by a mechanical vacuum pump. Heat is then supplied to the oil bath by a heating mantle. It is important not to heat the system before evacuation since anthracene oxidizes at elevated temperatures in air. The temperature of the system is kept constant at 110°C by a Thermo-O-Watch Controller, limit model L-6.

Results. Sublimation proves to be a far superior method for purifying anthracene than the recrystallization method. Crude anthracene subjected to sublimation (sample 6) forms yellow powdery crystals containing 26 ppm naphthacene. In a colloidal suspension the material fluoresces blue-green as indicated in Table 9. During operation, the condenser of the sublimer develops a series of condensed anthracene layers which exhibit successive changes in color from white, yellow, yellow-green to green. Sublimation should be suspended when the yellow layer first appears. This usually occurs when 70-75% of the charge has been sublimed.

A second sublimation does not produce a purer product, but a subsequent recrystallization from benzene solution gives a reasonably good material (sample 7) containing 16.6 ppm of naphthacene. The main disadvantages of sublimation is the small size of charge and slowness of operation (2 - 3 hours).

Dimerization of Anthracene

When solutions of anthracene are exposed to direct sunlight or ultraviolet light (310-375 millimicrons) dimerization occurs depositing dianthracene as a relatively inert and sparingly soluble compound. The reaction is:



Pringsheim (32) suggests that the absorption of the exciting light brings the anthracene molecule directly into the electronic state from which emission can take place. The molecule is highly reactive while in this state, and if a substance with which it can react (a second excited anthracene molecule) is present, reaction may occur before the molecule returns to the ground state with fluorescence emission. The reacting molecules are "quenched" and the dimer should show no fluorescence characteristics. The dimer is reported (35) to melt at 270-280°C with the reformation of anthracene.

Experimental Technique. A one to two per cent solution of crude anthracene in xylene is irradiated by ultra-violet light (310—375 millimicrons) for periods up to seventeen hours. A glass cooling coil is inserted into the reaction beaker to keep the temperature in the range of 21-31°C. A magnetic stirrer is employed to increase the surface area in contact with the ultra-violet rays. The insoluble dimer is filtered and washed with fresh solvent. Attempts to sublime anthracene or other volatile impurities from dianthracene at temperatures below 200°C and pressures of 50 microns showed that such volatile materials were not present. The dimer is converted back to anthracene by heating, in a nitrogen atmosphere, to 180-270°C. The decomposition temperatures of the dimer were studied by means of differential thermal analysis.

A second method of converting dianthracene to anthracene was employed by subjecting dianthracene to repeated zone refining in a nitrogen atmosphere at temperatures slightly above the melting point of anthracene monomer. After five passes of the heater, (1.3 inches per hour) the dimer is completely converted to anthracene as noted by the complete melting of the material in the direct area of the zone refiner heater.

Naphthacene (Matheson, Coleman and Bell Co., catalog no. 9082, melting point 340-342°C) was subjected to the same techniques as described above for anthracene to determine if a dimer is formed when exposed to ultra-violet rays.

Table 10

DIMERIZATION OF ANTHRACENE TO DIANTHRACENE

Run 1

Charge - 4.375 g. anthracene, 700 ml xylene

TIME (min.)	TEMPERATURE SOLUTION (°C)	YIELD (grams)	PER CENT YIELD (wt.)
0	21	0	0
115	27	0.6805	15.6
235	29	1.2308	28.2
445	31	1.8771	42.9
625	31	2.2695	51.9

Run 2

Charge - 7.1607 g. anthracene, 175 ml. xylene

TIME (min.)	TEMPERATURE SOLUTION (°C)	YIELD (grams)	PER CENT YIELD (wt.)
0	22	0	0
330	28	1.8194	25.4
1010	31	4.315	60.1

Results. The conversion of anthracene to dianthracene using ultra-violet light as a function of exposure time is summarized in Table 10. A study of the thermal decomposition of dianthracene by means of differential thermal analysis indicates a melting point for the dimer of 266.3°C. With rapid heating, there was no evidence of anthracene in the sample. However, with slow heating rates, decomposition started at 160°C and continued at an accelerating pace until it was complete at about 270°C. Such samples, on re-freezing showed complete reconversion to anthracene, melting at 214.5°C. The zone refining of dianthracene, a technique not previously reported in the literature, converted the dimer to exceptionally high yields of blue-fluorescent anthracene (42 passes at a rate of 1.3 inches per hour).

Analysis of the dimer by the fluorescence technique, shown in Table 9 indicates that the dimer exhibits no fluorescence chracteristics as predicted by Pringsheim (32).

Pure naphthacene did not form a dimer after 10 hours of exposure to ultra-violet light. This would seem to indicate that complete separation of anthracene and naphthacene is possible by the dimerization technique. However, fluorescence analysis of the anthracene formed (sample 9) from the dimer, which has been decomposed back to anthracene does not appear to show a significant improvement over untreated crude anthracene. It is postulated that these results occur because naphthacene dimerizes to some extent when in solution with anthracene forming either a naphthacene dimer or a naphthacene-anthracene dimer. This can be related to the fact that pure naphthacene shows no fluorescence characteristics. In a solid solution with anthracene the naphthacene fluoresces by means of sensitized fluorescence or excitation migration.

In a similar manner the naphthacene molecules are excited into the electronic state where they are highly reactive and can react with a second activated naphthacene molecule to form the dimer.

Co-distillation of Anthracene

The co-distillation of anthracene with ethylene glycol (8) has been used by Mikada (26), Feazle and Smith (9) and by Musicant (25) to produce anthracene equivalent to commercially available scintillation grades.

Apparatus. The apparatus used for co-distilling anthracene is shown schematically in Figure 7. The design of the apparatus is a modification of one suggested by Musicant (25). The condenser chamber consists of a 4 inch O.D. by 13 inch long section of Pyrex. The chamber is loosely fitted with a grooved aluminum top containing 1/4 inch O.D. copper tubing which serves as a cold finger condenser. The aluminum top also acts as a safety release in case of excessive pressure. A nickel-chromium wire screen is placed in the bottom of the chamber to collect condensed anthracene. Thre reactor is a two-neck, 500-ml Pyrex round bottom flask. A plug of cotton is placed in the connecting section between the reactor and the condenser chamber to prevent vapors from flowing directly into the bottom of the condenser chamber. A 1/2 inch resistance heater tape is employed to prevent condensation of anthracene in the 3/4 inch O.D. side tube. Heat is supplied to the reactor by a heating mantle. All joints are ball joints to enable assemblage of the apparatus.

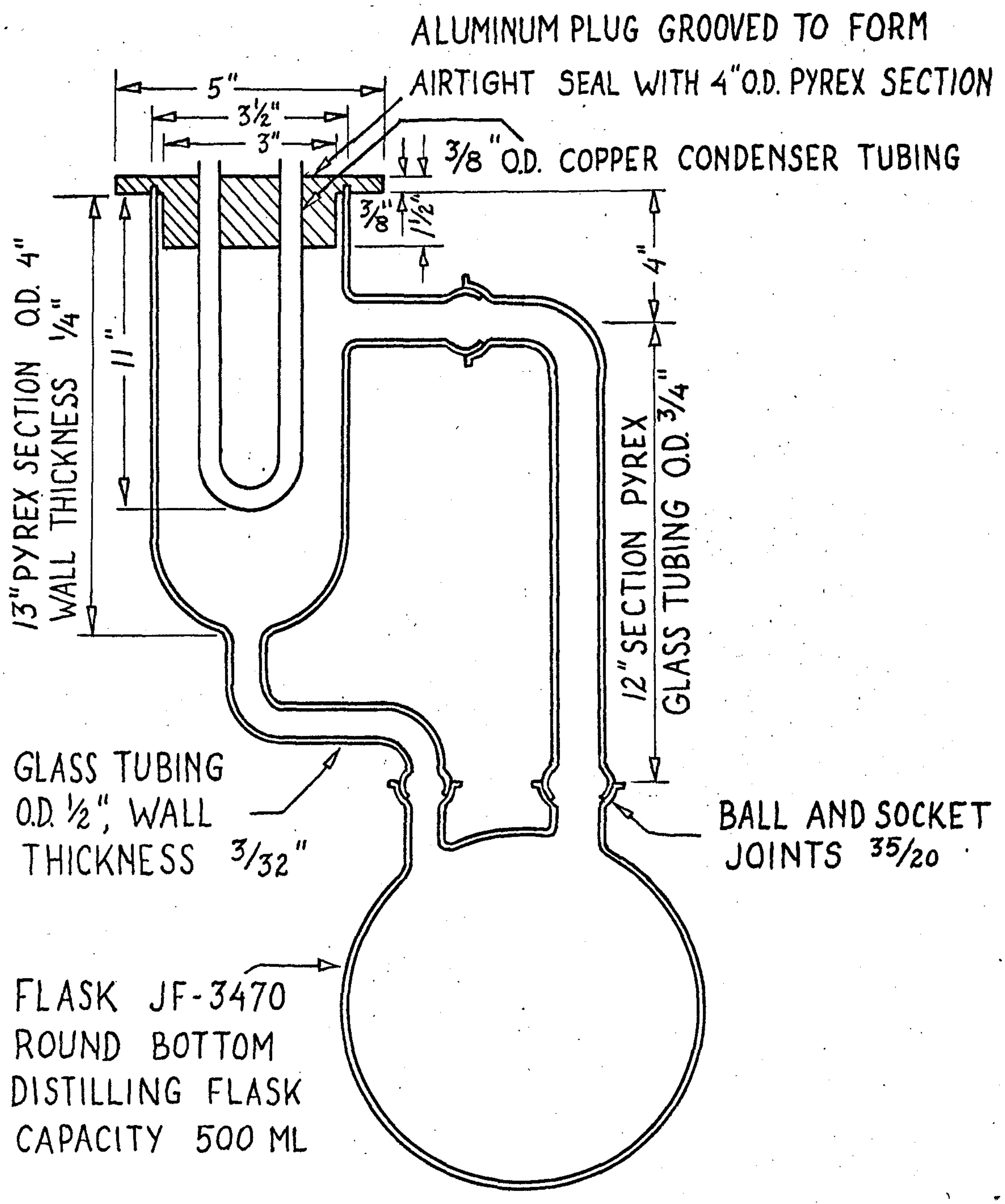


FIGURE 7
CO-DISTILLATION APPARATUS
NEWARK COLLEGE OF ENGINEERING
MELVIN DRUIN
SCALE : 1.5" = 12"

Experimental Technique. Twenty five grams of washed, once-recrystallized anthracene and 300 ml of ethylene glycol are charged directly into the round bottom flask. Powerstats supplying power to the resistance tape and the heating mantle are set at 65 and 100 volts respectively. Anthracene is condensed as fine particles on the cold finger condenser, sides of chamber wall and on the wire screen while ethylene glycol is recycled back to the round bottom flask. Heating is discontinued after 8-10 hours. Anthracene is then filtered and washed 4 or 5 times with distilled water to remove adhering ethylene glycol.

The original anthracene was co-distilled three successive times and various samples so obtained were analyzed. The results are reported in Table 9.

Crude anthracene was also co-distilled once with ethylene glycol and analyzed by the fluorescence technique as reported in Table 9.

Results. Table 9 gives the analytical results on the co-distilled anthracene analyzed by the fluorescence technique. The co-distillation of anthracene with ethylene glycol proves to be the most superior purification technique encountered (see Figure 5). The material so obtained is believed to be adequate for crystal growth and subsequent electrical measurements. One co-distillation, two co-distillations and three co-distillations of washed, once-recrystallized anthracene produce scintillation grade anthracene of 2.50 ppm, 1.20 ppm and 0.470 ppm naphthacene content. It is apparent that anthracene so prepared is purer than commercially available zone refined (sample 15) and synthetically prepared-zone refined (sample 16) anthracene of 0.68 ppm and 0.60 ppm naphthacene content respectively.

Co-distilled anthracene prepared from crude coal tar anthracene contains 3.00 ppm naphthacene. This indicates that washing and recrystallization prior to co-distillation is not needed.

Zone Refining of Anthracene

The theory and technique of zone refining as first disclosed by Pfann (30) has been applied to organic compounds by Henington, Handley and Cook (17), Wynne (44) and by Czorny (7). The basis for zone refining is the passage in one direction of a series of molten zones through a rod of impure material. Impurities, in the charge, travel with or opposite to the zone depending on their ability to raise or lower the melting point of the material.

The full details of the purification of anthracene by zone refining can be found in the thesis by Czorny (7).

The following is quoted from the Abstract of this thesis.

> "The segregation coefficient of anthracene from naphthacene was found to be about 0.6 at a refining rate of 3 in./hr. Calculations showed that 60 zone passes are required for ultimate purification under the experimental conditions employed here. This was confirmed by experiment."

Experimental Technique. A Fisher zone refiner with an automatic recycle was employed by the author to zone refine anthracene and dianthracene (see page 39). The material to be zone refined is introduced as a fine powder into a heavy walled Pyrex tube sealed at one end, 6 mm I.D. by 2 mm wall thickness. The tube is sealed off under a nitrogen atmosphere using the same technique employed for the crystal containers (see page 99). The number of cycles made by the heating element were recorded on a Bristol temperature recorder according to the technique described by Gumprecht (14). Instead of inserting the thermocouple into the material being refined as suggested by Gumprecht the thermocouple was taped to the outside surface of the Pyrex tube at a point corresponding to the beginning of the heating cycle.

Results. Zone refining of anthracene produces highly purified materials believed adequate for single crystal growth as indicated in Table 9. Anthracene so prepared is second only to multiple co-distilled material in naphthacene content. The main disadvantages of zone refining are the excessive number of zone passes required (60 passes at a rate of 1.5 inches per hour) and the relatively small size of charge.

CONCLUSIONS AND RECOMMENDATIONS OF PURIFICATION OF ANTHRACENE

The most promising methods of purification of anthracene, which were chemical synthesis, washing, recrystallization from solvents, sublimation, dimarization, co-distillation and zone refining have been investigated. The relative merits of each method were explored and discussed with particular attention to co-distillation which is considered by the author to be the most applicable. Both crude coal tar anthracene and washed, once-recrystallized anthracene have given material of comparable purity by co-distillation. Therefore it is recommended that the processes of purification of crude anthracene prior to single crystal growth be three successive co-distillations with ethylene glycol.

METHODS OF GROWING SINGLE CRYSTALS

A single crystal is a monolithic solid in which the molecules are arranged in a regularly repeating pattern. Many techniques have been developed for growing single crystals of organic compounds. It is the purpose of the author to grow organic single crystals with controlled amounts of crystal imperfections and selected impurities. This involves stringent requirements both on the selection of the method of crystal growth and the implementation of the technique.

In general, the method selected for the growth of single crystals depends on the chemical properties, crystal structure, and the melting point of the material. Due to differences in these properties, a method suitable for growing crystals of one material may be quite useless for another material. Many trials are often necessary before good crystals of a given material may be produced. Crystals growing is often more a combination of art and "divine faith" than a science. Buckley (6) has written, "It should be remembered that, in the preparation of large clear crystals, the touch of the artist is about as important as the application of established scientific principles."

From Sublimation

Single crystal flakes of anthracene have been produced by Lipsett (22) and Nakada (26) by means of sublimation. The chief advantages of this method are that the crystal grown is not contaminated with a solvent and the crystal flakes are convenient for resistivity measurements as slicing is not required. However, crystal habit (nucleation orientation) cannot be controlled.

From Solution

Techniques for growing single crystals of anthracene have been reported by Lipsett (22) and by Kallman and Pope (20). Advantages of growth of crystals from solution are that less demand is placed on power supplies, low temperatures well below the melting point of the pure substance are employed, and the problem of finding a suitable crucible material is non-existent. Contamination of the crystal with a solvent is a problem. The rate at which crystals can be grown from solutions is generally much smaller than the rate of growth from the pure melt. Common rates of linear growth from solution are in the order of 10^{-2} cm per hour, while rates from the pure melt are centimeters per hour.

From The Melt

In the past the most successful technique for preparing single crystals has been growth from the melt, composition of the melt being near that of the desired crystal. Although first used for metals, the method is suitable for the growth of organic crystals. The main advantages are that contamination of the crystal with a solvent is non-existent, large growth rates are possible and large single crystals can be prepared. Many organic materials cannot be grown into single crystals from the pure liquid phase because the substance melts with irreversible decomposition and there exists a solid state phase transformation between the melting point and the temperature to which the crystal is finally cooled. Single crystal growth from the melt can be accomplished in a wide variety of methods. These include: Tammann's method of growing single crystals, the method of Obeimov and Schubnikov, Bridgman's method, Kapitza's method, Czochralski's method, the method of Nacken, the method of Kyropoulos and the method of Stober. Detailed description of each method are given by Buckley (6).

From the Melt by the Bridgman Method. The method of Bridgman (5) has been used successfully for the growth of large single crystals of anthracene by Lipsett (21,22), Nakada (26), Sangster and Irvine (36), Feazel and Smith (9), and Pimentel and McClellan (31). The principle of this method is as follows. A specially shaped container is filled with the material to be grown into a crystal. The crystal is grown in an inert atmosphere from the melt in the sealed container which is slowly lowered through a temperature discontinuity which includes the freezing point of the substance. Crystallization of the melt occurs progressively upwards from the bottom of the container as it is lowered through the temperature discontinuity. The furnaces employed in the use of the Bridgman technique are designed so as to produce a large temperature gradient along the path of the moving container at the point of crystallization. The lowering of the container must be slower than the velocity of crystallization in the direction of the container. If the velocity is faster, portions of the melt will be forced to solidify before the orientating influence of the advancing crystal face has reached the section. The result is the formation of a differently orientated crystal. If the purity of material, the thermal conditions in the furnace, the shape of the container and the rate of lowering the container are suitable, a single crystal can be grown.

DESIGN CRITERIA

The growth of single crystals by the Bridgman method depends on the design of a suitable crystal growing apparatus and auxiliary equipment with the following design criteria:

(a) establishment and control of the correct temperature distribution within the furnace

(b) crystal container which initiates growth at a single point or constriction

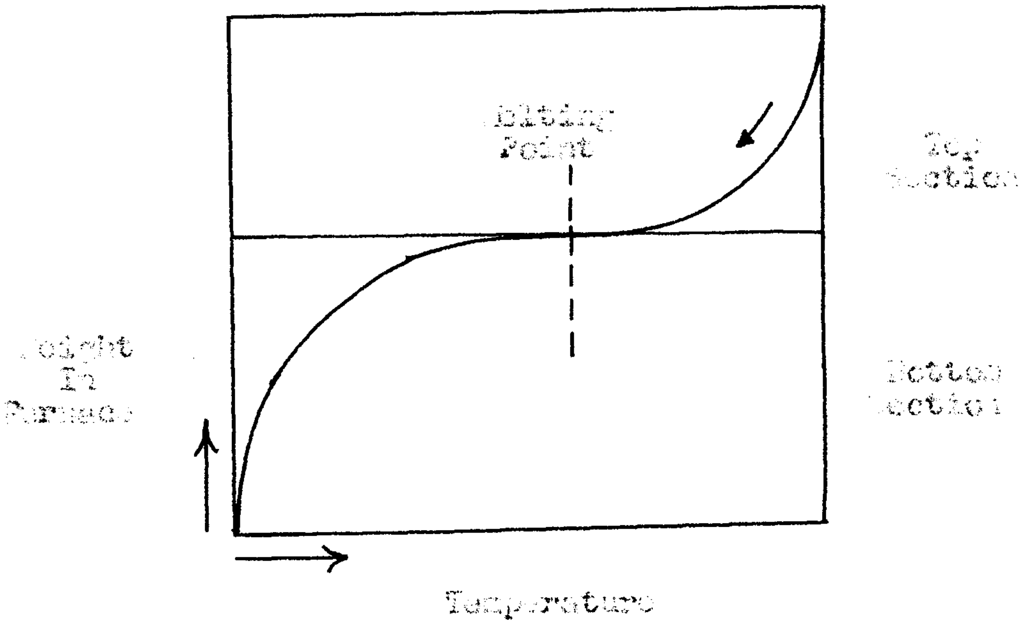
(c) convenience in operation involving the insertion and removal of the crystal container and the inspection of the material in the container during melting and growth

(d) a lowering mechanism which lowers the container smoothly and continuously through the furnace at constant rates of the order 0.5 to 3 inches/day

(e) a convenient operation in maintenance of the furnace

Temperature Gradient Within The Furnace

The ideal form of a temperature gradient as recommended by Lipsett (22) is shown schematically.



> "The temperature at the top of the furnace is in the upper right-hand corner of the diagram. This should not be high enough to cause any decomposition of the material. The temperature in the top section of the furnace should decrease fairly gradually until the lowest part of the top section is reached, and then should abruptly drop. The heat input to the furnace should be adjusted so that the melting point of the material is approximately in the mid-point of the sharp temperature drop. In the bottom section of the furnace the temperature may fall off more rapidly than in the top, provided the fall is not so large as to interfere with the annealing of large crystals, and if convenient the temperature at the bottom of the furnace may be that of the room." (22)

The horizontal gradient, in any horizontal plane of the furnace, should be uniform (horizontal). This condition is attained through proper insulation of the furnace.

Crystal Container

Material of Construction. The melt and the growing crystal are housed in the same container. Since the melt phase is in intimate contact with the container wall, there must not be any reaction between the melt and the container material. Should reaction occur, the melt phase becomes contaminated with the container material. The container material must also have a thermal coefficient of expansion close to that of the crystal. If this condition is not satisfied and the grown portion of the crystal tends to stick to the container as they are being cooled, large stresses caused by differential thermal contraction will arise between the container and the crystal. A small disturbance such as a chemical reaction or an imperfection in the container wall may induce nucleation which may prevent single crystal growth. Thus it is important to select a material of construction for the crystal container that has a smooth, non-reactive surface.

The object of all crystal containers is to initiate the growth of a single crystal at a constriction or point. Should the wall of the container above the constriction slope gradually outwards to the full diameter, the chances of obtaining a good single crystal are increased. A crystal container may be designed either to produce a seed crystal (large single crystals are later grown in another container from the seed) or a single crystal by a process of self-seeding.

Self-seeding. Tammann (41) was the first to grow single crystals by the method of self-seeding. He constructed a tube of uniform cross section and tapered it to a fine capillary at one end. As the bottom section is first cooled below the melting point, several seeds of different orientation are produced. Certain directions are more suitable for the rapid extension of the crystal. Providing the tube is long enough, one of the seeds would have the opportunity to grow outwards to the full diameter by squeezing to one side all other grains. The narrower the tube, the shorter the length of tube required. Statistically there will be fewer competing grains, the narrower the tube.

Seed Crystal. Some investigators have used seed crystals to grow single crystals (22,29,40). A section of a seed crystal grown is introduced into another container with new material added above the seed. The main disadvantage with using seed crystals is that it is impossible to see the liquid-solid interface. Thus it is difficult to control growth on the seed and still be certain that the seed itself is not completely melted.

Convenience of Operation of the Furnace

The crystal container should be inserted and removed from the furnace with little difficulty in a period of

5-10 minutes. The furnace should not have to be disassembled during this operation.

During melting and growth the condition of the material should not be determined by having to lift the container momentarily out of the furnace. The sudden change in temperature will produce large stresses in the crystal which can cause dislocations and other imperfections.

Lowering Mechanism

The crystal container must be lowered smoothly and continuously through the furnace at a constant rate of the order of 0.5 to 3 inches per day. These rates have proved successful for single crystal growth of anthracene by the Bridgman technique (9,21,22,36). The rate of growth is dependent on the rate of diffusion of the latent heat of fusion at the liquid-solid interface. The rate must be such that the temperature of the growing nucleus is less than its melting point. The rate of growth is also dependent on the rate of formation of nuclei large enough to grow at the temperature of the liquid-solid interface.

Convenient Operation in Maintenance of the Furnace

A well designed furnace requires little maintenance. The most likely malfunction of the furnace would be in the resistance heaters. All heater leads should be connected to external wiring by means of short screws and nuts. It has been found (21) that hard soldered joints at these points tend to break after a number of heating and cooling cycles. The furnace should also be designed with ease in operation and maintenance in mind. Each section of the furnace should be independently maintained, that is, one section at a time can be disassembled.

DESCRIPTION OF FURNACE

The furnace is a modification and refinement of one described by Lipsott (21) and is composed of six major parts; the upper heating zone, the lower heating zone, the bottom section and three transite plates. Each heating zone consists of an inner Pyrex tube heated by a wrapping of resistance wire and an outer Pyrex pipe which provides thermal insulation.

The Upper Heating Zone

The upper heating zone consists of an outer Pyrex pipe section conforming to the dimensions shown in Figure 8, and an inner heated Pyrex tube section shown in Figure 9. The ends of both sections have been ground square and fire polished. Three 24/40 standard taper outer joints sealed to the Pyrex pipe allow for temperature measurements and control. The Pyrex pipe is insulated with a covering of aluminum foil, 3/4-inch thick magnesia (rolled diameter of 4.5 inches) and an outer cover of cheese cloth painted with three coats of a saturated solution of sodium silicate in water. Holes are cut at intervals in the insulation to serve as windows. These windows allow observation of the progress of melting and growth. When not in use, these holes are plugged with glass wool. The crystal may easily be viewed by holding a light against a

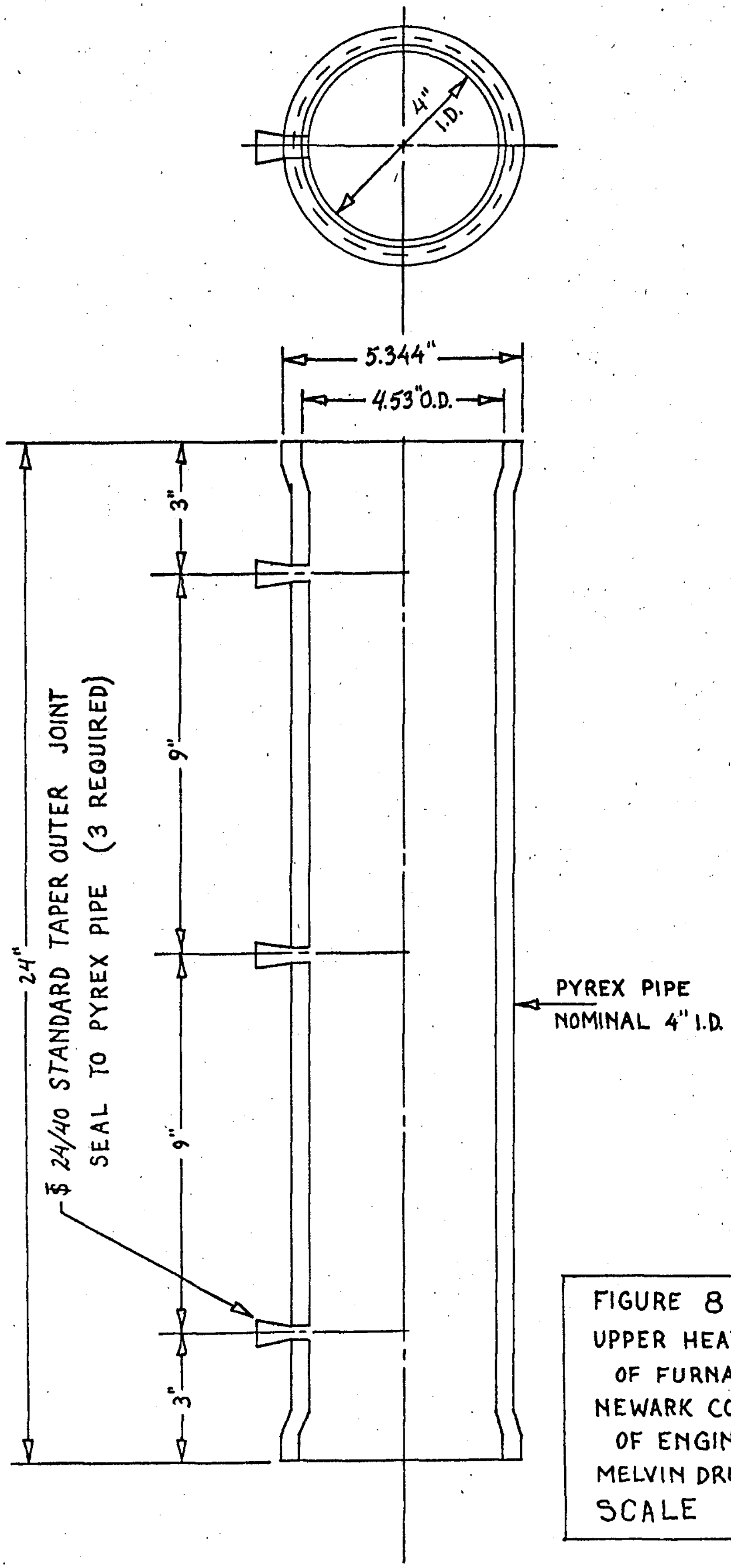
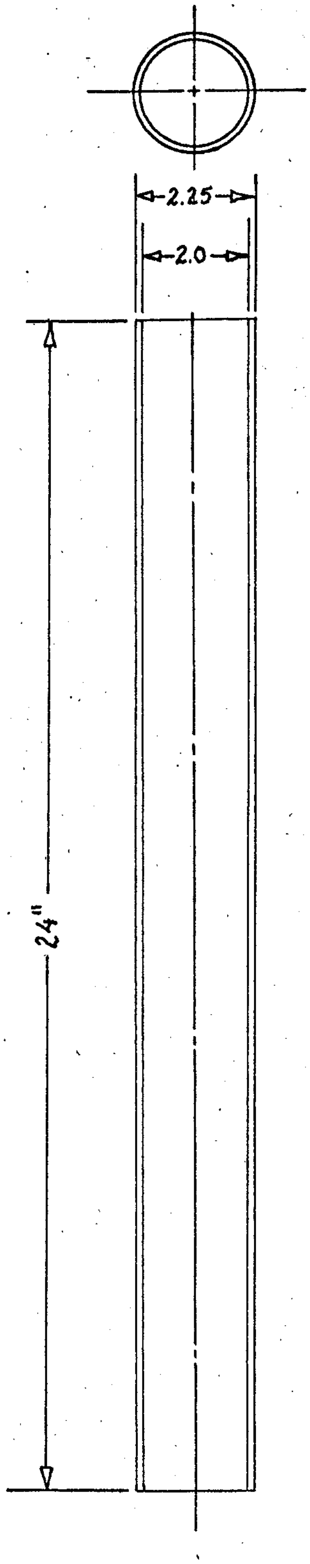


FIGURE 8
UPPER HEATING ZONE
OF FURNACE - SECTION 1, PART A
NEWARK COLLEGE
OF ENGINEERING
MELVIN DRUIN
SCALE 3" = 1'-0"



PYREX TUBING
MEDIUM WALL
ENDS CUT SQUARE
AND FIRE POLISHED
G-8530

FIGURE 9
UPPER HEATING ZONE
OF FURNACE - SECTION 1, PART B
NEWARK COLLEGE
OF ENGINEERING
MELVIN DRUIN
SCALE 3" = 1'-0"

window while looking in at a directly opposite window. The insulation also shields from light any material to be grown into a crystal which is sensitive to photochemical reactions (under certain conditions this is the case for anthracene).

The inner Pyrex tube has three separately controlled resistance heaters R_1, R_2 and R_3 shown in Figure 18, which create the temperature gradient along the length of tubing. The heaters are each made of 20 feet of 22 gage chromel resistance wire, wound at 3/16 inch spacings covering a section 7.5 inches in length. Each heater was constructed in the following manner:

(a) Three strips of ½" asbestos tape were moistened and applied vertically to the inner Pyrex tube, spaced at 120° intervals.

(b) Two strips of asbestos tape were moistened and applied circumferentially about the inner Pyrex tube at both ends of the heating section.

(c) The asbestos strips were dried with a heating lamp. When dry, the strips adhered to the walls of the Pyrex tube.

(d) The resistance wire was attached to the asbestos strip at one end of the heating section and wrapped tightly around the Pyrex tube. Care was taken to maintain the correct spacing between turns.

The total resistance per heater, including two 2.5—foot long leads, is 21 ohms. Each lead was insulated with sections of Pyrex tubing and led through a 1/8 inch diameter hole in the top transite plate (Figure 13) to a terminal strip bolted directly to the top transite plate. At the terminal strip further wiring connections were made to power leads. By selecting a total resistance per heater of 21 ohms the furnace might prove useful for growing crystals with melting points considerably higher than that of anthracene.

The Lower Heating Zone

The lower heating zone consists of an outer Pyrex pipe section and an inner Pyrex tube section shown in Figures 10 and 11 respectively. Two 24/40 standard taper outer joints are sealed to the outer Pyrex pipe. The outer Pyrex pipe is insulated in the same manner as the Pyrex pipe of the upper heating zone. The inner Pyrex tube has one heater, R_4, shown in Figure 16. The heater is 20 feet of 22 gage chromel resistance wire wrapped on a logarithmic spacing starting with 1/16 inch at the top and increasing to 1/4 inch at the bottom of the section. The "afterheater" has been included to avoid plastic deformation which occurs if the crystal is cooled too quickly. This is achieved by minimizing thermal losses

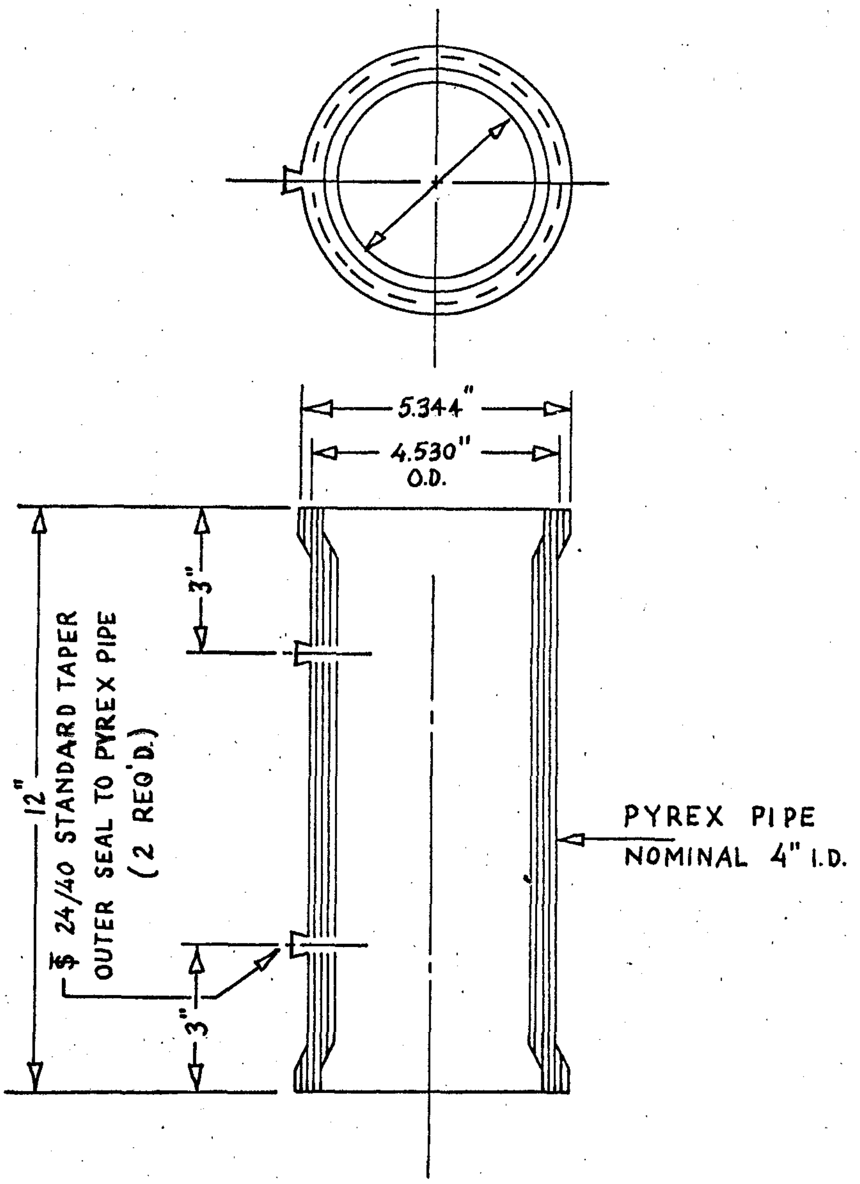
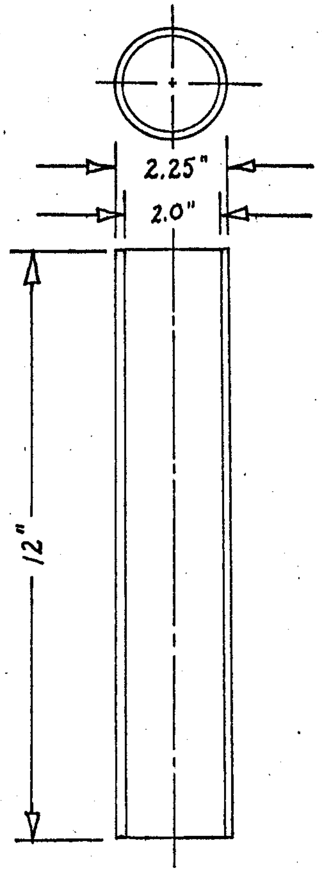


FIGURE 10
LOWER HEATING ZONE
OF FURNACE-SECTION 2, PART A
NEWARK COLLEGE
OF ENGINEERING
MELVIN DRUIN
SCALE 3"=1'-0"



PYREX TUBING
MEDIUM WALL
ENDS CUT SQUARE AND
FIRE POLISHED G-8530

FIGURE 11
LOWER HEATING ZONE
OF FURNACE-SECTION 2, PART B
NEWARK COLLEGE
OF ENGINEERING
MELVIN DRUIN
SCALE 3" = 1'-0"

from the sies of the crystal and thus forcing most of the heat to flow uniformly along the length of the crystal. With the use of afterheaters, Bonnett and Sawyer (2) have grown germanium crystals with etch pit densities of less than one hundred per cm^2. The two heater leads were insulated with sections of Pyrex tubing and led through 1/8 inch diameter holes in the bottom transite plate (Figure 13) to a terminal strip bolted directly to the transite plate.

Bottom Section

The bottom section of the furnace consists of a section of Pyrex tubing shown in Figure 12. The section is held against the bottom transite plate by two tube clamps. A 2 inch diameter rubber stopper is placed in the bottom of the section while a crystal is being grown. This helps to prevent loss of heat by convection and protects the crystal container from accidental breakage.

Transite Plates

The top, middle and bottom transite plates were grooved on a lathe according to the dimensions given in Figure 13. The outer groove (O.D. 5 11/32 inch) houses the outer Pyrex pipe and the inner groove (O.D. 2 8/32 inch) the Pyrex tube. Thermocouples, resistance heater leads and the fiberglass cord pass out of the furnace through 1/4 inch, 1/8 inch and 1/8 inch diameter holes respectively drilled in the top transite plate.

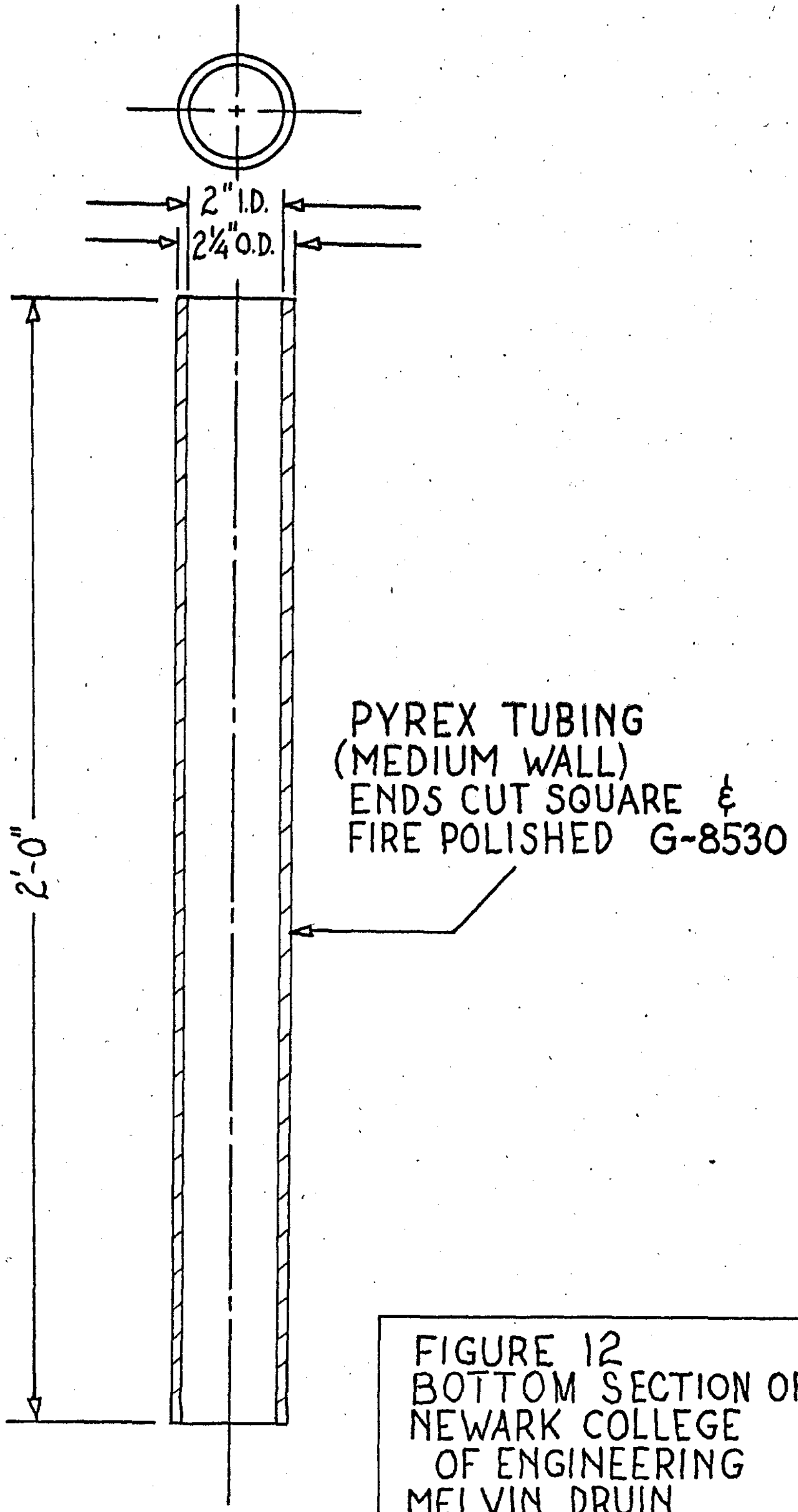


FIGURE 12
BOTTOM SECTION OF FURNACE
NEWARK COLLEGE
OF ENGINEERING
MELVIN DRUIN
SCALE 3" = 1'-0"

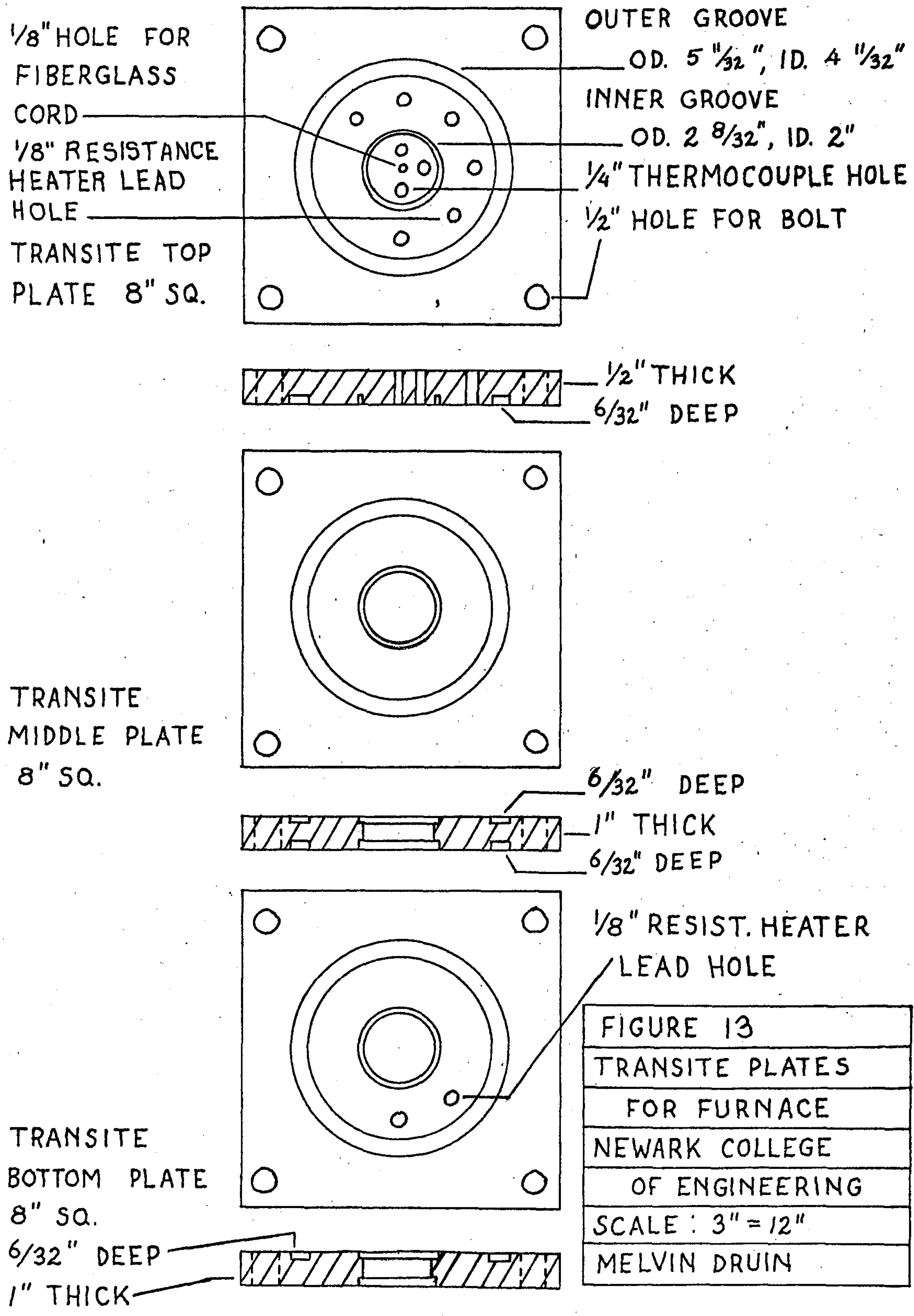


FIGURE 13
TRANSITE PLATES FOR FURNACE
NEWARK COLLEGE OF ENGINEERING
SCALE : 3" = 12"
MELVIN DRUIN

The middle transite plate supports the upper heating zone and divides the annuli of the upper and lower heating zones. The plate permits the upper section to be maintained above the melting point of the solid while the lower section is held several degrees below its freezing point.

The bottom transite plate supports and insulates the lower heating zone. Two 1/8 inch diameter holes were drilled to allow the resistance heater leads to pass out of the furnace to a terminal strip bolted directly to the transite plate.

Each transite plate has four 1/2 inch holes by which plates are bolted directly to the unistrut frame which extends from floor to ceiling. The unistrut makes possible a convenient operation of maintenance by permitting either heating section to be separately disassembled by merely lowering or raising the bottom or top transite plate (see Figures 19 and 20).

DESCRIPTION OF CRYSTAL CONTAINER

Many types of containers have been employed for growing single crystal (5,18,22,39). In all cases the object is to initiate the growth of a single crystal at a constriction or point. The Pyrex crystal container used by the author (Figure 14) is a modification of the type used by Huber and his associates (18) and by Lipsett (22). A difficulty encountered by Lipsett when using this type of container is that the latent heat of fusion of anthracene at the liquid-solid interface can be conducted away only with considerable difficulty. The problem can be solved by decreasing the rate of descent of the crystal container through the furnace.

With the design in Figure 14, a single crystal can be grown even if it is not possible to achieve a single nucleus at the point of constriction. In the bottom capillary portion of the container it is probable that the growth is multi-crystalline throughout. Since the walls of the container above the capillary portion slope fairly gradually outwards to the full diameter, it is highly probable that one of the growing grains will predominate provided the container is sufficiently long. This process of self-seeding is recommended over the use of a seed crystal. Inability to see the liquid-solid interface makes it difficult to control growth of a seed crystal and still be certain

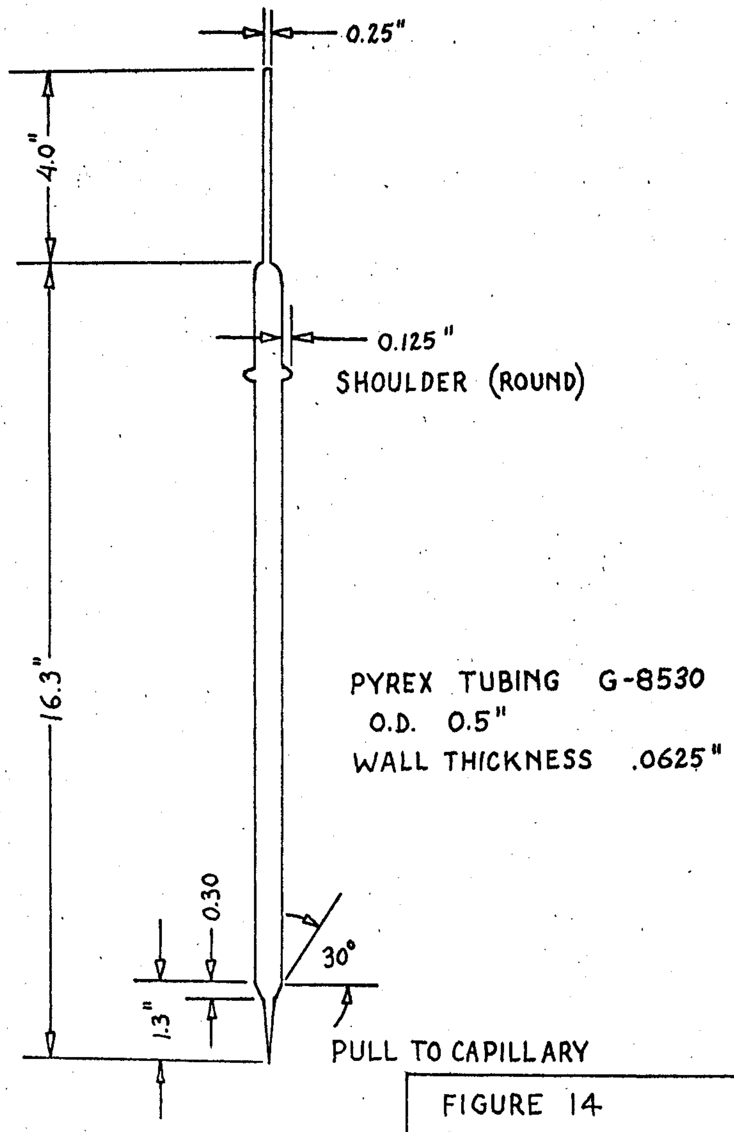


FIGURE 14
CRYSTAL CONTAINER
NEWARK COLLEGE
OF ENGINEERING
MELVIN DRUIN
SCALE 3"=1'-0"

that the seed itself has not been completely melted. A second reason for using a long crystal container is that anthracene cannot be melted in air without serious oxidation or charring at the surface. Thus the charge to the crystal container is anthracene powder or flakes which are sealed off in vaccum. When melted in the furnace the anthracene fills only a small section of the container. The small (0.125 inch) round shoulder is used for attaching the fiberglass cord to the crystal container.

A second crystal container was designed by the author, shown in Figure 15, as an improvement over the design shown in Figure 14. The upper section of the container is a reservoir section used to contain the material during the loading of the crystal container. Such a section eliminates the loading problems encountered in the original design (diameter of opening too small and loading time too long). To increase the probability that only one single crystal is formed, an S curve section has been included in the design of Figure 15. If several nuclei are formed at the point of the first capillary section, they will grow through the section until the first curved portion is reached. It is highly probable that only one of the growing grains will be properly oriented to grow past this section. There are five additional curved portions of the S curve which ensures one surviving

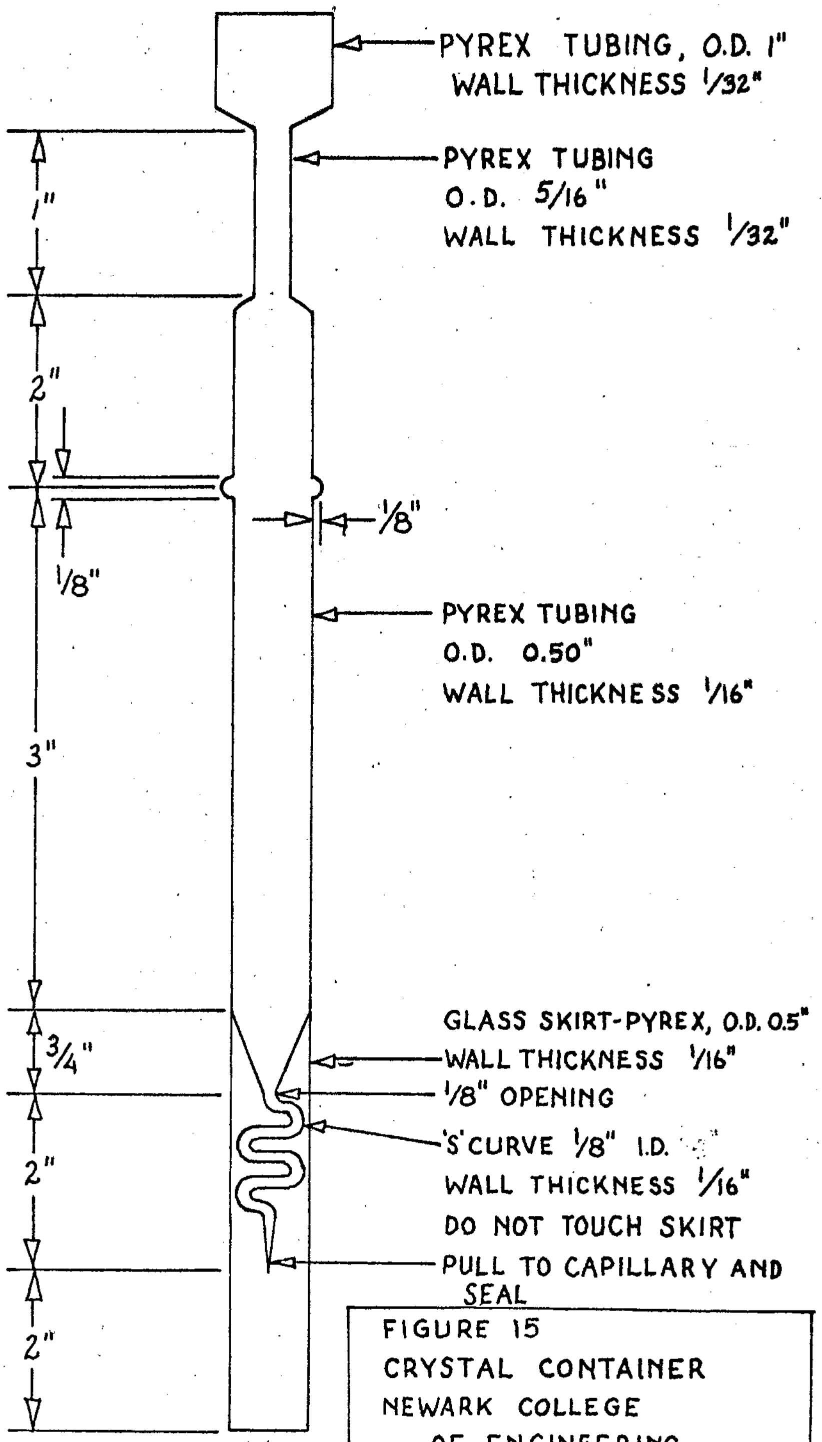


FIGURE 15
CRYSTAL CONTAINER
NEWARK COLLEGE
OF ENGINEERING
MELVIN DRUIN

grain to serve as the unique seed for the remainder of the charge. A Pyrex skirt has been included to protect the S curve section during the loading of the material into the container. The skirt may also be used as a guide when rasing the crystal container through the furnace. The container is raised to a position in the furnace such that the end of the container (skirt) is immediately below the middle transite plate. Thus the cpaillary point is at a point 22.5 inches below the surface of the top transite plate.

DESCRIPTION OF AUXILIARY EQUIPMENT

Crystal Container Lowering Mechanism

The crystal container which is suspended in the furnace by a 0.034 inch-diameter fiberglass wire (Figures 19 and 20) is lowered by the motor and gear train mechanism shown in Figures 16 and 17. Specifications are:

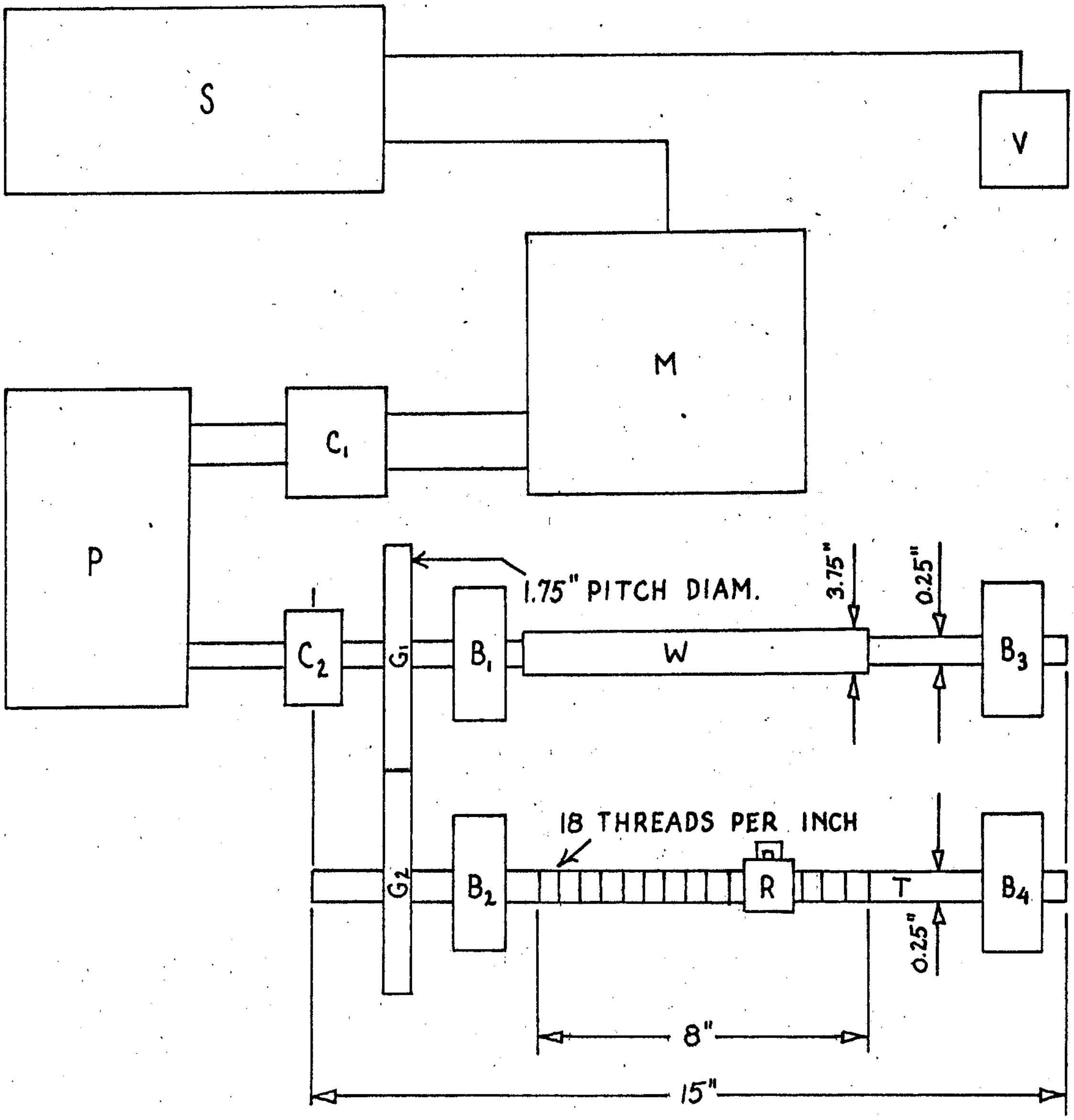
"M" 1/70 hp Bodine DC gearhead motor, 40 inch-pounds torque, 1.6 RPM minimum output speed.

"P" Insco speed reducer, model 00141, ratios of input to output speeds are 1000/1, 500/1, 250/1, 100/1, 50/1, 25/1, 10/1, 5/1, 2.5/1, and 1/1.

"S" Heller S-12 DC motor controller, reversible.

The traveler rod was grooved on a lathe with 18 threads per inch. Guide ring R guides the fiberglass wire off and on the winding rod W in a single wrapping of uniform spacing. This is necessary to prevent overlapping of the fiberglass wire which would result in a variability of rate of travel. The guide ring R is prevented from rotating by a 2 inch steel pin which extends from its base to a grooved slot in the supporting table. Two steel spur gears of 1.75 inch pitch diameter allow the winding rod W and the traveler rod T to rotate at the same rate. Both rods are supported at each end by two cast iron pillow blocks.

The fiberglass wire passes from the winding rod W over two pulleys mounted above the furnace, through a 1/8 inch hole in the top transite plate. A small weight is attached to the wire, by means of a swivel hook, which keeps the wire taut when no crystal container is suspended in the furnace. Calibration and reliability of the lowering mechanism is summarized in Tables 12, 13 and 14.

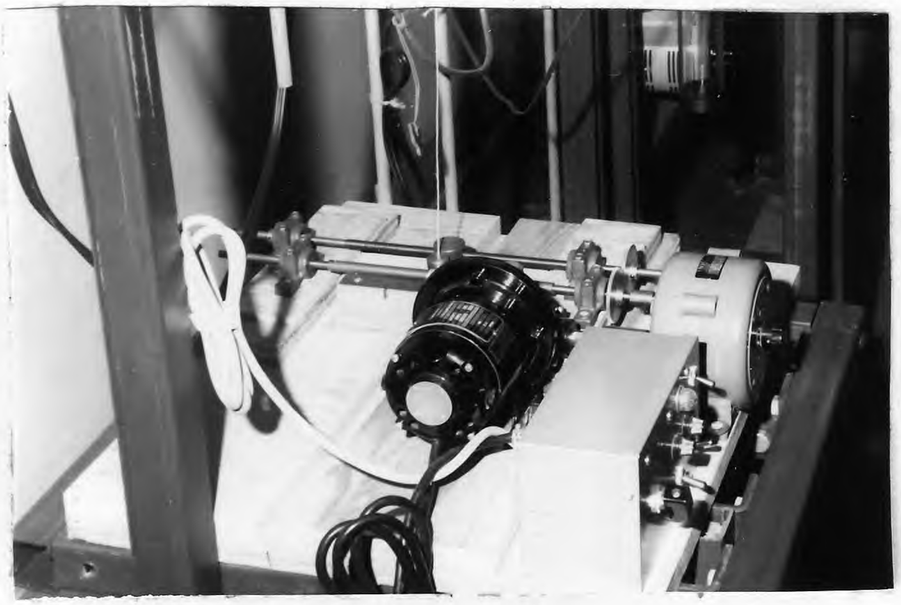


KEY

B - PILLOW BLOCK
C - SLEEVE COUPLING
G - SPUR GEAR
M - 1/70 H.P. BODINE MOTOR
P - SPEED REDUCER
R - GUIDE RING
S - S-12 CONTROLLER
T - TRAVELER ROD
V - 110 VOLTAGE SUPPLY
W - WINDING ROD

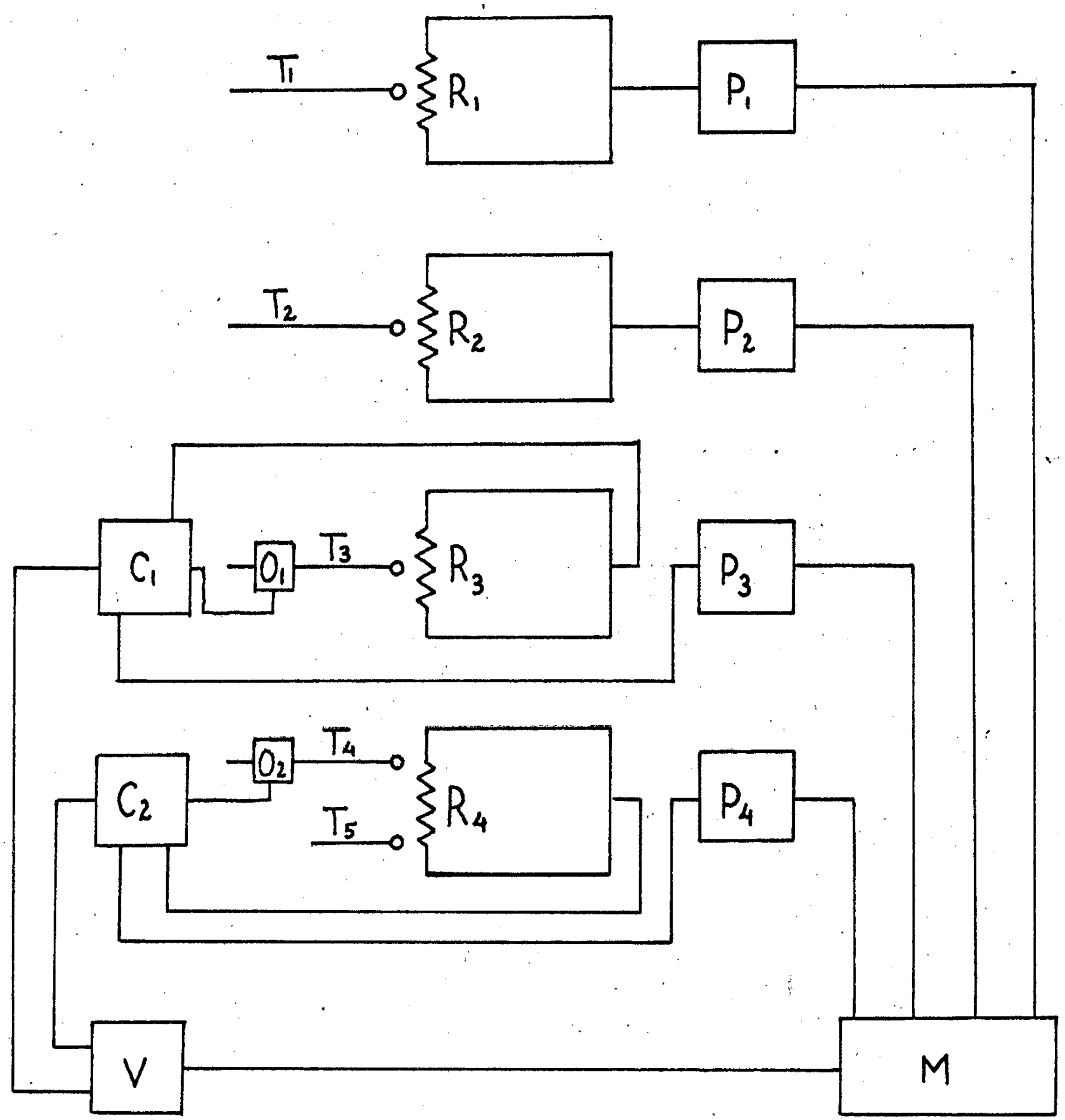
FIGURE 16
DRIVE SYSTEM FOR
LOWERING OF
CRYSTAL CONTAINER
NEWARK COLLEGE
OF ENGINEERING
MELVIN DRUIN

FIGURE 17, DRIVE SYSTEM FOR LOWERING OF THE CRYSTAL CONTAINER



Temperature Controls

The circuit diagram for the electrical supply to the resitance heaters R_1, R_2, R_3 and R_4 and the temperature control circuits are shown in Figure 18. Voltages to R_1 and R_2 are controlled by variable transformers, type 116. Thermometers T_3 and T_4 which bracket the critical crystal-growing zone actuate capacitance controllers (Therm-O-Watch limit model L-6). The action of the Therm-O-Watch is based on the fact that once the oscillator head (clips onto thermometer) is tuned, a slight increase in the capacity of its circuit due to the closeness of a liquid (Mercury) near the sensing clip will cause oscillations to cease and the relay in the amplifier to operate. The amplifier contains two 110 volt outlets that are turned alternately on and off in response to the action of the oscillator head. Thus the Therm-O-Watch automatically switches current on and off to heaters R_3 and R_4 as required to maintain constant temperature. With adjustable thermometers, range 0 to 250°C, the sensitivity of the controller is ± 0.5°C at 215°C. The calibration of the temperature gradient maintained inside the furnace is summarized in Table 11.



KEY
C ~ I^2R CONTROLLER
M ~ MULTIPLE SWITCH
O ~ OSCILLATOR
P ~ POWERSTAT
R ~ RESISTANCE HEATER
T ~ THERMOMETER
V ~ 110 VOLT SUPPLY

FIGURE 18
HEATING ELEMENTS AND
FURNACE CONTROLS
NEWARK COLLEGE
OF ENGINEERING
MELVIN DRUIN

Thermocouples

The thermocouples used were 24 gage copper-constantan insulated with fiberglass. Originally one thermocouple was used to determine the vertical temperature gradient in the furnace. This method was also used by Lipsett (21,22). The thermocouple was inserted through the 1/4 inch hole in the top transite plate and measurements of temperature were determined at ten different points inside the furnace tube with a Leeds and Northrup potentiometer. Since the time required to collect the data was at least 30 minutes the method was discarded. Ten thermocouples were installed at ten points inside the furnace tube as described and numbered as follows:

#1 6 inches below the surface of the top transite plate
#2 12 " " " " "
#3 22 " " " " "
#4 23.5 " " " " "
#5 24.5 " " " " "
#6 26 " " " " "
#7 27.5 " " " " "
#8 28.5 " " " " "
#9 29.5 " " " " "
#10 30.5 " " " " "

The thermocouples enter the furnace through three 1/4-inch diameter holes drilled in the top transite plate.

The thermocouple leads are connected to a Thermo Electric 12 position rotary selector switch. This switch is connected to the potentiometer and an ice bath (cold junction). Calibration of the temperature gradient maintained inside the inner Pyrex tube is summarized in Table 11.

Details of the assembled furnace and auxiliary equipment are presented in Figures 19 and 20. The furnace has an over-all height of 5 feet. A longer furnace may be made merely by stacking a third heated section on top of the upper heating zone.

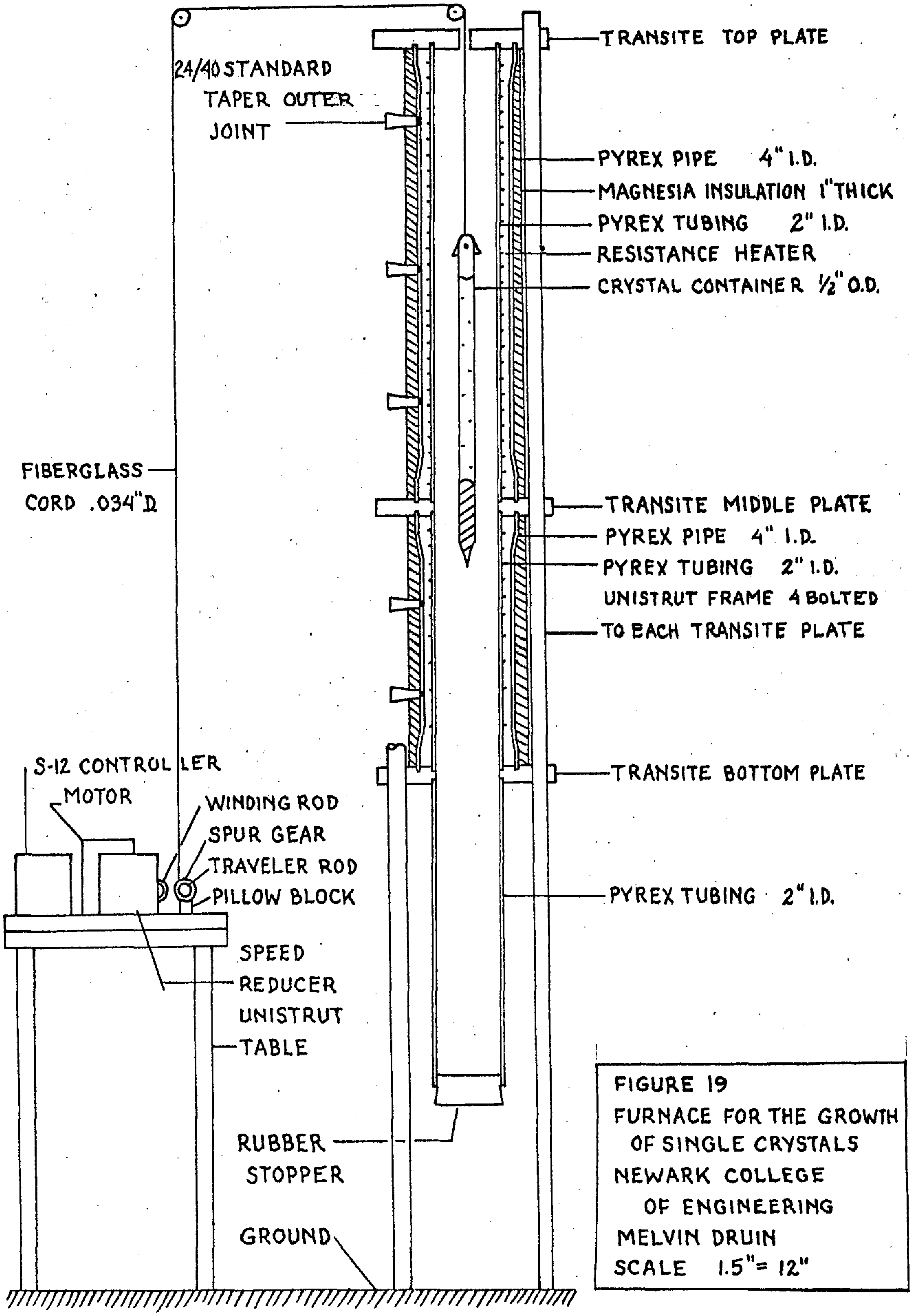
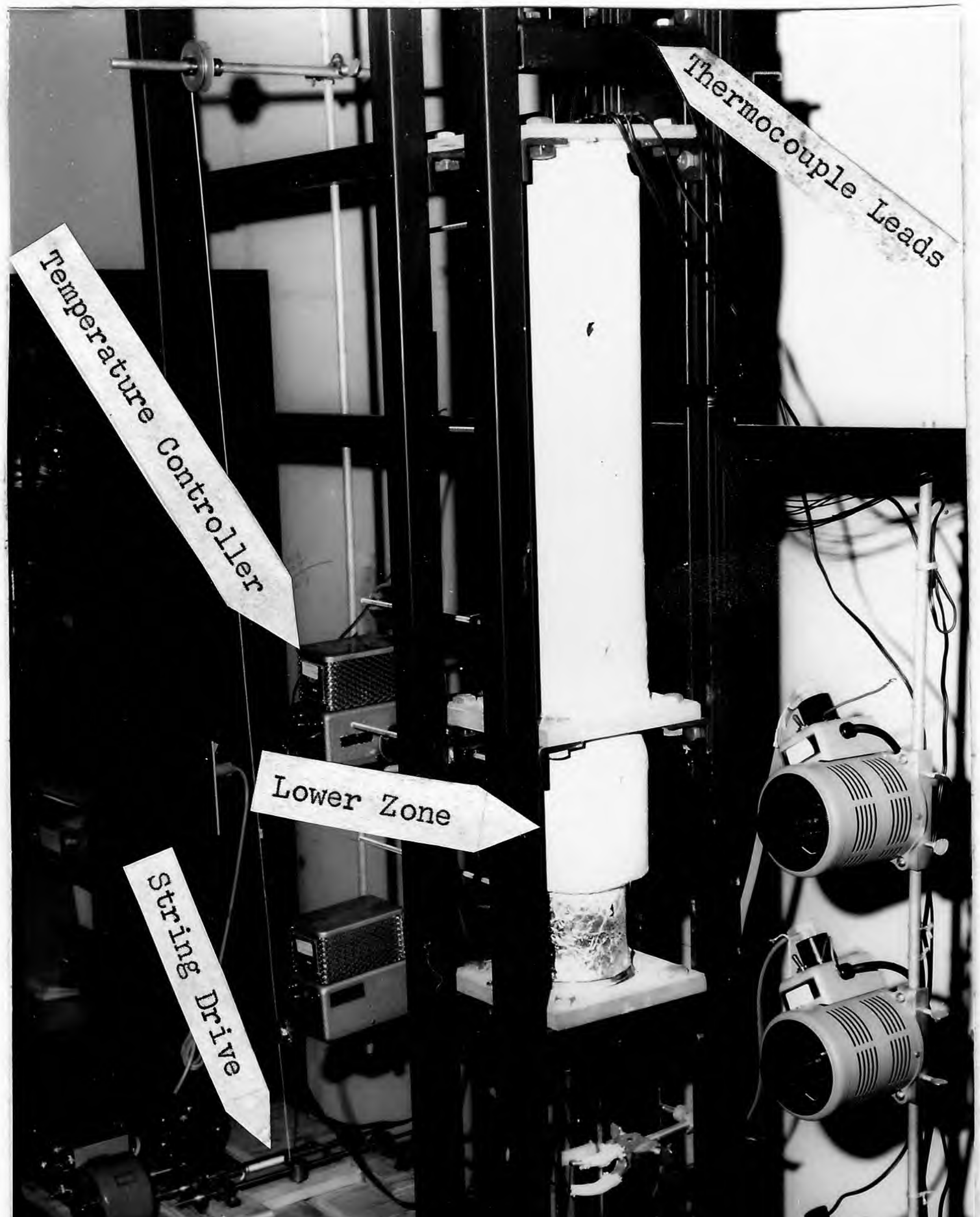


FIGURE 19
FURNACE FOR THE GROWTH OF SINGLE CRYSTALS
NEWARK COLLEGE OF ENGINEERING
MELVIN DRUIN
SCALE 1.5" = 12"

Figure 20

Two Zone Bridgman Furnace



DETERMINATION OF VERTICAL TEMPERATURE GRADIENT MAINTAINED IN THE FURNACE

In order to grow a single crystal of anthracene, for example, the correct temperature distribution within the furnace must be established. The best form of the vertical temperature gradient within the furnace has been discussed on page 56. The vertical temperature gradient within the furnace was determined by use of the 10 copper constantan thermocouples installed inside the inner Pyrex tube. Oscillator heads O_1 and O_2, shown in Figure 18, were clipped on thermometers T_3 and T_4 with the bottom of the sensing clip at 210°C and 139°C respectively. Powerstats P_1, P_2, P_3 and P_4 were set at 35, 25, 60 and 60 volts respectively. These settings which were arrived at through trial result in the desired temperature gradient.

Temperatures within the critical crystal growing zone (230° to 197°C) of the furnace show a maximum variation of less than 1°C for a period of three days as shown in Table 11. A plot of the average temperature (during the three day period) versus the distance from the surface of the top transite plate is shown in Figure 21. The vertical temperature gradient desired in a Bridgman furnace has thus been accomplished. Temperatmres at the top of the furnace are not high enough to cause decomposition of the

Table 11

TEMPERATURE GRADIENT AND FLUCTUATIONS IN FURNACE

DATE	TIME	VOLTAGE (VOLTS)				THERMOMETER TEMPERATURE (°C)					THERMOCOUPLE READING (mv)									
		P_1	P_2	P_3	P_4	T_1	T_2	T_3	T_4	T_5	1	2	3	4	5	6	7	8	9	10
5/1/63	10:00AM	35	25	60	60	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	1:30PM	35	25	60	60	205	213	208	138	54	12.23	11.61	11.71	10.81	9.09	8.55	8.12	7.52	6.64	5.64
	2:45PM	35	25	60	60	211	218	208	138	55	12.44	11.84	11.61	10.81	9.09	8.50	8.06	7.47	6.61	5.61
	4:30PM	35	25	60	60	214	221	208	139	54	12.67	12.03	11.64	10.83	9.12	8.55	8.11	7.52	6.64	5.61
5/2/63	10:15AM	35	25	60	60	211	218	208	139	54	12.32	11.81	11.72	10.85	9.13	8.55	8.13	7.53	6.65	5.62
	11:50AM	35	25	60	60	212	220	208	139	54	12.41	11.85	11.60	10.86	9.13	8.53	8.10	7.52	6.64	5.62
	2:30PM	35	25	60	60	212	220	208	139	54	12.45	11.91	11.61	10.90	9.14	8.53	8.09	7.50	6.64	5.63
	7:00PM	35	25	60	60	210	221	208	139	56	12.52	11.91	11.64	10.82	9.11	8.51	8.08	7.49	6.64	5.62
5/3/63	11:00AM	35	25	60	60	212	221	208	139	54	12.43	11.89	11.64	10.92	9.15	8.54	8.10	7.52	6.64	5.62
	1:25PM	35	25	60	60	212	221	208	139	54	12.53	11.93	11.63	10.92	9.10	8.53	8.09	7.50	6.63	5.63

Table 11 (Continued)

TEMPERATURE GRADIENT AND FLUCTUATIONS IN FURNACE

DATE	TIME	THERMOCOUPLE TEMPERATURE (°C)									
		1	2	3	4	5	6	7	8	9	10
5/1/63	10:00AM										
	1:30PM	253.9	242.6	244.5	228.2	196.2	186	177.7	166.5	148.6	128.5
	2:45PM	257.6	246.9	242.2	228.2	196.2	185	176.5	165.5	148	127.6
	4:30PM	261.7	250.3	242.8	228.3	197	186	177.5	166.5	148.6	127.6
5/2/63	10:15AM	255.5	246.3	244.5	228.6	197.3	186	177.8	166.7	148.8	128
	11:50AM	257.1	247	242.1	228.7	197.3	185.6	177.3	166.5	148.6	128
	2:30PM	257.8	248.1	242.2	229.5	197.4	185.6	177.1	166	148.6	128.2
	7:00PM	259	248.1	242.8	228.2	196.6	185.2	177	165.8	148.6	128
5/3/63	11:00AM	257.4	248.1	242.8	230	197.5	185.8	177.3	166.5	148.6	128
	1:25PM	259.2	248.5	242.6	230	196.5	185.6	177.1	166	148.5	128.2
	Average	258.2	247.9	242.8	228.9	197	185.6	177.2	166.2	148.5	128

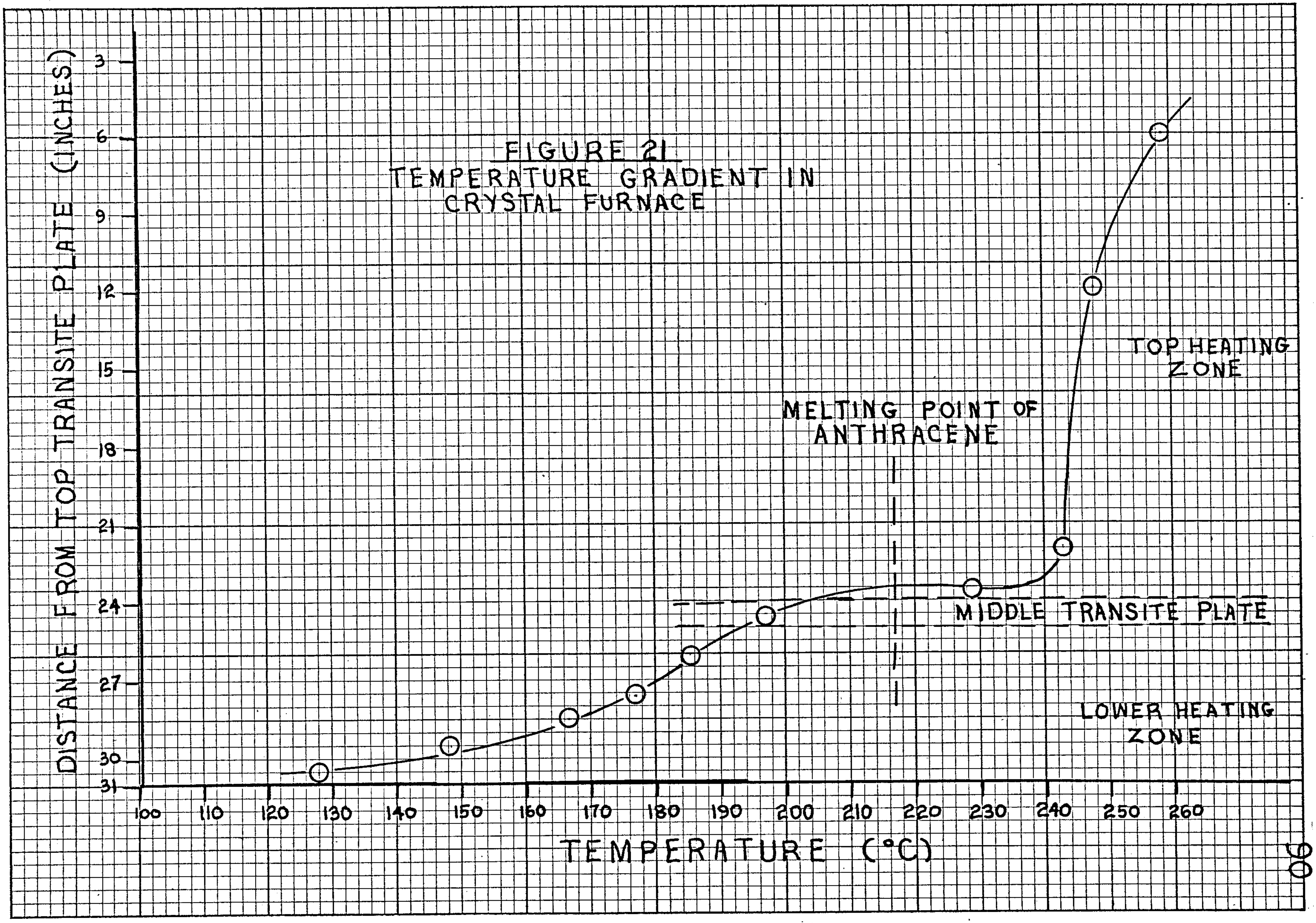


FIGURE 21
TEMPERATURE GRADIENT IN
CRYSTAL FURNACE

anthracene. The temperature in the upper heating zone decreases gradually until the lowest portion of the top heating zone is reached. At this point the temperature abruptly drops from 240° to 200°C in a distance of 1/2 inch. The melting point of anthracene is found approximately at the mid-point of the sharp temperature drop. In the lower heating zone of the furnace the temperature falls off more rapidly than in the upper zone. However, it is expected that the gradient is not so large as to interfere with the annealing of the single crystal. With the type of vertical temperature gradient established in the furnace, little regulation of temperature is required. A slight decrease or increase in the temperature of the furnace leaves the liquid-solid interface unmoved at a point 23.5 inches below the surface of the top transite plate.

CALIBRATION OF CRYSTAL CONTAINER LOWERING MECHANISM

The crystal container lowering mechanism shown in Figures 16 and 17 was calibrated by lowering a weight (equal to the approximate weight of loaded crystal container) continuously through the furnace at various rates governed by the speed control knob on the Heller S-12 motor controller. The Insco speed reducer was kept constant at a ratio of input/output of 1/1. Lowering time and distance traversed were recorded.

Results

The results of the calibration of the crystal container lowering mechanism are shown in Table 12, Table 13, Figure 22 and Figure 23. The minimum lowering speed attainable is 0.490 inches/day, and maximum speed 13.9 feet/hour. A comparison of Tables 12 and 13 indicates that the lowering speeds can be increased 18-21.4% by putting the high-low switch of Heller S-12 motor controller to high setting.

Fluctuations of Lowering Speed

A weight (equal to approximate weight of loaded crystal container) was lowered smoothly and continuously through the furnace for a period of seven days. The control settings were selected so as to give a rate of descent of 1 inch per day, a rate which is used to grow single crystals of anthracene. Table 14 indicates that

Table 12

CALIBRATION OF CRYSTAL CONTAINER LOWERING MECHANISM (LOW SETTING)

Heller S-12
    Forward-stop-reverse switch - reverse
    High-low switch - low

Insco speed reducer
    Ratio of input/output - 1/1

Heller S-12 Speed Control Setting	LOWERING TIME (min.)	MEASURED DISTANCE LOWERED (Inches)	RPM OUTPUT	LOWERING RATE (Inches/day)
5	3	7.03	1.99	3370
5	6	14.15	2.00	3390
4	3	6.35	1.80	3050
4	6	12.88	1.82	3080
3	3	5.63	1.59	2700
3	4.5	8.44	1.59	2700
3	6	11.25	1.59	2700
2	3	4.69	1.32	2250
2	6	9.47	1.34	2250
1	3	4.08	1.16	1950
1	6	8.15	1.15	1950
Off	3	3.25	0.922	1560
Off	6	6.55	0.925	1570
10	3	1.70	0.481	820
10	5	2.88	0.487	826
9	6	2.05	0.290	492
9	6	2.02	0.286	486

Table 13

CALIBRATION OF CRYSTAL CONTAINER LOWERING MECHANISM (HIGH SETTING)

Heller S-12
    Forward-stop-reverse switch - reverse
    High-Low switch - high

Insco speed reducer
    Ratio of input/output - 1/1

Heller S-12 Speed Control Setting	Lowering Time (min.)	Measured Distance Lowered (inches)	RPM Output	Lowering Rate (inches/day)
5	3	8.34	2.36	4000
5	5	13.88	2.36	4000
4	3	7.72	2.19	3710
4	5	12.84	2.18	3700
3	3	6.72	1.90	3220
3	6	13.58	1.92	3260
2	3	5.75	1.63	2760
2	3	5.78	1.63	2760
1	3.5	5.64	1.37	2320
1	3	4.76	1.35	2280
Off	3	3.92	1.11	1880
Off	3	4.00	1.13	1920
10	5	3.47	0.589	1000
10	8	5.50	0.584	990
9	4	1.64	0.348	591
9	6	2.47	0.349	591

Table 14

FLUCTUATION OF LOWERING SPEED

Heller S-12
    Forward-stop-reverse switch - reverse
    High-low switch - high
    Speed control switch - 10

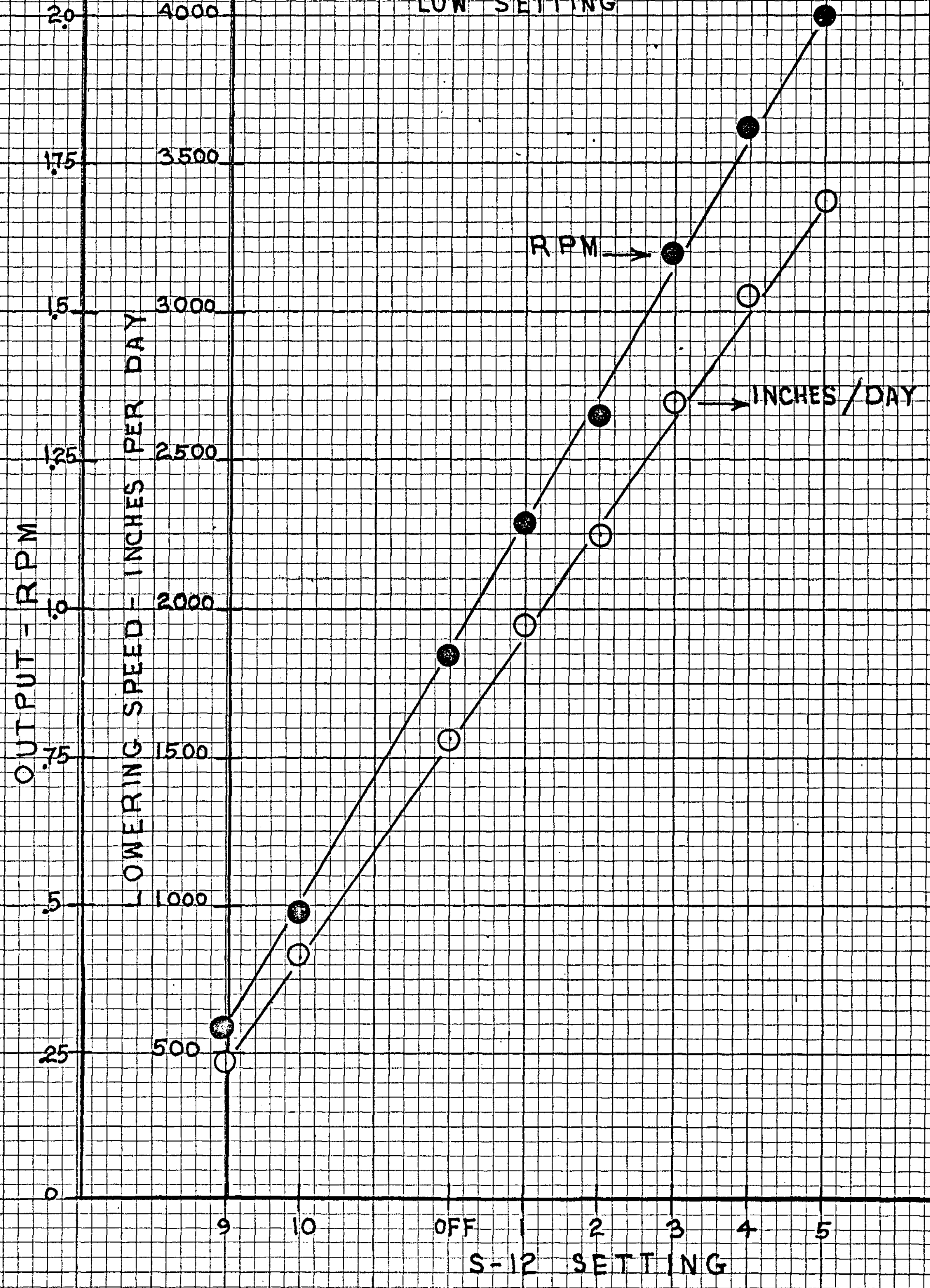
Insco speed reducer
    Ratio of input/output -2000/1

Date	Time	Lowering Time (min.)	Measured Distance Lowered (inches)	Lowering Rate (in./day)	Lowering Rate Deviation From Mean (d)	Lowering Rate Square of Deviation From Mean (d^2)
5/31	1:20 PM	0	0	0	0	0
6/3	11:30 AM	4210	2.81	0.962	+0.012	1.44 (10^{-4})
6/4	11:50 AM	5670	3.74	0.949	-0.001	1 (10^{-6})
6/6	11:05 AM	8505	5.58	0.944	-0.006	36 (10^{-6})
6/7	2:30 PM	10,150	6.66	0.944	-0.006	36 (10^{-6})

Mean = 0.950 $\Sigma (d)^2 = 2.17 (10^{-4})$

Standard deviation = ± 0.0085 in./day

FIGURE 22
CALIBRATION OF CRYSTAL CONTAINER LOWERING MECHANISM
LOW SETTING



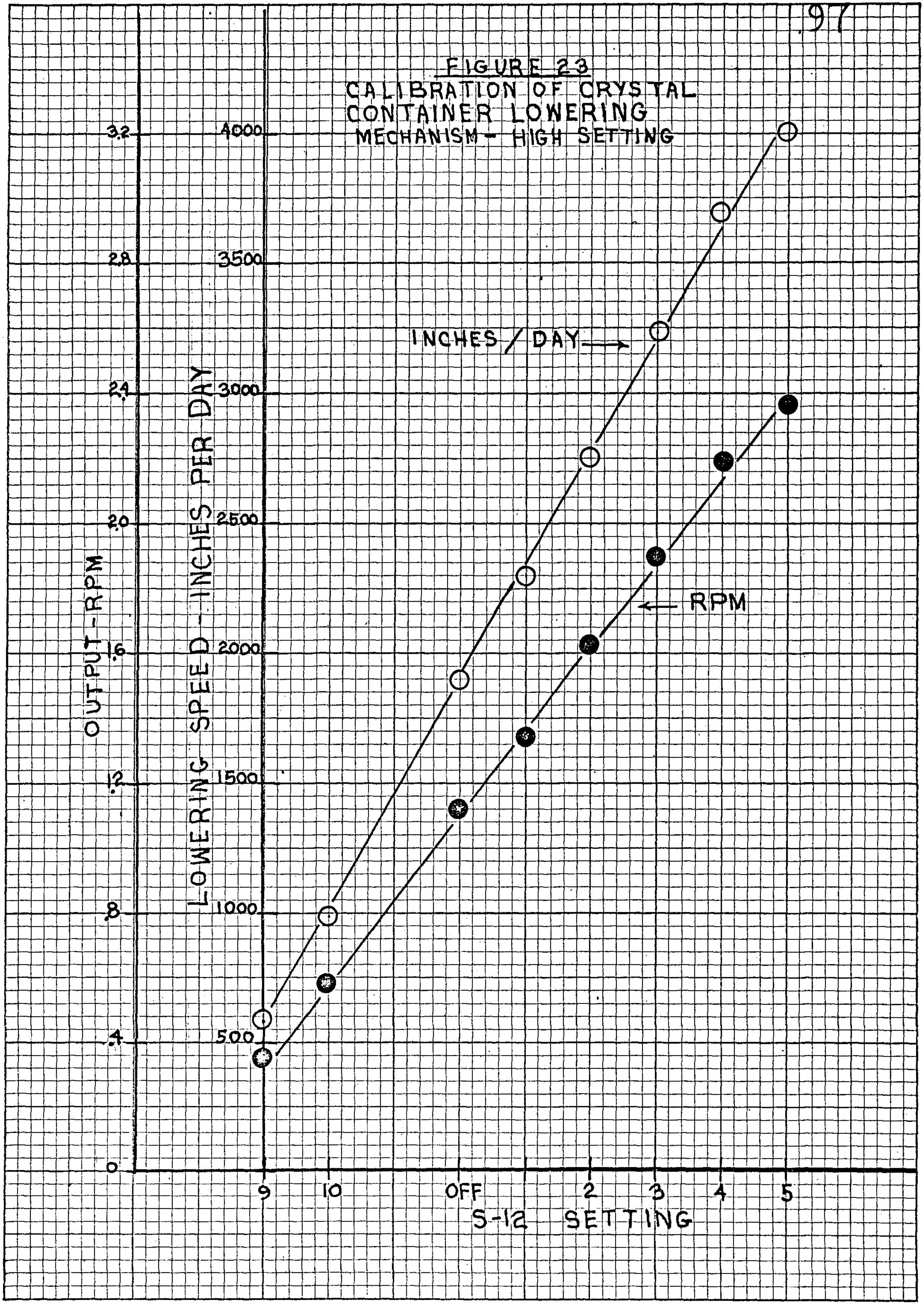


FIGURE 23
CALIBRATION OF CRYSTAL CONTAINER LOWERING MECHANISM- HIGH SETTING

at the selected settings the rate of descent in the furnace can be maintained at a speed of 0.950± 0.0085 inches/day.

PROCEDURE FOR GROWING SINGLE CRYSTALS

Loading Crystal Container

The material to be grown single crystal form is first pulverized finely by crushing with a clean spatula, on a glass watch glass. The material is collected and introduced into the crystal container (Figure 14), which has previously been cleaned with an alchohol-sodium hydroxide cleaning solution. Approximately 12-13 grams of material are packed tightly into the container to a height of 12 inches.

A constriction is pulled in the crystal container above the rounded shoulder. The container is then evacuated until a pressure of 10 microns is attained. Care must be taken at the start of evacuation that the powdered material is not drawn out of the container. This is accomplished by controlling the vacuum so that the initial pressure drop occurs slowly. An inert atmosphere of helium or nitrogen gas is introduced into the container and the contents are again evacuated to 10 microns or less. This procedure is repeated 3 or 4 times to sweep out all air and the container is then sealed off (at the previously made constriction) under a total pressure of 10 microns or less. The crystal is grown in an inert atmosphere because materials such as anthracene may not be melted in air without serious oxidation or charrring.

Inserting Crystal Container Into Furnace

Power to the furnace is first turned on. Powerstats P_1, P_2, P_3 and P_4 and Thermo-O-Watch controllers C_1 and C_2 are set at the necessary values in order to obtain the required vertical temperature gradient within the furnace (Table 11). The fiberglass cord is lowered out of the bottom section of the furnace. The small weight which keeps the wire taut when no crystal container is suspended in the furnace is removed from the swivel hook and is replaced by a sling which is attached to the crystal container directly below the small round shoulder. The fiberglass cord is wound up on the winding rod W so as to raise the crystal container through the lower and upper heating sections at a rate of 491 inches/day. Raising of the crystal container proceeds until the entire container is in the upper heating zone which is maintained at a temperatue above the melting point of the material.

Lowering of Crystal Container

When the material is molten (after 2 hrs.), the crystal container is lowered smoothly and continuously through the furnace at a rate of 0.950 ± 0.0085 inches per day by the gear train mechanism shown in Figures 16 and 17.

During the descent of the crystal container, the ten thermocouple temperatures are measured with the potentiometer in order to check that all heaters are functioning properly. Observations of the progress of melting and growth are performed by viewing the crystal container through the small holes cut in the outer magnesia insulation. The lowering rate is checked by measuring the actual distance traversed for a given time interval.

RESULTS OF GROWING SINGLE CRYSTALS

When growing single crystals the operational procedures and furnace described previously are employed. The methods described have been used with success to produce single crystals of anthracene and ethyl-p-aminobenzoate with diameters of 1/2 inch. The operating conditions are summarized in Table 15.

Anthracene (blue-violet fluorescence grade)

Blue-violet fluorescent grade anthracene purchased from Matheson, Coleman and Bell Co. and used without further purification was grown into a single crystal with dimensions of 1/2 inch in diameter and 6 inches in length. The crystal was grown in a helium atmosphere at a rate of 0.960 inches/day over a total period of twenty days (June 12 to July 2, 1963). During this growth period temperatures within the critical growing zone of the furnace showed a maximum variation of less than 1°C. The average temperatues at ten positions within the inner Pyrex tube are shown in Table 15.

Discussion of Results. The crystal shows large zones of single character, gross evidence of the presence of impurities (naphthacene) and several faults as shown in Figure 24. The crystal is not clear throughout. It

Table 15

GROWING SINGLE CRYSTALS

MATERIAL	TIME PERIOD (DAYS)	VOLTAGE (VOLTS)				THERMOMETER TEMPERATURE (°C)					AVERAGE THERMOCOUPLE READING (mv.)									
		P_1	P_2	P_3	P_4	T_1	T_2	T_3*	T_4*	T_5	1	2	3	4	5	6	7	8	9	10
ANTHRACENE (Blue-Violet Fluor.) Grade	20	31	25	60	60	200	213	200	139	58	11.54	11.4	10.95	10.31	8.72	8.29	7.84	7.32	6.59	5.58
ANTHRACENE (From Dimer)	24	31	25	60	60	198	210	200	139	56	-	-	10.94	-	8.71	8.22	7.83	7.32	6.58	5.58
ETHYL-P-AMINO BENZOATE	28	18	15	35	30	98	101	86	48	35	-	-	4.43	-	3.20	2.59	2.36	2.21	2.03	1.87

* Controlled by Thermo-O-Watch Controllers C_1 and C_2

\- Thermocouple Faulty

Table 15 (Continued)

GROWING SINGLE CRYSTALS

MATERIAL	TIME PERIOD (DAYS)	AVERAGE THERMOCOUPLE TEMPERATURE (°C)									
		1	2	3	4	5	6	7	8	9	10
ANTHRACENE (Blue-Violet Fluor.) Grade	20	241	238.5	230.5	218.5	189	180	172.5	163	147.5	127
ANTHRACENE (From Dimer)	24	-	-	230.4	-	188.5	179.8	172.4	163	147.4	127
ETHYL-P-AMINO BENZOATE	28	-	-	103.5	-	76.7	63	57.7	54.3	49.8	46

\- Thermocouple Faulty

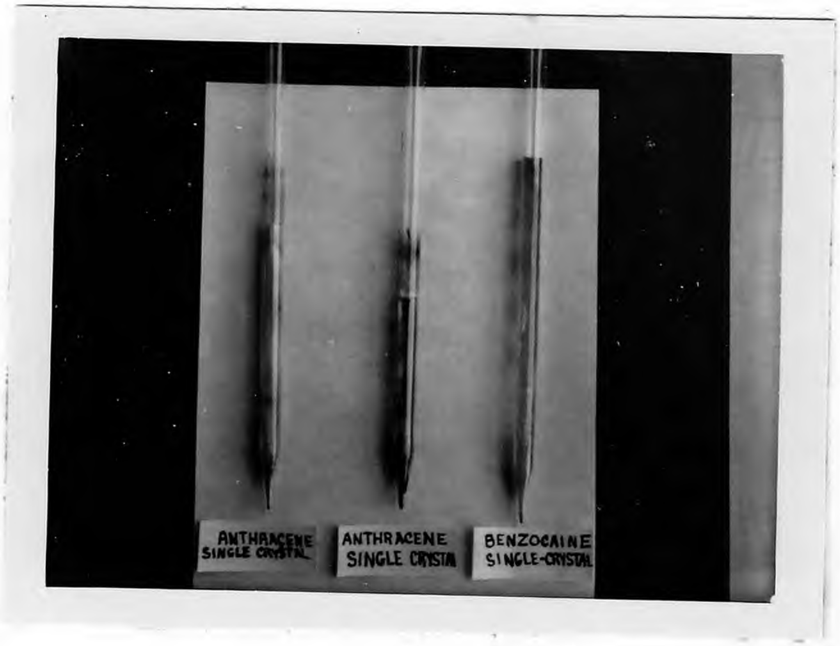


FIGURE 24, SINGLE CRYSTALS; Anthracene (Blue-violet fluorescence grade), Anthracene (from the dimer) Ethyl-p-aminobenzoate (benzocaine) has a light brown color throughout the main section and a dark brown color at either end. The impurity concentration of the crystal is not of a uniform nature as demonstrated by observation under ultra-violet light (310-375 millimicrons). The brown portions fluoresce a variety of shades of green indicating variations in naphthacene concentration.

Anthracene (prepared directly from the dimer)

A single crystal of anthracene was prepared directly from its dimer, dianthracene, with dimensions of 1/2 inch in diameter and 4 inches in length. The crystal was grown in a nitrogen atmosphere at a rate of 0.983 inches/day for a total period of 24 days (Aug. 24 to Sept. 17, 1963). Preparation of the dimer by exposing a solution of anthracene to ultra-violet light was previously discussed. The dimer was then loaded into the crystal container and inserted into the furnace. After a period of two hours during which it was exposed to temperatures slightly above the melting point of anthracene the dimer was converted to anthracene. Temperatures within the furnace showed a maximum variation of less than 1°C during the 24 day growth period. Average temperatures at ten positions in the furnace tube are shown in Table 15.

Discussion of Results. The crystal shows large zones of single character, gross evidence of the presence of impurities (naphthacene) and many faults as shown in Figure 24. It may be seen that the crystal contains a greater number of faults and more sections of a polycrystalline nature than does the crystal grown from the blue fluorescence grade anthracene. The impurity concentration of the crystal becomes greater in the direction of growth. This may be readily observed by means of ultra-violet light.

More attention must be paid to the purity of the initial charge to the container as this has a definite influence on the resulting crystal. Fluorescence analysis of the blue-violet grade anthracene and the technical anthracene purified by the dimerization method establish the impurity concentrations as 1.6 and 119 ppm naphthacene in anthracene. As demonstrated, the greater the impurity concentration in the initial charge the greater the pile up of impurity in the direction of growth and the greater the number of faults.

Ethyl-p-aminobenzoate

Reagent grade ethyl-p-aminobenzoate (benzocain), purified by sublimation methods similar to those previously discussed for anthracene, was grown into a 7 inch by 1/2 inch diameter single crystal. The crystal was grown in a nitrogen atmosphere at a rate of 0.976 inches/day for a total period of 28 days (July 10 to Aug. 7, 1963). Temperatures in the furnace proper were measured by the iron-constantan thermocouples at ten points inside the furnace tube and showed a maximum variation of less than 1°C. Average temperatures during the growth period are shown in Table 15.

Discussion of Results. The crystal shows large zones of single character and little evidence of the presence of impurities as shown in Figure 24. There are many faults which resemble air bubbles. These faults were created as a result of sealing the container under a nitrogen atmosphere of 1-2 pounds/sq. inch gage, instead of the usual pressure of 10 microns or less. As the container was heated the nitrogen expanded and bubbled through the material.

CONCLUSIONS AND RECOMMENDATIONS

A furnace was designed and built for growing of large single crystals of organic compounds by the Bridgman technique. Single crystals of anthracene and ethyl-p-aminobenzoate with diameters of 1/2 inch have successfully been grown in the furnace. It has been shown that the purity of the initial charge to the crystal container has a definite influence on the resulting crystal. An improved design of the original crystal container, with a primary view to insure that only one single crystal is indeed formed in the process has been performed. It is believed that this container will eliminate many of the problems encountered by this author in the process of growing single crystals.

High purity anthracene of fluorescent quality has been prepared by multiple co-distillation of 90-95 percent anthracene with ethylene glycol. Anthracene prepared by this method is purer than zone refined anthracene, having a 0.470 ppm naphthacene content. It is believed that this material will be adequate for crystal growth and subsequent electrical measurements. Co-distillation is generally applicable to many organic compounds which are of interest as semiconductors.

It is recommended that a three-neck, two-liter Pyrex round bottom flask be substituted for the reactor of the co-distillation apparatus which is currently in use. Larger quantities of pure anthracene may then be produced and with a Therm-O-Watch limit model L-6 the temperatue of the system may be controlled more accurately.

Zone refining of anthracene is not recommended although it produces an excellent quality of material because of the excessive number of zone passes required and the relatively small size of charge. Similarly snythetic preparation is not recommended because of the relatively complicated and tedious process involved and the small yields of satisfactory anthracene produced.

A very simple fluorescence technique for quantitative analysis of traces of naphthacene in anthracene has been developed. This method employs a colloidal suspension of the sample. Sensitivity approaching 0.1 ppm naphthacene in anthracene has been obtained. For rapid semiquantitative analysis, it provides a visible fluorescence color correlation with the level of impurity. The method is convenient to use because it employs small samples and uncomplicated manipulative techniques.

Further work is required to determine the ultimate sensitivity of the fluorescence technique. The sensitivity of this method can probably be extended to 0.01 ppm naphthacene content by determining the optimum colloidal concentrations, using a purer standard prepared from co-distillation and by employing a more sensitive photomultiplier tube particularly in the 510 mu range. It is recommended that an R.C.A. 1P22 photomultiplier tube, which is twice as sensitive at this level, be used in place of the R.C.A. 1P28.

BIBLIOGRAPHY

(1) Adams, R., and Johnson, J. R., *Laboratory Experiments in Organic Chemistry*, Fourth Edition. New York: The Macmillan Co., 1960, pp. 80, 73-84.

(2) Bennett, D. C., and Sawyer, B., *Bell System Tech. J., 35*, 1956, pp. 637.

(3) Bowen, E. J., and Lawley, P. D., "Crystal Size and Fluorescence Intensity, *Nature*, *164*, 1949, pp. 572.

(4) Brenner, *Materials in Design Engineering*, *51*, April, 1960, pp. 12-13.

(5) Bridgman, P. W., *Proc. Am. Acad. Arts Sci.*, *60*, 1925, pp. 305.

(6) Buckley, H. E., *Crystal Growth.* New York: John Wiley and Sons, Inc., 1951.

(7) Czorny, Bohdan, *The Electrical and Optical Properties of Organic Semiconductors*. M.S. Thesis, Newark College of Engineering, Newark, New Jersey, 1963.

(8) Eastman Kodak Co., *U.S. Patent* 2,213,755.

(9) Feazel, C. E., and Smith, C. D., *Rev. Sci. Instr.*, *19*, 1948, pp. 817.

(10) Fieser, Louis F., *Experiments in Organic Chemistry*, Third Edition. Boston: D.C. Heath and Company, 1955, pp. 159-64.

(11) Franck, J., and Teller, E., "Migration and Photochemical Action of Excitation Energy in Crystals," *J. Chem. Phys*. *6*, 1938, pp. 861.

(12) Furst, Kallmann and Brown, "Fluorescence Efficiencies of Organic Compounds," *J. Chem. Phys.*, *26*, 1957, pp. 1321-22.

(13) Ganguly, S. C., "Fluorescence of Anthracene in Presence of Naphthacene," *Nature*, *151*, 1943, pp. 673.

(14) Gumprecht, D. L., "A Cycle Counter for Zone-Refining Systems," *Chem. Eng.*, November, 1962, pp. 140.

(15) *Handbook of Chemistry and Physics*, C. D. Hodgman, R. C. Weast and S. M. Selby (eds.), Forty-Third Edition. Cleveland, Ohio: Chemical Rubber Publishing Co., 1961-62, pp. 806.

(16) Hannay, N. B., *Semiconductors*. A.C.S. Reinhold Publishing Co., New York: 1959, Chapt. 15 by Garrett.

(17) Hennington, Handley and Cook, "Zone Refining Organics." *Chem. and Ind.*, *16*, April, 1956, pp. 292.

(18) Huber, O., Humble, F., Schneider, H., and Steffen, R., *Helv. Phys. Acta*, *22*, 1949, pp. 410.

(19) Inockuchi, H., *Bull. Chem. Soc. Japan*, *29*, 1956, pp. 131.

(20) Kallman, H., and Pope, M., "Preparation of Thin Anthracene Single Crystals," *Rev. Sci. Instr.*, *29*, 1958, pp. 993.

(21) Lipsett, F. R., "Furnace for the Growth of Naphthalene and Anthracene Crystals," *Rev. Sci. Instr.*, *29*, May, 1958, pp. 423-24.

(22) Lipsett, F. R., "On the Production of Single Crystals of Naphthalene and Anthracene," *Can. J. Phys.*, *35 No. 3*, March, 1957, pp. 284-294.

(23) Lipsett, F. R., and Dekker, A. J., "Fluorescence Spectra of Some Organic Solid Solutions," *Can. J. Phys.*, *30*, 1952, pp. 165-73.

(24) Mette, H., and Pick, H. Z., *Physik*, 134, 1953, pp. 566.

(25) Musicant, Louis, *Private Communication* Irvington, New Jersey, October 25, 1963.

(26) Nakada, Ichiroch, "The Optical Properties of Anthracene Single Crystals," *J. Phys. Soc. of Japan*, *17 No. 1*, January, 1962, pp. 113-118.

(27) Northrop, D. C., and Simpson, O., "Electronic Properties of Aromatic Hydrocarbons, Fluorescence Transfer in Solid Solutions," *Proc. Roy. Soc. (London)*, A234, 1956, pp. 136-49.

(28) Parker, C. A., and Rees, W. T., "Fluorescence Spectrometry A Review," *The Analyst*, *87*, 1962, pp. 83-111.

(29) Petrauskas, A. A., and Gaudry, F. J., *Appl. Phys.*, *20*, 1949, pp. 1257

(30) Pfann, William G., *Zone Melting*. New York: John Wiley and Sons, Inc., 1958.

(31) Pimentel, G. C., and McClellan, A. L., *J. Chem. Phys.*, *20*, 1952, pp. 270.

(32) Pringsheim, Peter, *Fluorescence and Phosphorescence*, First Edition. New York: Interscience Publishers, Inc., 1949.

(33) Riehl, N. V., *Zhur. Fiz. Khim.*, *6*, 1955, pp. 959.

(34) Robertson, J. M., *Rev. Mod. Phys.*, *30*, 1958, pp. 155.

(35) Rodd, E. H., *Chemistry of Carbon Compounds*, Vol. 111 B. Amsterdam: Elsevier Publishing Company, 1956, pp. 1362.

(36) Sangster, R. C., and Irvine, J. W., *J. Chem. Phys.*, *24* 1956, pp. 670.

(37) Shpol'ski, E. V. S., Ilina, A. A., and Bazilevich, V. V., "Fluorescence Spectra of Anthracene, 1, 2-Bezanthracene, and Some of Their Derivatives," *Dokl. Akad. Nauk SSSR*, *62*, *1948*, pp. 227-30. *Chem. Abs.*, *43*, 1949, 498a.

(38) Sloan, *Physics and Chemistry of the Organic Solid State*. New York: Interscience Publishers, 1963, pp. 192.

(39) Stockbarger, D. C., *Rev. Sci. Instr.*, *7*, 1936, pp. 133.

(40) Takaki, H., Nakamura, S., Nakamura, Y., Hayashi, J., Furukawa, K., and Aso, H. J., *J. Phys. Soc. (Japan)*, *9*, 1954, pp. 204.

(41) Tammann, G., *Metallography*, translated by Dean and Swenson. New York: The Chemical Catalog Co., 1925, pp. 26.

(42) Van Duuren, B. L., "Effects of the Environment of the Fluorescence of Aromatic Compounds in Solution," *Chem. Revs.*, *63*, August, 1963, pp. 325-351.

(43) Van Duuren, B. L., and Bardi, C. E., "Reflectance Fluorescence Spectra of Aromatic Compounds in Potassium Bromide Pellets," *Anal. Chem.* *35*, 1963, pp. 2198-2202.

(44) Wynne, Edwin A., "Application of Zone Refining to the Purification of Organic Compounds," *Microchem. J.*, *5*, 1961, pp. 175-183.