PART 1

THE USE OF A COULTER COUNTER TO QUANTITATIVELY
DETERMINE MOLD IN CARBONATED SOFT DRINKS

PART 2

THE INVESTIGATION OF DIMERIC HALOGEN

ADDITION TO PIASELENOLE

PART 3

ULTRASONIC ATTENUATION OF METAL CHELATES

by

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The Use of a Coulter Counter to Quantitatively
Determine Mold in Carbonated Soft Drinks

By

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Abstract

A method for the rapid, quantitative screening
of carbonated soft drinks for mold at levels
well below what is normally detected by candling
and which is quantitatively more reliable than
counting mold clumps is proposed. It involves the
use of a Coulter Counter and can detect as few as
10 mold filaments per milliliter of the original
soft drink. Soft drinks containing pulp pose a
problem that is only partially solved. Dead mold
in the soft drink is completely separated by a
density gradient salt solution, but live mold uses
the pulp as a growth base and is not separated.

INTRODUCTION

Present accepted methods of determining the amount of mold in food materials are accomplished in one of two ways, direct counting under a microscope or by the use of a Howard's Cell.[1] Both methods require visual inspection and are limited in the total number of determinations made by one person per day. In addition mold clumps encountered are difficult to measure quantitatively. This lack of quantification prohibits the use of these methods in precise determinations.

A method was desired to determine the total amount of mold particles in carbonated beverages that would allow one operator to do more determinations with better reproducibility and more accuracy than is presently available. Mold is a frequent contaminant of bottled carbonated beverages and if proper cleaning of bottling machinery and bottles is not assured, mold that would grow in such an ideal environment would be bottled with the beverage. The method presented here was developed to monitor mold contamination in soft drinks.

In systematic classification, molds are not distinctly separate botanical groups. Molds are fungal growths consisting of a network of branched mycelium (singular-hypha) and reproductive units called spores. There are two types of mycelium: septate - individual disjoint cells, and nonseptate - no separate cells but long multi-nuclei tubes with shared protoplasm. Mold growth is conducted in two directions, vegetative mycelium penetrate the growth medium for food and the aerial mycelium (the fuzzy characteristic) produce spores.[2]

A Coulter automatic counter (Figure 1) was used to determine the amount of mold present in a given sample. Particles suspended in an electrolyte can be sized and counted by passing them through an aperture with a specified path of current flow for a given time.

Particles pass through the aperture and displace an equal
volume of electrolyte causing a change in the resistance in
the path of the current. The magnitude of the change is directly
proportional to the volumetric size of the particle and the number
of changes in a given time is proportional to the number of
particles in suspension.[3,4,5]

EXPERIMENTAL

A. Chemicals.   All chemicals used were reagent grade.

A saturated salt solution was prepared by adding 7 g
NaCl per 25 ml of distilled, deionized water. Density = 1.25g/ml.

Formalin was used to fix the mold concentration.

A surfactant, BRIJ-35 (Technicon), and 85% H_3PO_4 were used
to break up the oil film in samples that contained pulp.

Isoton (Coulter Diagnostics), an isotonic buffered saline
solution, was used as the diluting agent.

n-Hexyl alcohol was used to prevent bubble formation that
would interfere with the determination.

B. Equipment.

A Bausch and Lomb model WN4242 microscope with a 15x
ocular, equipped with a 100 μ scaler, and a 21x focusing lens
was used in careful examination of all samples.

A Waring blender on low setting effectively homogenized
each sample. Microscopic examination at 315x of random aliquots,
taken from each sample homogenized in this manner, showed that
no mycelial clumps or spore groupings were left in the sample.
Individual particles were observed that covered a size distri-
bution of 4 - 80 μ , the smaller particles being mostly spores.

The density gradient was prepared in a buret. Separation
was quantitative and complete in about 12 hours. The time of
separation can be markedly reduced to about 15 minutes by

preparing the density gradient in a centrifuge tube and centrifuging. The mold settles in the bottom 1 - 2 ml and can be collected.

A millipore filtration method can be applied to beverages without pulp. An aliquot or the entire sample can be passed through a millipore filter of pore size 1.2μ or smaller. The mold particles were collected on the filter and quantitatively collected by washing the filter with a fine stream of salt solution.

A Coulter Counter model A was used to determine the number of mold particles in each sample. The instrument employs a 100μ aperture and a sampling volume of 500 lambda. From the calibration data of the instrument used, a threshold value of 6 and an aperture current setting of 5 was found to allow the counting of all particles of size distribution $2 - 100\mu$. By varying the threshold and aperture current settings, the size range of the particles detected can be changed. In this case, all particles smaller than 2μ were considered background. A limit of detection of 10 particles per milliliter of the original sample was found based on a 10 oz bottle of original soft drink.

C. Procedure.

All samples studied were of 10 oz volume (295 ml) and were handled on an "as received" basis. Each sample was homogenized and 20 ml of formalin was added. A 20 ml aliquot of the homogenized solution was added to a buret containing 25 ml of the saturated salt solution and a density gradient was formed. Mixing was done by moving a small magnetic stirring bar up and down inside the buret with a larger magnetic stirring bar held outside the buret. Nothing more was done to the sample if

there was no pulp present. If pulp was present, 1 ml of 85%
H_3PO_4 and 1 ml of the surfactant (BRIJ-35) were added to the
buret before the gradient was formed. The same procedure was
used in a centrifuge tube when centrifuging was to be employed.

The mold was quantitatively collected in the bottom 1 - 2
ml of the salt solution.

The collected mold particles were diluted to a volume of
100 ml with Isoton. Care was taken to make sure that the sample
was homogenious and a dilution series was made to eliminate
the effect of coincidence.

One small drop of n-hexyl alcohol was added to each test.
Data were collected using a Coulter Counter model A.
Replicate determinations were made.

DISCUSSION

Carbonated beverages can be classified into two categories,
fruit drinks - those that are made from the pulp of fruits, and
non-fruit drinks - those with no pulp. In both types, when mold
was present, it was found throughout the entire sample but
primarily on the walls of the vessel or, in the case of broken
or cracked bottles, floating on the surface. Beverages that
contained pulp had mold using the pulp as a growth base with
vegetative mycelium penetrating the cell structure of the pulp
filaments. This was observed under careful microscopic examination.
No material other than mold or pulp was seen in these examinations.

To determine the total amount of mold in a given sample of
the carbonated beverage, it was necessary to assure thorough
mixing of mold throughout the sample and to fix the concentration
so that no continued growth would take place. This was accomplished
by homogenizing the sample with a Waring blender and adding

formalin to inhibit aerial and vegetative mycelial growth. All samples were handled on an "as received" basis. It was found that at least 5 minutes for homogenization was necessary to separate the mold filaments.

The method gives excellent results for carbonated beverages that do not contain pulp. Pulp containing beverages present a problem in that it is impossible to separate the vegetative mycelial phase from the pulp which is used as a growth base. The method presented gives total mold and pulp together but the exact ratio of pulp to mold is unknown as it appeared to vary with each sample.

The mold was separated from the beverage sample by either using a density gradient or by millipore filtration. Densities of various carbonated beverages were determined (Table 1) and were used to form a density gradient with a saturated salt solution so that the mold in the homogenized sample, being heavier, falls to the bottom where it is collected. Millipore filtration is straight forward and the mold is washed off the filter and collected. Microscopic examination of the density gradient solution and the millipore filter showed no residual mold particles to be present and therefore both methods are quantitative.

A Coulter Counter model A was used in the determination. The instrument allows control over the sizing of the particles to be determined only on the lower end. The maximum size is set by the aperture. The data (Table 2) are reproducible well within the limits of detection by the instrument. The instrument error is 3% at 10,000 counts. In a large volume of collected data, 90% is within 1% of the mean value. This is excellent in contrast to the visual methods mentioned previously which may differ by as much as 20% between replicate determinations.

The effect of coincident passage of particles through the aperture must be taken into consideration. By forming a dilution series, the effect of coincidence can be seen and can be corrected. Concentrated samples must be corrected for coincidence, while dilute samples need not be corrected.[5] Analysis of the dilution series data show a linear relationship of dilution versus counts per 500 lambda. This indicates that the total amount of mold determined in this manner is indeed a true measure of the total amount of mold present in the original sample.

Very minute amounts of mold cannot be determined with a Coulter Counter. The diluting electrolyte, Isoton, while having a very small background, in conjunction with the instrument error prohibits very small concentrations to be determined. The detection limit was found to be 10 mold particles per milliliter of original beverage.

This method, while being accurate and reproducible, is also simple to implement. No chemical training is required and replicate determinations can be made in as little as five minutes after the mold is quantitatively collected.

Table I

Density Values of Soft Drinks
Determined by Pycnometric Methods

TABLE I   Density values of soft drinks determined by
            pycnometric methods

Type	Density
Pepsi	1.043
Mountain Dew	1.042
Orange Soda	1.042
Diet Pepsi	1.042

Table II

Dilution Series Determination
in counts/500 lambda
Corrected for coincidence

TABLE II Dilution Series determination in counts/500 lambda
corrected for coincidence

Pepsi Sample 1

Dilution	Count 1	Count 2	Count 3	Count 4	Average
0 fold	41075	41114	41068	40996	41063
5 fold	8175	8223	8268	8197	8215
10 fold	4454	4198	4321	4185	4289
20 fold	2242	2329	2367	2275	2303
50 fold	966	943	942	910	940
100 fold	506	515	507	511	509
200 fold	374	361	353	345	358
500 fold	169	151	189	184	173
1000 fold	132	137	157	146	143

Diet Pepsi Sample 2

Dilution	Count 1	Count 2	Count 3	Count 4	Average
0 fold	6905	6963	6874	6897	6909
5 fold	1452	1326	1388	1430	1399
10 fold	818	814	762	748	785
20 fold	450	432	434	424	435
50 fold	250	248	302	338	284
100 fold	116	127	124	115	120

Mountain Dew Sample 3

Dilution	Count 1	Count 2	Count 3	Count 4	Average
0 fold	27490	27205	27453	27482	27405
5 fold	5285	5752	5148	5808	5498
10 fold	2996	3087	3233	2971	3071
20 fold	1391	1452	1651	1573	1516
50 fold	635	641	653	606	633
100 fold	380	388	382	373	380
200 fold	201	188	192	193	193
500 fold	87	91	80	79	84

Orange Soda Sample 4

Dilution	Count 1	Count 2	Count 3	Count 4	Average
0 fold	21130	21094	21126	21113	21115
5 fold	4254	4175	4249	4226	4226
10 fold	2172	2247	2269	2227	2228
20 fold	1132	1178	1311	1209	1207
50 fold	454	407	406	421	422
100 fold	294	291	266	302	288
200 fold	176	179	181	165	175

Orange Soda Sample 5

Dilution	Count 1	Count 2	Count 3	Count 4	Average
0 fold	9940	9894	9879	9885	9899
5 fold	2025	1936	1961	2014	1984
10 fold	902	920	856	872	887
20 fold	486	507	442	397	458
50 fold	212	233	213	200	214
100 fold	127	133	117	90	116

Isoton Diluting Solution

	Count 1	Count 2	Count 3	Count 4	Average
	10	11	7	13	10

Figure 1

Coulter Counter Sample Stand
(Courtesy - Coulter Electronics Inc.)

FIGURE 1

Coulter counter sample stand

(Courtesy- Coulter Electronics Inc.)
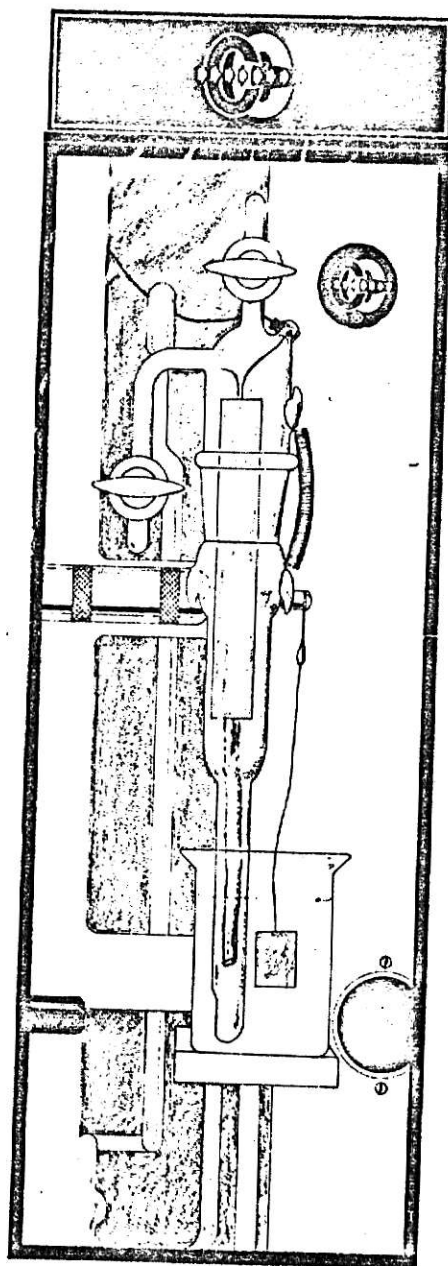
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PART 2

The Investigation of Dimeric Halogen
Addition to Piaselenole

The Investigation of Dimeric Halogen Addition to Piaselenole

By

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Abstract

The affinity of 2,1,3 benzoselenadiazole (piaselenole) for dimeric chlorine and bromine has been investigated. A 1:1 adduct is formed between piaselenole and both Cl_2 and Br_2. The adduct, upon reaction with water or gentle heating, liberates the chlorine or bromine dimer, however, the yields are too low to make the adduct an effective solid halogenation reagent. At slow flow rates, piaselenole quantitatively removes halogens from contaminated air streams. In addition, the Raman spectral assignments for dimeric chlorine and bromine in an associated molecular form have been found.

INTRODUCTION

Several years ago, a paper was published in which the compound 3,3' diaminobenzidine was proposed as a colorimetric reagent for selenium. The method was a good one but the structure put forth as the selenium containing compound (1) was questionable.

(1)
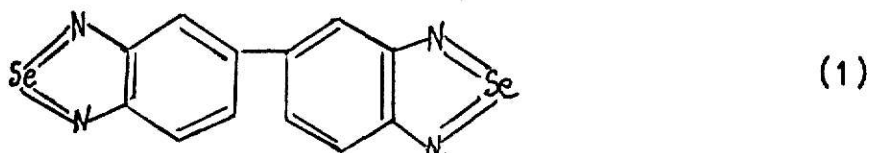
It was believed that the N=Se=N group did not exist. To simplify the study, only one half of the molecule (1) was prepared using o-phenylene diamine and selenious acid to produce the compound 2,1,3 benzoselenadiazole, or as it is commonly called − piaselenole (2).

(2)

Work by Bunting[3] with this compound led to a cobalt adduct which is a potential reagent for trace amounts of water. His structural studies supported the structure (2), shown above. During these investigations, an attempt to chlorinate the piaselenole produced a yellow compound which he observed would "corrode a spatula". In previous work undertaken to chlorinate the six-membered ring on the molecule (2), it was found that the same conditions for the chlorination of benzene were needed; reflux at elevated temperatures over iron filings. If only chlorine gas was introduced into the reaction vessel, a yellow material was recovered that was said to contain dimeric chlorine.[11]

Piaselenole has a planar, ortho-quinoid structure[6,7] and undergoes quarternization reactions with alkyl halides in preference to reaction with the selenium atom.[8,9] The compound has been proven to be very versatile in the area of trace analysis.[1-5]

This work consisted of the following areas:

1. Identification of the exact compound that corroded a stainless steel spatula.

2. Obtaining evidence as to the structure of the piaselenole – chlorine reaction product.

3. Investigation of chlorine adduct as a possible solid chlorination reagent, hopefully for cis chlorinations.

4. Measuring the ability of piaselenole to act as a scrubbing agent for the removal of halogens from contaminated air streams.

EXPERIMENTAL

A. Chemical.

Preparation of Piaselenole: An aqueous solution of o-phenylene-diamine (Eastman Chemical) + hydrochloric acid (Mallinckrodt), to form the dihydrochloride salt, was mixed with an excess of an aqueous solution of selenium dioxide (Apache Chemical). The resulting precipitate is collected and recrystallized to obtain the pure product characterized by white needles that have a melting range of 74 - 76°C.

Reaction with Chlorine Gas: A known amount of piaselenole was dissolved in carbon tetrachloride. Chlorine was bubbled slowly into the solution at a slow flow rate (less than 15ml/10 sec.) through a glass frit until excess chlorine came off. Methyl Orange was used as a visual indicator since chlorine bleaches out the orange color. The Cl_2 adduct precipitated out of solution when one mole of piaselenole had absorbed one mole of chlorine gas. (Table 1) The yellow precipitate was collected and found to decompose in the presence of heat or light.

Reaction with Bromine Liquid: A known amount of piaselenole was placed in a volume of water. The piaselenole was then titrated with a 0.25% Br_2 solution (1.25 ml Br_2 (Allied Chemical) per 500 ml water) dropwise with constant stirring. The piaselenole absorbed Br_2 changing the white material into a yellow-orange colored material. One mole of piaselenole absorbs one mole of Br_2 (Table 1). At the end point of the titration, the adduct began to turn a bright orange-red color.

TABLE 1

Mole Ratio Determinations
  A. Chlorination.
  B. Bromination.

TABLE 1

Mole Ratio Determinations

A. Chlorination. Chlorine gas.

Sample	Moles of piaselenole	Time of reaction	Flow rate	Moles of chlorine	Ratio Cl_2:piaselenole
1	5.46×10^{-3}	599.7 sec.	$\frac{10ml}{14\ sec}$	6.53×10^{-3}	1.20 : 1
2	5.48×10^{-3}	629.8 sec.	$\frac{10ml}{14\ sec}$	6.68×10^{-3}	1.21 : 1

B. Bromination.   0.25% Bromine solution.

Sample	Moles of piaselenole	Ml of bromine solution added	Moles of bromine	Ratio Br_2:piaselenole
1	6.14×10^{-3}	127.10	6.14×10^{-3}	1 : 1
2	5.32×10^{-3}	110.69	5.35×10^{-3}	1 : 1
3	7.11×10^{-3}	147.32	7.12×10^{-3}	1 : 1

Chlorination and Bromination Reactions: The chlorine and bromine adducts were prepared as described and in darkness to prevent photodecomposition. A known amount of piaselenole was reacted quantitatively. The adduct was then collected and transferred to the reaction vessel. An excess of the material to be halogenated, making the adduct the limiting reagent, was added to the reaction vessel. The reaction was allowed to proceed under gentle heating for thirty minutes to one hour. A high boiling substrate, decyl alcohol, was added to double the volume present and a fractional distillation undertaken. Fractions were identified by their boiling points with the desired fractions being collected in vessels calibrated in one tenth milliliter units.

Test of Piaselenole as a Scrubbing Agent:

A. As a Solid.

A sample of piaselenole was packed in a glass column of 1" diameter. A mixture of halogen and air, in varying concentrations and varying flow rates, was passed over the sample. A methyl orange sample was used as a visual detector for chlorine. Excess bromine also possessed its characteristic red color. At slow flow rates, no chlorine or bromine was detected passing the piaselenole sample until the sample was saturated with the halogen. It was noted that the packed sample of piaselenole exhibited a decomposition gradient where the end exposed to the halogen-air mixture would decompose upon saturation while the other end would still be white. An attempt to stop the decomposition by stirring the piaselenole sample proved ineffective in stopping the

decomposition but still absorbed all halogen coming
over the sample.

B. As a Liquid.

The procedure for this is the same as for the preparation
of the chlorine adduct. Twenty seven common and uncommon
solvents were tested. (Table 2) Only chlorine was tested
in this manner. All chlorine was absorbed until the pia-
selenole was saturated. This method is better than the
previous method since the adduct formed can be collected
and the piaselenole can be regenerated, in most cases, to
be used again.

B. Instrumental.

All Raman spectra were taken with a Spex Industries model
1451N Spectrometer. Samples were analyzed as solids in capil-
laries and in pellet form with the use of a rotating platform.
The pure piaselenole samples were very stable but the chlorine
and bromine adducts were burned up with prolonged exposure
to laser radiation. The rotating samples extended the length
of time that a sample could be kept in the laser but the adducts
still burned.

Excitation was done with a Spectra Physics model 164 Argon Ion
Laser that employed a model 265 Exciter. Two lines were used:
the 514.5 nm line at 80 mW power and the 488.0 nm line at 140
mW power. A model 310A broad band polarization rotator was used
for polarization. In addition a Spectra Physics model 375 dye
laser and model 376 dye circulator was used to give excitation
at the 611.4 nm line at 140 mW power.

TABLE 2

Adduct Formation From Various Solvents

Table 2

Adduct Formation From Various Solvents

Solvent	Solubility of piaselenole	Ppt. rate of adduct	Adduct Stability in solution (hrs)
Carbon Disulfide	s	fast	50+
Chloroform	s	fast	50+
Methylene Chloride	s	slow	50+
Carbon Tetrachloride	m	slow	24
Chlorobenzene	s	slow	-
Benzene	s	slow (d)	-
Toluene	s	fast	50+
Xylene	s	fast	50+
Pentane	m	fast	12
Hexane	m	fast	50+
Cyclohexane	m	fast	50+
Ethyl Acetate	s	slow	-
Acetone	s	slow	-
MIBK	s	no ppt	-
MEK	m	no ppt	-
1,4 - dioxane	s	d	-
Ethylene glycol	m	d	-
Methanol	m	d	-
Ethanol	m	d	-
n-Propanol	m	d	-
Petroleum Ether	m	fast	12
Nitrobenzene	s	fast	50+
Pyridine	s	d	-
Aniline	m	d	-
Mineral Oil	i	-	-
O-147, OAI Lube Oil	m	fast	50+
"3 in 1" Oil	m	fast	50+

Solubilities denoted as: s - soluble, m - moderately soluble,
i - insoluble
Decomposition is denoted by d

O-147, OAI Lube Oil, Tenneco Chemicals Inc., Nuodex Div. Batch 10418

"3 in 1" Oil, Boyle - Midway Inc., New York, N. Y.

RESULTS AND DISCUSSION

During the previous investigations, it became clear that both Cl_2 and Br_2 could be removed from a gas stream. Many compounds will also do this but usually by an oxidation - reduction process where the scrubbing agent is destroyed. In this case, piaselenole was found to remove both chlorine and bromine quantitatively until it became saturated with the halogen. The halogens can also be stripped away when water is added to the adduct and the scrubbing agent regenerated. By using a light oil as a substrate, this may be of commercial value.

Attempts to employ the halogen adducts as solid halogenation reagents were successful to a limited extent (Table 3). Low yields characterized the attempts to halogenate. An attempt to place the dimeric halogen onto a double bond in a cis configuration was unsuccessful. The trans isomer was predominant. However, it is possible that the cis isomer was formed in larger yields but the heating during the fractional distillation may have caused a rearrangement to the trans isomer. Attempts to chlorinate toluene, methylcyclohexane, and ethylbenzene gave no chlorination results. Iso-pentane was the only other compound tried that gave chlorination results, but the separation of each fraction could not be accomplished because the boiling points were too close together. The yields were very low, but the largest fraction obtained was that associated with the tertiary substituted product. In all attempts, a large amount of black residue was noted after each halogenation. This was due to decomposition products.

Product yields from these attempts indicate that as a halogenating reagent, it is rather ineffective. Other reaction conditions may prove that the halogen adducts will be very good solid

halogenating reagents. The compound is restricted by its high molecular weight, 253.98 for the chlorine adduct and 343.09 for the bromine adduct, and the tendency to decompose which makes the adduct rather hard to handle.

The stability of the halogen adducts was determined (Table 4). Decomposition in the presence of light and room temperature was noted within a few minutes. At room temperature, in the absence of light, decomposition was complete within one hour. When kept at freezer temperatures in the absence of light, the adduct has been kept for two months with no decomposition and appears to be indefinitely stable under these conditions. The bromine adduct was found to decompose under all conditions.

The Raman spectra for pure piaselenole and for the chlorine and bromine adducts are presented in figures 1 to 4. Raman spectroscopy was chosen for the investigation of the structure of the adducts because the vibrational modes of the halogens are strong.

The strong peaks at 790 cm^{-1} and 302 cm^{-1} with the 514.5 nm line were found to shift when other excitation lines were used and subsequently were found to be instrumentation errors.

Solid samples of the chlorine and bromine adducts were found to burn when subjected to laser radiation when a capillary tube was used to hold the sample. A pellet of the solid material placed on a spinning platform and subjected to laser radiation was found to burn albeit less readily than in the capillary tube.

Inorganic dimeric chlorine is reported to have a frequency assignment of 557 cm^{-1} and bromine has an assignment of 316 cm^{-1}.[12] Comparison of the Raman spectra obtained give dimeric chlorine in the adduct an assignment of 520 cm^{-1}. The assignment for dimeric bromine in the adduct is a broad band with two peaks at 214 cm^{-1}

and 236 cm^{-1}. The broad band is due to the burning of the sample. These positions were observed to disappear upon continued exposure to laser light at the same time that decomposition was noted in the sample. No frequencies associated with a selenium-halogen bond were observed.

Previous work on piaselenole has shown that the selenium atom is rather inactive towards anything except metals which readily react with chalcogens. The nitrogens are the observed reactive sites. The crystal structure data of Luzzati[6] give a nitrogen - nitrogen distance of 2.38 Å, which would be just right for a halogen to sit between the nitrogens in a bridging configuration. The chlorine - chlorine distance is reported at 1.99 Å and the bromine - bromine distance is 2.29 Å.[13] It is believed that the lone electron pair on the nitrogen is associated with the halogen in the same manner as the formation of a quarternary salt. A slight polarization in the dimeric halogen could interact with a slight reverse polarization between the nitrogens to allow hydrogen bonding between the atoms.

On the basis of the Raman spectra, the observed reactivities of the halogen adducts, and previously reported information, it is believed that dimeric halogens are indeed associated with piaselenole in the adducts.

TABLE 3

Halogenation of Cyclohexane and Cyclohexene

    A. Chlorination of Cyclohexane
    B. Bromination of Cyclohexane
    C. Chlorination of Cyclohexene
    D. Bromination of Cyclohexene

TABLE 3

Halogenation of Cyclohexane and Cyclohexene

A. Chlorination of Cyclohexane.

Moles of piaselenole	Ml of fraction collected	Moles of $C_6H_{11}Cl$	% yield
7.296×10^{-3}	0.32	1.855×10^{-3}	25

B. Bromination of Cyclohexane.

Moles of piaselenole	Ml of fraction collected	Moles of $C_6H_{11}Br$	% yield
7.360×10^{-3}	0.26	2.130×10^{-3}	28

C. Chlorination of Cyclohexene.

Moles of piaselenole	Ml of fraction collected		Moles of $C_6H_{10}Cl_2$	% yield
8.968×10^{-3}	trans	0.28	2.166×10^{-3}	24
	cis	0.09	0.707×10^{-3}	7

D. Bromination of Cyclohexene.

Moles of piaselenole	Ml of fraction collected		Moles of $C_6H_{10}Br_2$	% yield
8.669×10^{-3}	trans	0.24	1.761×10^{-3}	20
	cis	0.12	0.899×10^{-3}	10

TABLE 4

Stability of Halogen Adducts

TABLE 4

Stability of Halogen Adducts

Conditions	Decomposition		
Room temperature, light	Cl_2 adduct	–	10 minutes
	Br_2 adduct	–	6 minutes
Room temperature, no light	Cl_2 adduct	–	55 minutes
	Br_2 adduct	–	15 minutes
$-8\ ^{\circ}C$, light	Cl_2 adduct	–	72 minutes
	Br_2 adduct	–	15 minutes
$-8\ ^{\circ}C$, no light	Cl_2 adduct	–	2 months +
	Br_2 adduct	–	23 minutes

FIGURE 1

Raman Spectra of Piaselenole
    514.5 nm excitation line
    Field width - 3 K
    Filter   - 1.3
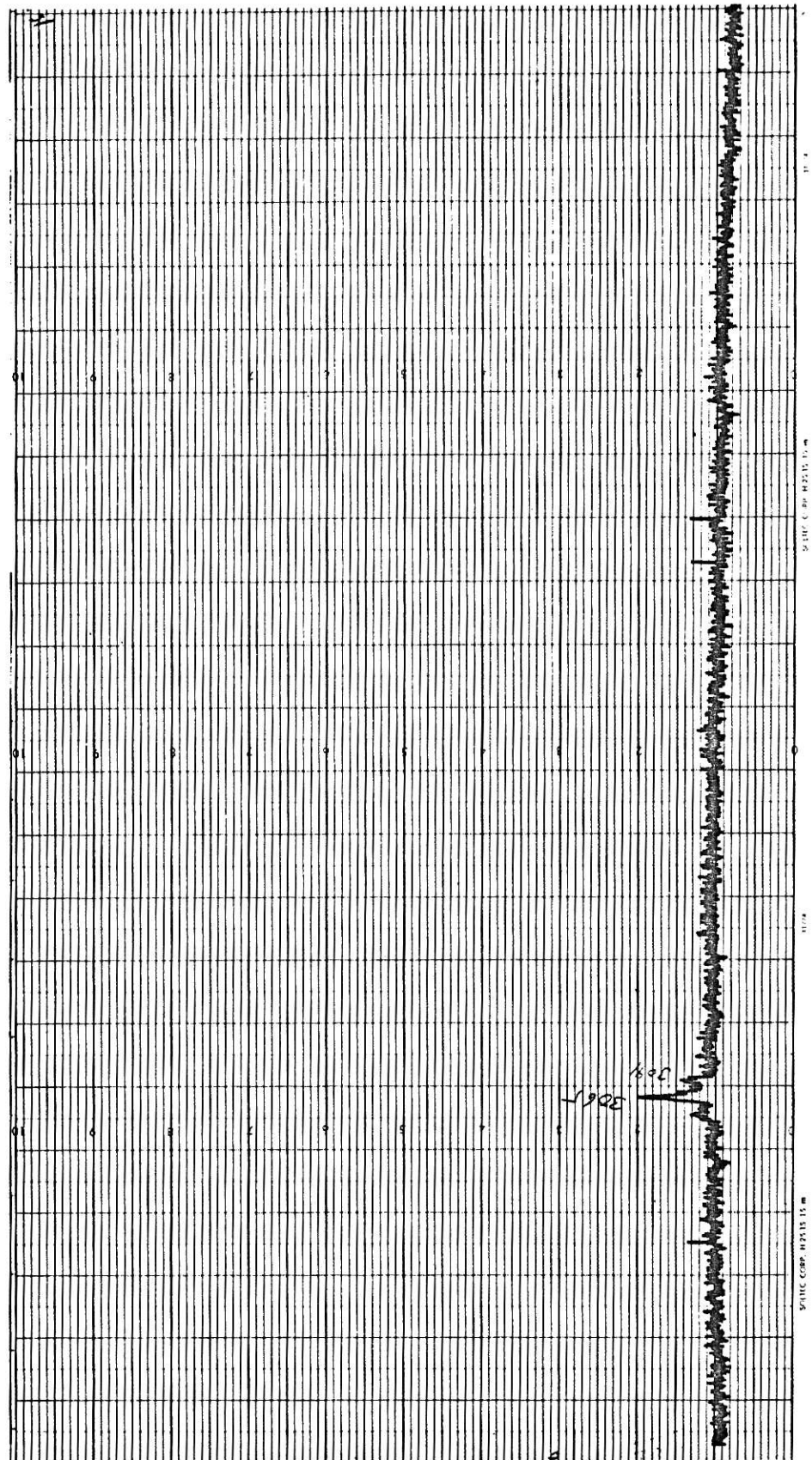   Power - 80 mW
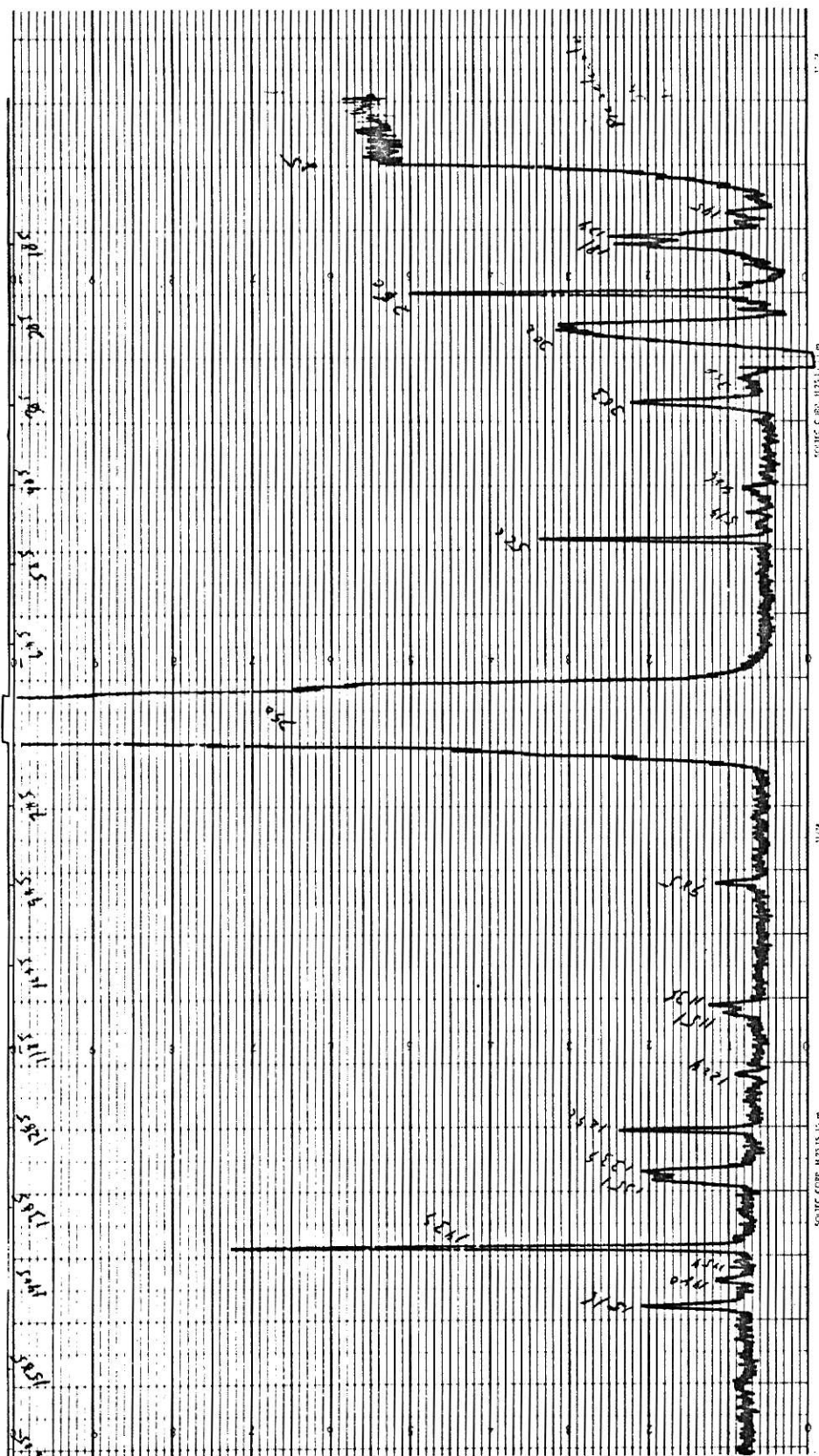
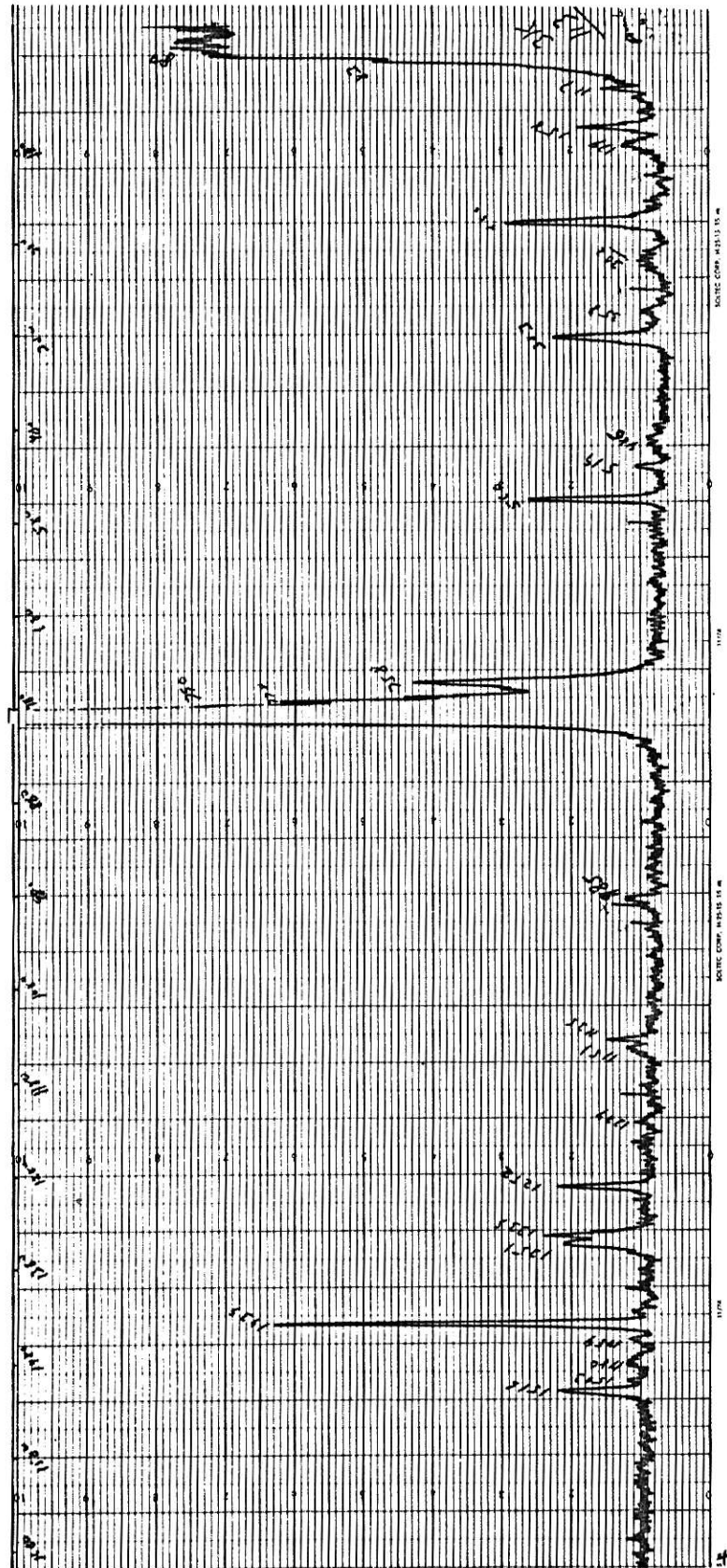FIGURE 2

Raman Spectra of Piaselenole
   514.5 nm excitation line
   Field width - 3 K
   Filter - 1.3
   Power - 80 mW

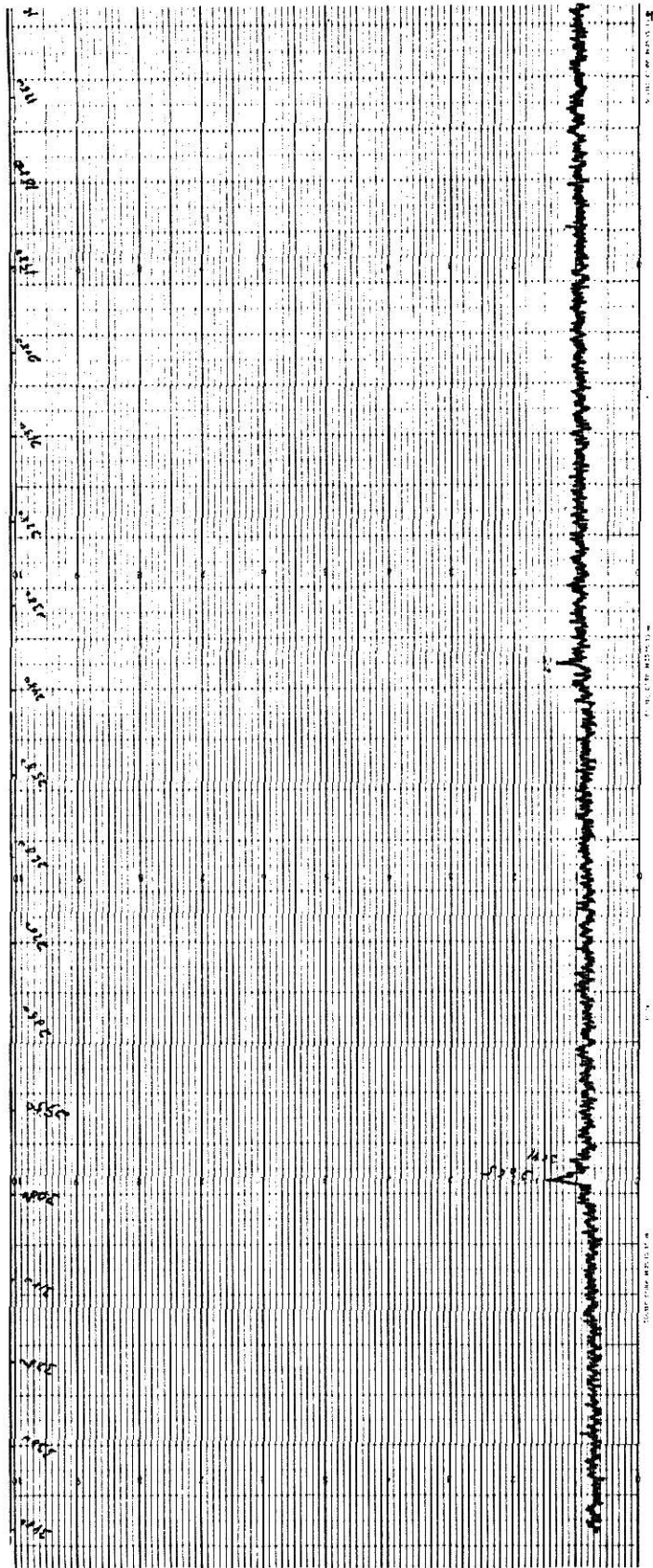Same sample as in figure 1
taken after 45 minutes

FIGURE 3

Raman Spectra of Cl_2 Adduct
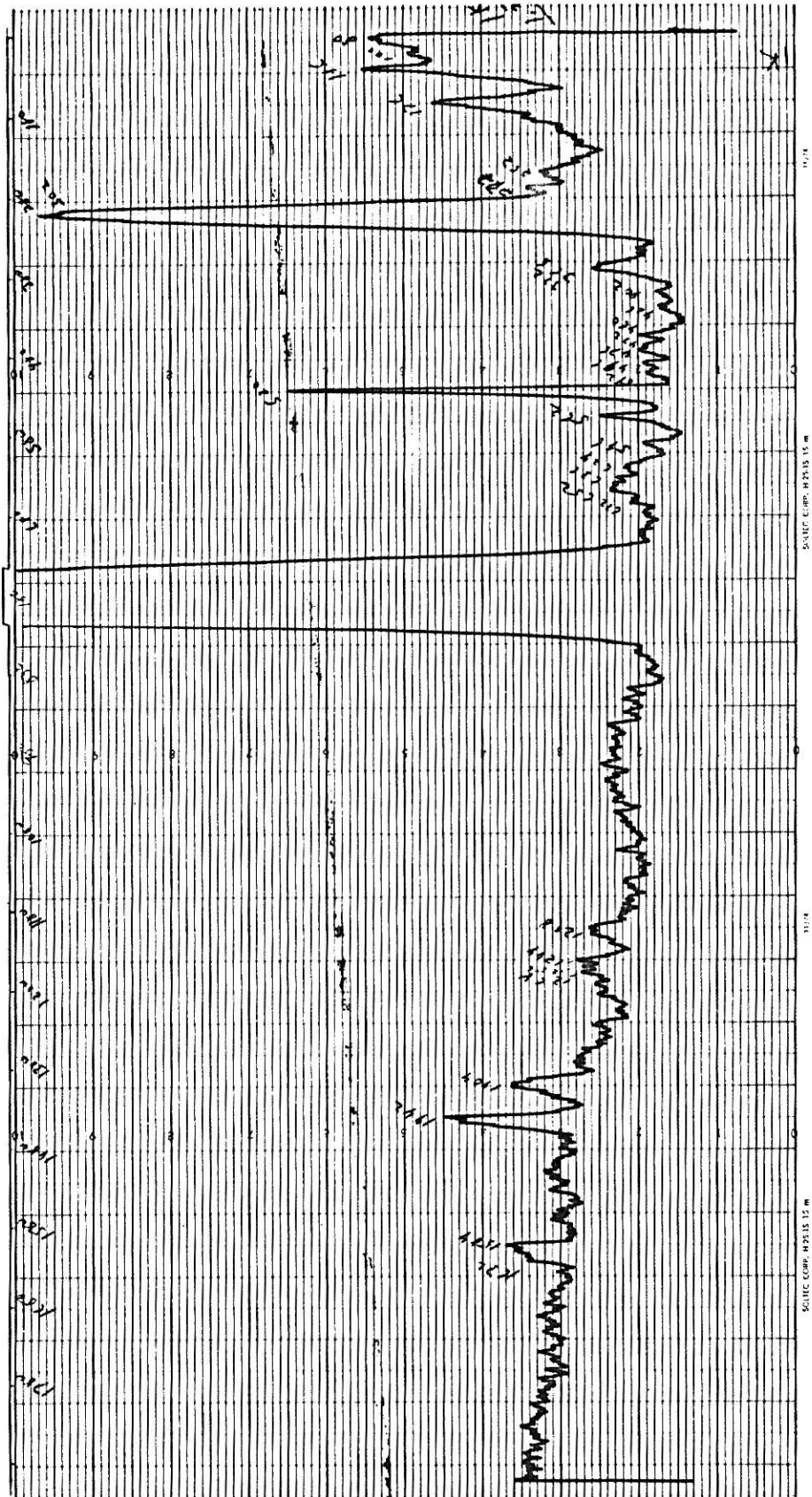514.5 nm excitation line
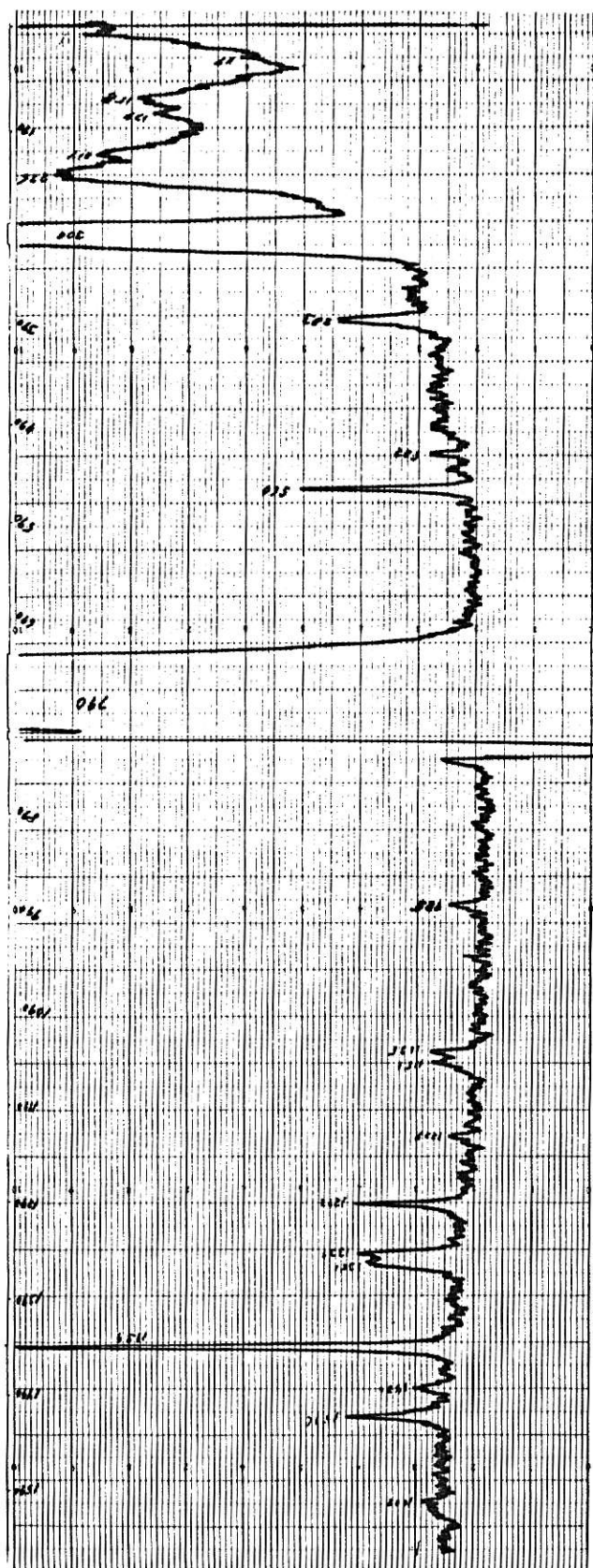Field width - 1 K
Filter - 1.3
Power - 80 mW

FIGURE 4

Raman Spectra of Br_2 Adduct
514.5 nm excitation line
Field width - 1 K
Filter - 1.3
Power - 80 mW

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Acknowledgements

PART 3

Ultrasonic Attenuation of Metal Chelates

Ultrasonic Attenuation of Metal Chelates

By

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Abstract

Reaction rates and activation parameters for the removal of adducts from several metal chelates in organic solvents has been determined by ultrasonic absorption. The ability of the metal chelates to hold onto adducts appears to be dependent upon the coordination sphere of the metal and the polarity of the ligand. The type of solvent used also has an effect. A complete analysis of the factors involved in adduct association is not possible yet as the number of associated adducts remain unknown at this time.

INTRODUCTION

Work has been going on in this research group for many years to determine just what takes place when a metal chelate is extracted from an aqueous phase into an organic phase. That work has led to the discovery that there are definite numbers of water and organic solvent molecule adducts surrounding the metal chelate and that these appear to reach a definite number at the moment of extraction. This has led to the need to determine the rate at which these adducts exchange as well as the energies involved. Ford (13), of this group, built an ultrasonic instrument that was barely sensitive enough to work with metal chelates. Bartner (14), also of this group, improved the sensitivity of the instrument by nearly an order of magnitude. The work presented here utilizes this instrument to make the actual rate and energy measurements on several metal chelates in various organic solvents.

A general approach to studying fast reactions is represented by relaxation methods, in which an external parameter, i.e., pressure, temperature, or electrical field density, is rapidly changed to induce a perturbation of the existing equilibria and subsequently observing the re-equilibration process. If the perturbation is small, then linearized rate equations can be applied and the equilibration process can be characterized by a discrete spectrum of relaxation times.

Direct methods of relaxation processes include pressure shock, T jump, electrical pulse, dielectric-loss methods, and acoustic absorption. Generally, the direct methods have advantages as the different steps of a chemical transformation occur on a time or frequency axis and interpretation requires only minor difficulties.[1,2,3]

The ultrasonic technique makes use of the fact that the temperature and pressure of a solution can be varied periodically by the passage of an acoustic wave through the solution. If the frequency is varied slowly enough, any equilibria sensitive to temperature or pressure changes will alter in phase with the acoustic wave. As the frequency of the wave is increased, some point is reached at which the phase of the periodic change in the equilibria begins to lag that of the acoustic wave. This phase lag leads to an energy absorption and this can be related to the rate constants of the equilibria.

The mathematical model for relaxation techniques has been considered extensively.[4-12] In general, the chemical relaxation is characterized by a relaxation time constant, τ. Interpretation of τ in terms of various reactions is presented in Table 1.[6] Activity coefficients are not included here and may be required in non-buffered solutions.

Given the reaction:

$$A \underset{K_r}{\overset{K_f}{\rightleftharpoons}} B + C$$
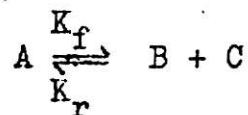
the displacement, y, at time, t, from the equilibrium concentrations, a_o, b_o, c_o, in the recombination reaction may be described as:

$$\frac{dy}{dt} = (K_f + K_r(b_o + c_o))(y_{eq} - y)$$

where y_{eq} is the corresponding equilibrium value of y at time t. Since $\tau^{-1} = K_f + K_r(b_o + c_o)$, this may be rewritten as:

$$\tau \frac{dy}{dt} + y = y_{eq} \tag{1}$$

The stress is due to a sound wave, therefore,

$$y_{eq} = A \sin \omega t,$$

where A is the amplitude and ω is the frequency ($\omega = 2\pi f$).

Table 1

The Interpretation of the Relaxation Time for Various
Reactions

TABLE 1

The interpretation of the relaxation time for various reactions.

A. Single Step Reactions.

1) $A \rightleftharpoons B$ $\qquad$ $1/\tau = K_f + K_r$

2) $2A \rightleftharpoons A_2$ $\qquad$ $1/\tau = 4K_f a^* + K_r$

3) $A + B \rightleftharpoons C$ $\qquad$ $1/\tau = K_f a^* + K_r$
   (B = buffered)

4) $A + C \rightleftharpoons B + C$ $\qquad$ $1/\tau = K_f c^* + K_r c^*$
   (C = catalyst)

5) $A + B \rightleftharpoons C + D$ $\qquad$ $1/\tau = K_f(a^* + b^*) + K_r(c^* + d^*)$

6) $A + B + C \rightleftharpoons D$ $\qquad$ $1/\tau = K_f(a^*b^* + a^*c^* + b^*c^*) + K_r$

B. Multi-step Reactions.

$$A \underset{K_{21}}{\overset{K_{12}}{\rightleftharpoons}} B \underset{K_{32}}{\overset{K_{23}}{\rightleftharpoons}} C$$

$$1/\tau_{AB} = K_{12} + K_{21}$$

$$1/\tau_{BC} = \frac{K_{12}K_{23}}{K_{12} + K_{21}} + K_{32}$$

The solution to equation 1 is then,

$$y = \frac{A}{1 + \omega^2 t^2} \sin \omega t - \frac{A \omega t}{1 + \omega^2 t^2} \cos \omega t.$$

The phase lag responsible for the absorption is given by the out of phase term in $\cos \omega t$. The amplitude, P, of a sound wave that has traversed a distance, d, in a fluid, can be expressed in an exponential form as,

$$P = P_o e^{-2 \alpha d}, \tag{2}$$

where P_o is the amplitude at d=0 and α is the absorption coefficient. The factor 2 is due to the sinusoidal characteristic of the wave which produces two pressure changes. The ratio of α / ω is proportional to the out of phase coefficient, $\frac{\omega t}{1 + \omega^2 t^2}$. In practice, α is measured experimentally and α / f^2 is plotted against log f. The relaxation time can then be found by fitting to the curve,

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f/f_c)^2} + B \tag{3}$$

where $f_c = (2 \pi \tau)^{-1}$ and $\omega = 2 \pi f$. A is a collection of constants and B is a constant introduced to account for the background absorption. In practice, A and B are found as described in figure 1.[6]

General Description of the Ultrasonic Instrumentation.[13,14]

An ultrasonic wave is an acoustic wave with a frequency higher than the limit of audio frequencies (greater than 10 KHz). The upper limit of the ultrasonic frequencies approaches the gigahertz range, which is the microwave region. A block diagram of the instrument used is shown in figure 2.

In order to induce an acoustic wave of a determined frequency,

Figure 1

Sigmoid Plot of $\dfrac{\alpha}{f^2}$ versus log f

$$\frac{\alpha}{f^2} = \frac{A}{1 + \left(\frac{f}{f_c}\right)^2} + B$$

$$\tau = \frac{1}{2\pi f_c}$$

LOG f

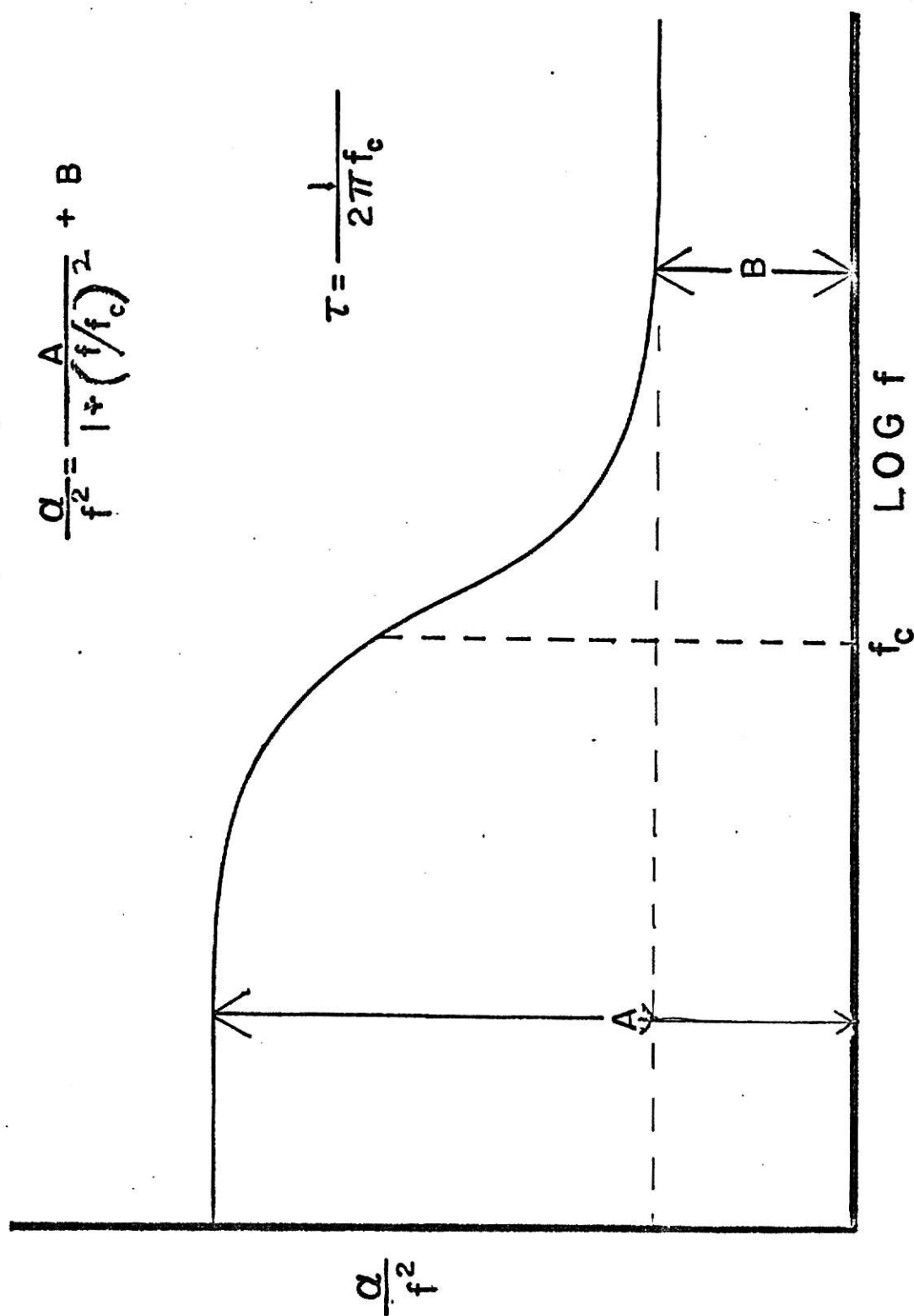f_c

$\dfrac{\alpha}{f^2}$

A
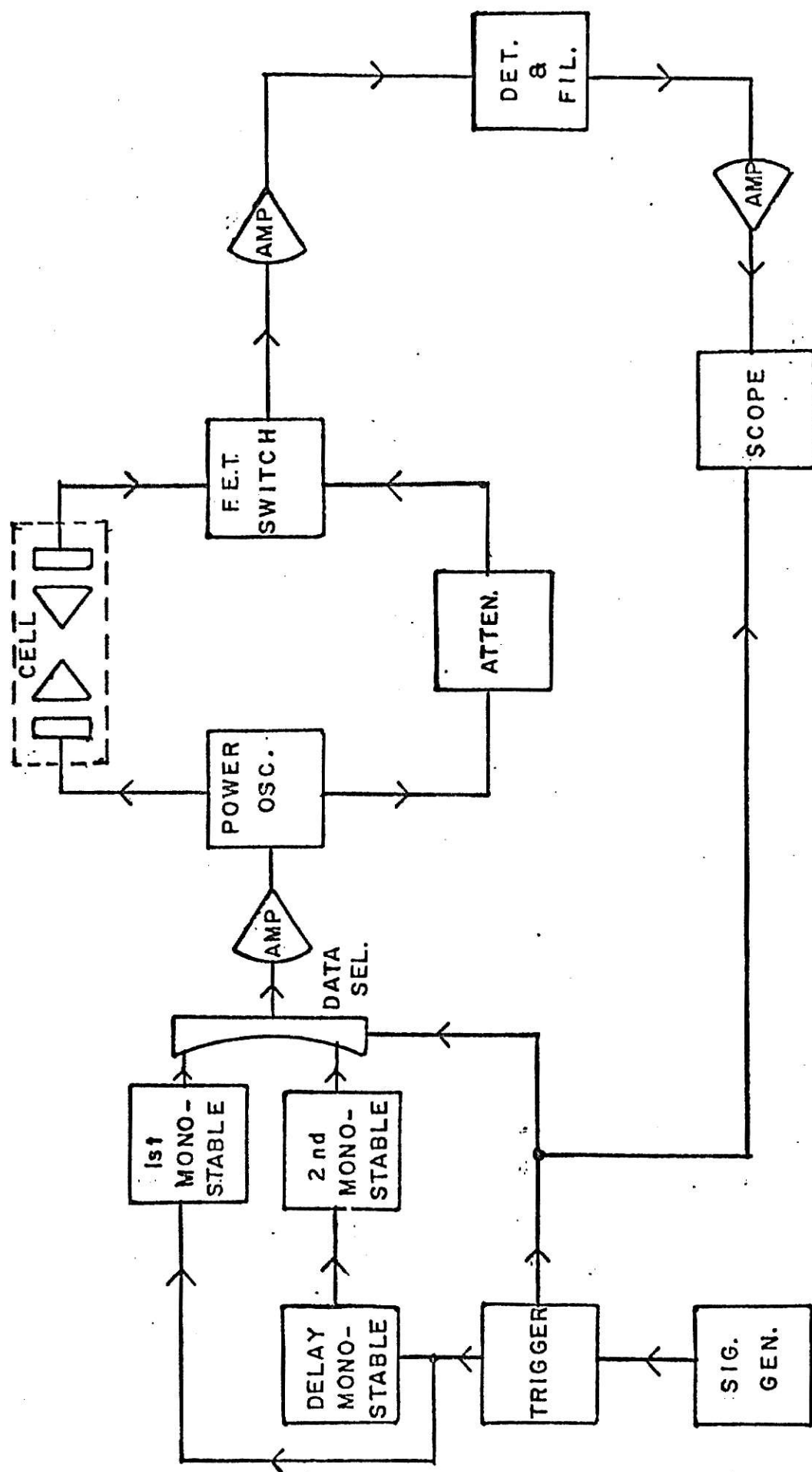
B

Figure 2

Block Diagram of the Ultrasonic Instrument

Figure 2.

an acoustic transducer is required. X-cut quartz crystals, coated
with a layer of chromium and then with a layer of gold on both
sides for electrical contact, are mounted on a drop plate so that
they face each other. A high powered radio frequency signal is
applied to the crystal causing it to vibrate at that frequency.
The resulting pressure wave is propagated through the medium to
the other quartz crystal, where it is again transduced to a voltage
signal. The crystals themselves have a fundamental frequency of
vibration. This is determined by the thickness of the crystal and
is found through the relationship:

$$f = \frac{2,870,000}{d} \text{ Hz},$$

where d is the thickness in millimeters. The crystals used in this
instrument have a d value of 5.74 millimeters, which corresponds
to a fundamental frequency of 0.5 MHz.

Although the crystals will vibrate at every harmonic, only
the odd harmonics will transduce pressure waves to the solution.
In this case, the odd harmonics of 0.5 MHz are 1.5 MHz, 2.5 MHz,
3.5 MHz, etc. The standing wave configuration of the crystal
prohibits the even harmonics from transducing pressure waves since
the nodes occur at the surface of the crystal. In contrast, the
nodes of the odd harmonics occur at the center of the crystal
with the maxima being at the surfaces of the crystal. Theoretically,
the crystals could be driven at all frequencies above the
fundamental but a great deal of power is required and most
crystal configurations cannot dissipate the heat generated in the
power generation.

The signal was applied to the transducers through the use of
a pulsed signal. A vacuum tube power oscillator of variable
frequency was used and a tuning capacitor enabled fine tuning of

the desired harmonic signal.

Two independent pulses are required: a high voltage pulse is used to drive the crystal transducer, and a low voltage pulse is taken into a calibrated attenuator network. The width of each pulse can be varied as can the delay time between each pulse. The high voltage and the low voltage multiplexed signals, after passing through the sample cell and attenuator network, respectively, are demultiplexed and fed into a wide band detector. The output is displayed on an oscilloscope as two out of phase gaussian curves, with the phase shift dependent upon the initial delay between the two pulses.

Measurements are then made on the heights of the peaks, which are directly proportional to the signal strength. In use, the crystals are initially moved so that the transmitting crystal is near the membrane. At all times, the crystals are maintained at a fixed distance. In this configuration, the signal is being transmitted mostly through the reference solution. The signal going to the attenuator network is matched to the signal passing through the cell by adjusting the attenuator, the pulse width, and the magnitude of the radio frequency pulse.

The crystals are then moved so that the detecting crystal is near the membrane. In this configuration, the signal is passing mostly through the sample solution and a decrease in the output amplitude of the detected signal indicates that an absorption has taken place. The attenuator network is adjusted to again match the two signals. The change in value of the attenuator network, in decibel calibration, divided by the change in distance traversed by the crystals gives the absorption coefficient in units of db/cm.

The cell used (figure 3) incorporates the design put forth by Corsoro et al.[15] This is a differential cell that blanks out the effect of solvent leaving only the absorption of the solute to be measured. This can readily be seen as:

$$P = P_o \, e^{-2d(\alpha_r - \alpha - \alpha_{sol})}$$

where α is the absorption coefficient of the solute, α_{sol} is the absorption coefficient of the solvent in the sample side, and α_r is the absorption coefficient of the solvent in the reference side. Since this is a differential cell, $\alpha_{sol} = \alpha_r$, then

$$\ln P/P_o = 2\alpha d.$$

Since $db = 20 \log P/P_o$,

$$\frac{2.303 \, db}{20} = 2\alpha d \quad \text{and} \quad \frac{db}{17.37 \, d} = \alpha.$$

The change in absorption per unit distance can be represented by,

$$\frac{\Delta db}{17.37 \, \Delta d} = \alpha,$$

where $\Delta \alpha = \alpha$, since $\alpha_o = 0$.

The cell is equipped with a water jacket to maintain isothermal conditions. The two halves are separated by an ultrasonic permeable membrane.
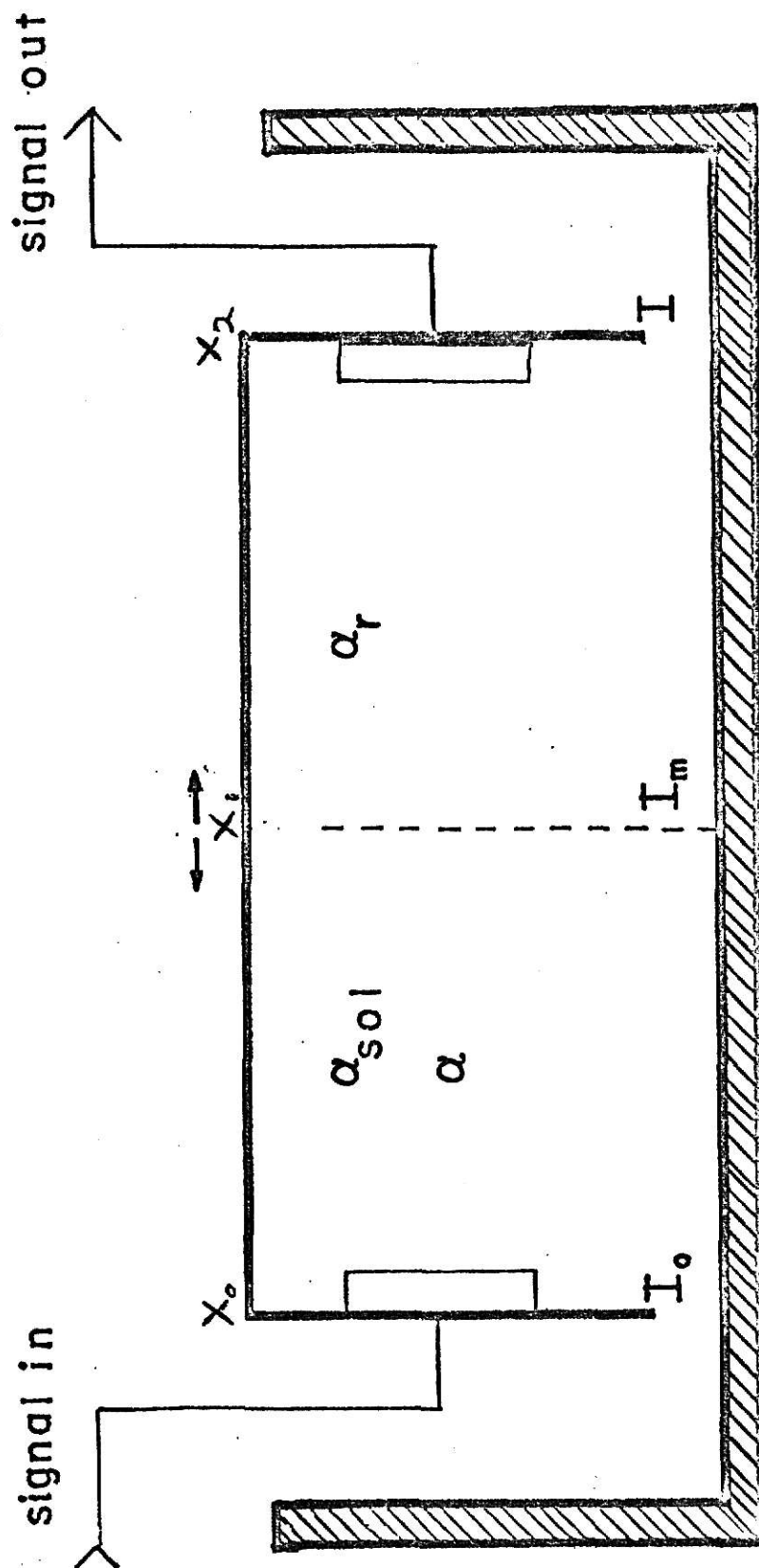
Figure 3

Differential Sample Cell

Figure 3.

Ultrasonic Induced Relaxation of Metal Chelates.

Previous work has shown that water interacting with metal chelates is an integral part of the solvent extraction process.[16-24] The method of ultrasonic relaxation is well suited to the study of this type of interaction. Ultrasonics has also been used in conjunction with the method of continuous variations to measure the chelate to metal ratio and to determine relaxation times and rate constants for the formation of chelates.[26-31]

It was desired to obtain rate constants and activation parameters of various metal chelates, using the same metals and varying the chelates, to determine a common denominator in the solvent extraction process and to see if it would be possible to predict extraction on an individual basis.

EXPERIMENTAL

The metal chelates prepared and the corresponding extraction solvents are listed in Table 2. All solvents used were reagent grade.

Metal salts were dissolved in distilled, deionized water and extracted with the chelating agent solublized in the solvent of choice. The metal chelate was then collected, crystallized, and re-crystallized to assure the purity of the chelate. 10^{-2} molar solutions of the metal chelates were prepared. This concentration was chosen because excessive absorption by a few chelates at higher concentrations prohibited detection of any signal.

Each side of the differential cell contained 500 ml. To one side, the metal chelate and solvent were added and solvent was added to the other. The crystal transducer system was set in place and the entire cell mechanism was encased in a plexiglas shell to

Table 2

Metal Chelates and Solvents

TABLE 2

Metal Chelates and Solvents

Metal Chelates	Solvent
$Cu(AcAc)_2$	chloroform
$Fe(AcAc)_3$	chloroform
$UO_2(AcAc)_2$	chloroform
$VO(AcAc)_2$	chloroform
$Cu(DEDTC)_2$	chloroform
$Fe(DEDTC)_3$	chloroform
$UO_2(DEDTC)_2$	chloroform
$VO(DEDTC)_2$	chloroform
$Fe(Bz)_3$	n-butanol
$UO_2(Bz)_2$	n-butanol
$VO(Bz)_2$	n-butanol

AcAc   = acetylacetone
DEDTC = diethyldithiocarbamate
Bz   = benzohydroxamic acid

protect the isothermal characteristic. Water from a Sargent-Welch constant temperature bath was circulated in the water jacket by an immersion pump. The bath can regulate temperature to within 0.01°C.

Absorption was measured for the metal chelate systems at two temperatures, measured with a thermometer that could be read to within 0.02°C. The experimental measurements were made as described previously. The transducers, being mounted on a drop plate, traversed the solution as the drop plate was driven by a 1/2 " diameter threaded steel rod. The drive screw has 13 threads per inch and is coupled to a General Electric motor, model 5SMY54HB1, through a gear system that reduces the motor speed by one third. A cog wheel at the end trips a microswitch six times per revolution. A Sodero TCeZ5E.97 space 40 ohm pulse counter counts the trips, which are used to tell how far the transducer has moved by using the conversion: 1 count = 0.0326 cm.

The primary device for measuring peak heights is a Tektronix type 531A oscilloscope. This is a 15 MHz scope with a rise time of 0.022 microseconds and uses a type 1A2 dual trace plug-in module. The scope is triggered externally from the synchronous of the pulsing system.

RESULTS AND DISCUSSION

The relaxations under study here involve the removal of adducts, associated water and solvent, from the metal chelates by an induced ultrasonic perturbation. In reactions reported where an induced perturbation has occurred, the recombination rate is much faster than the dissociation rate, making the dissociation the limiting process. This in turn means that the amount of dissociated material in solution is very small so that the effect of the recombination is not seen during the relaxation process and the relaxation time depends only on the rate of dissociation,

Table 3

Rate Constants and Activation Parameters

TABLE 3

Rate Constants and Activation Parameters

Chelate	T (^{o}K)	$f_c \times 10^{-6}$ sec	$\tau \times 10^8$ sec^{-1}	$K_f \times 10^{-7}$ sec	$E_a(\frac{Kcal}{mole})$
Cu(AcAc)$_2$	298.15	6.77	2.35	4.25	5.72
	300.15	7.22	2.20	4.54	
Fe(AcAc)$_3$	298.15	3.25	4.90	2.04	12.95
	300.15	3.77	4.22	2.36	
UO$_2$(AcAc)$_2$	298.15	3.37	4.73	2.11	13.63
	300.15	3.91	4.07	2.46	
VO(AcAc)$_2$	298.15	3.22	4.94	2.02	14.61
	300.35	3.84	4.14	2.42	
Cu(DEDTC)$_2$	298.15	3.65	4.36	2.29	15.39
	300.15	4.34	3.67	2.73	
Fe(DEDTC)$_3$	298.15	3.90	4.08	2.45	7.98
	300.15	4.26	3.74	2.68	
UO$_2$(DEDTC)$_2$	298.55	5.87	2.71	3.69	11.40
	300.35	6.73	2.36	4.24	
VO(DEDTC)$_2$	298.15	6.76	2.35	4.26	11.23
	300.35	7.63	2.09	4.78	
Fe(Bz)$_3$	298.15	4.24	3.75	2.66	12.16
	300.15	4.86	3.28	3.05	
VO(Bz)$_2$	298.15	7.88	2.02	4.95	5.85
	303.65	9.43	1.69	5.92	
UO$_2$(Bz)$_2$	296.15	4.89	3.26	3.07	9.65
	300.15	6.08	2.62	3.82	

AcAc = acetylacetone
DEDTC = diethyldithiocarbamate
Bz = benzohydroxamic acid

Table 4

Rate Constants and Activation Parameters

TABLE 4

Rate Constants and Activation Parameters

Chelate	T ($^\circ$K)	$K_f \times 10^{-7}$ sec	$\Delta G^{\ddagger}(\frac{Kcal}{mole})$	$\Delta H^{\ddagger}(\frac{Kcal}{mole})$	$\Delta S^{\ddagger}(\frac{cal}{mole\ K})$
Cu(AcAc)$_2$	298.15	4.25	-10.40	7.49	60.00
	300.15	4.54	-10.52		
Fe(AcAc)$_3$	298.15	2.04	-9.97	12.39	75.00
	300.15	2.36	-10.12		
UO$_2$(AcAc)$_2$	298.15	2.11	-9.99	13.86	80.00
	300.15	2.48	-10.15		
VO(AcAc)$_2$	298.15	2.02	-9.97	14.42	81.82
	300.35	2.42	-10.15		
Cu(DEDTC)$_2$	298.15	2.29	-10.04	15.30	85.00
	300.15	2.73	-10.21		
Fe(DEDTC)$_2$	298.15	2.45	-10.08	7.81	60.00
	300.15	2.68	-10.20		
UO$_2$(DEDTC)$_2$	298.55	3.69	-10.34	11.22	72.22
	300.35	4.74	-10.47		
VO(DEDTC)$_2$	298.15	4.26	-10.40	9.93	68.18
	300.35	4.78	-10.55		
Fe(Bz)$_3$	298.15	2.66	-10.13	12.23	75.00
	300.15	3.05	-10.28		
VO(Bz)$_2$	298.15	4.95	-10.50	31.24	140.00
	303.65	5.92	-10.78		
UO$_2$(Bz)$_2$	296.15	3.07	-10.14	30.11	135.00
	300.15	3.82	-10.41		

AcAc   = acetylacetone
DEDTC = diethyldithiocarbamate
Bz   = benzohydroxamic acid

Figure 4

Plot of $\dfrac{\alpha}{f^2}$ versus log $(f \times 10^{-6})$

$Cu(AcAc)_2$

or $\tau^{-1} = K_f.$[6]

Rate constants and activation parameters determined from the relaxation are presented in Tables 3 and 4 and in Figures 4 to 14.

The relaxation measured is due to the removal of both water and solvent adducts of the metal chelates. Since a differential cell is used, the effect of solvent is blanked out so that only the effect of the removal of the adducts is seen. At this time, it is not known what the exact process of adduct removal is since the number of water and solvent molecules associated with a molecule of metal chelate varies between chelating agents and between the type of solvent used. The instrument is also a limiting factor since the frequency range available for use, 2.5 - 9.5 MHz, is small compared to the total frequency spectrum and the quartz crystals used vibrate only on odd harmonics of 0.5 MHz, which allow only eight data points to allow a curve fit. The possibility that individual adduct molecules undergo individual relaxation about the interpolated relaxation frequency is entirely excluded from our consideration.

The fact that the relaxation is due to adduct removal and not ligand removal can be established from the Arrhenius activation energies. Removal of ligands would require energies in the range of 70 kcal/mole [33] while adduct effects of reported inorganic compounds require energies in the area of 10 kcal/mole.[6] The conditions of the reaction also prohibit the removal of a ligand, since there is no other material present that would exchange for the removed ligand.

The small range of frequencies used by the instrument restricted the use of a large temperature range in the determinations. A large temperature change could shift the relaxation out

Fig. 4
plot of $\frac{\alpha}{f^2}$ vs. $\log(f \times 10^{-5})$

Cu(AcAc)$_2$

o = 27.00°C
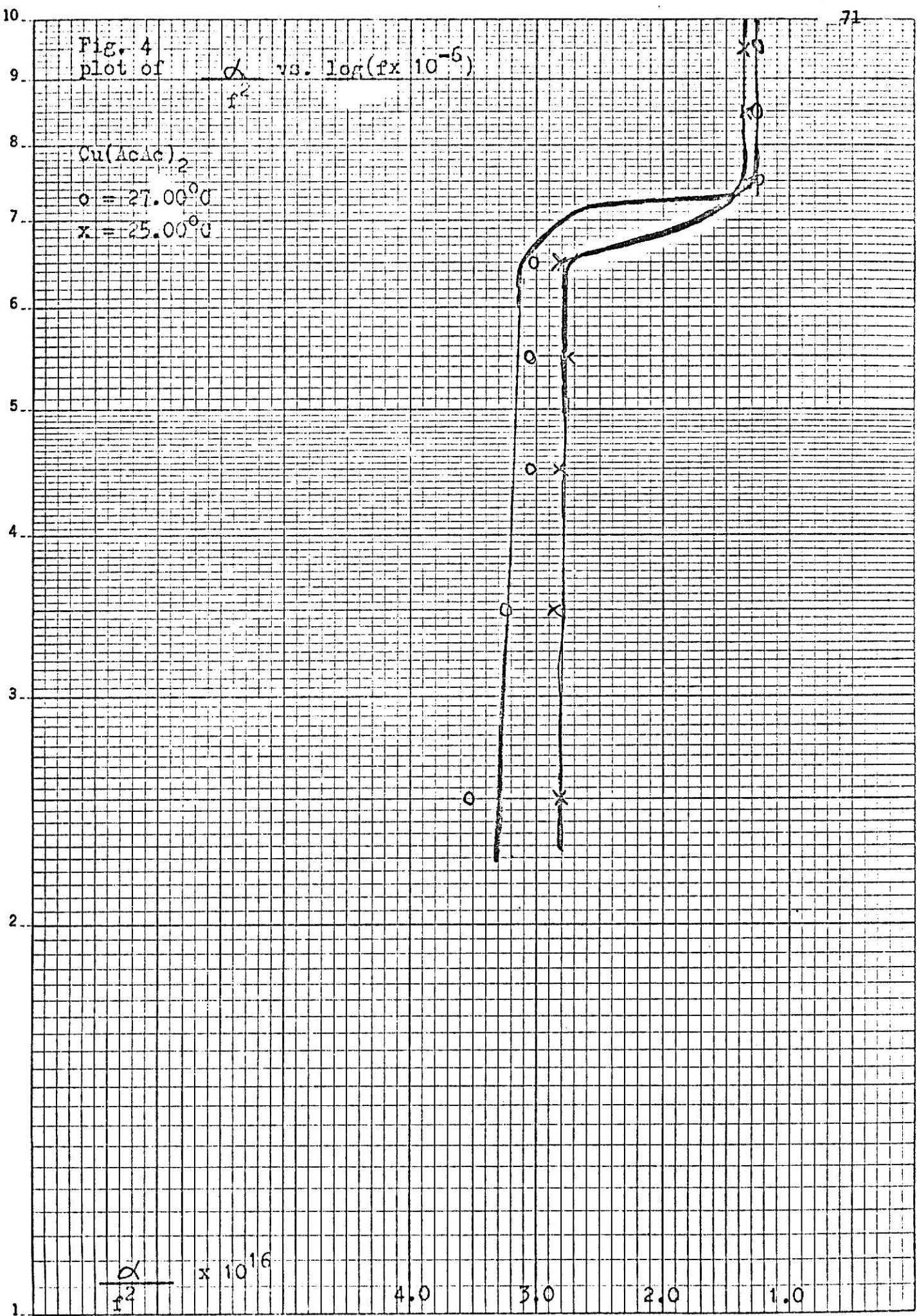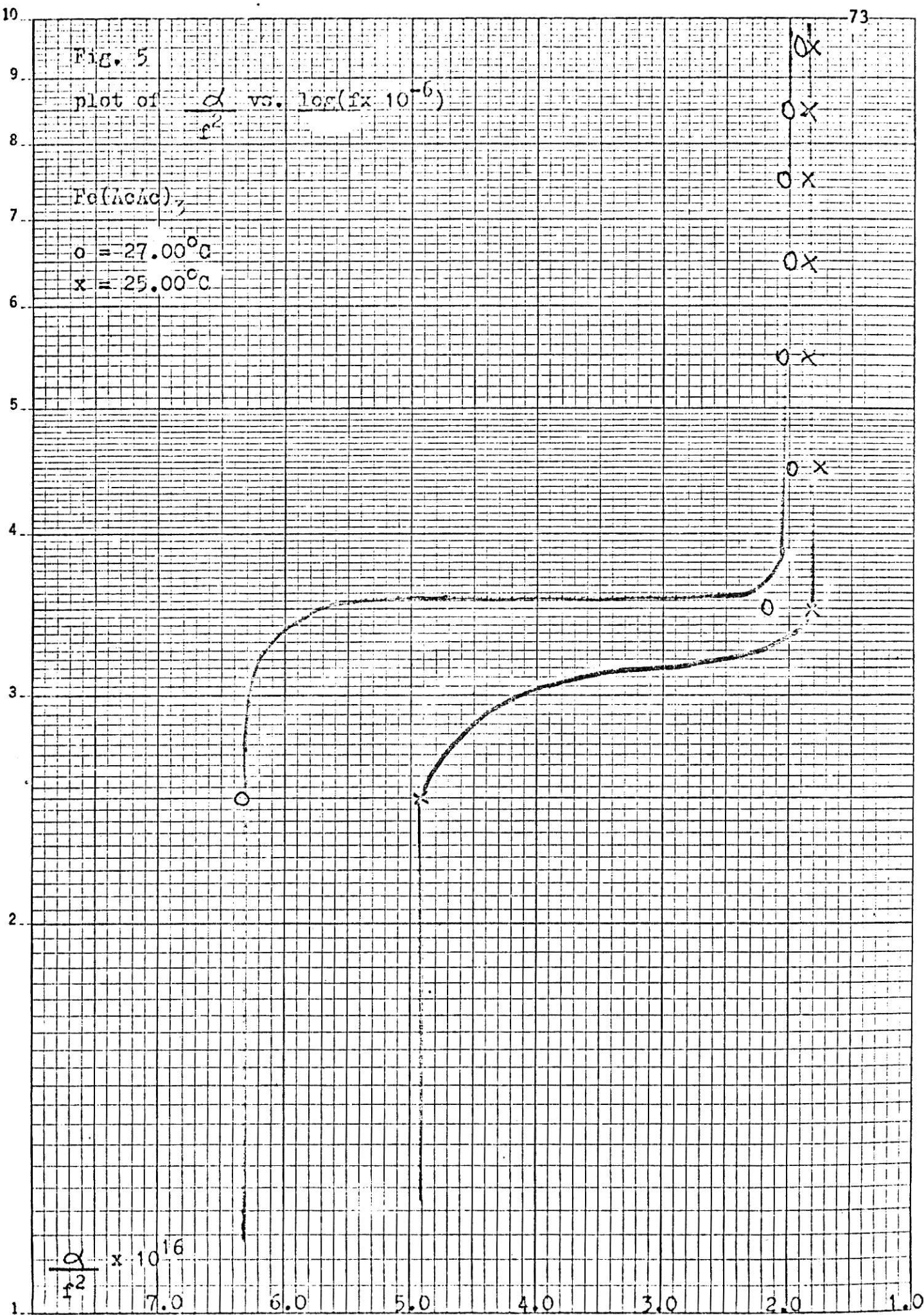x = 25.00°C

$\frac{\alpha}{f^2} \times 10^{16}$

Figure 5

Plot of $\dfrac{\alpha}{f^2}$ versus $\log (f \times 10^{-6})$

$Fe(AcAc)_3$

Fig. 5

plot of $\frac{\alpha}{f^2}$ vs. $\log(f \times 10^{-6})$

$Fe(AcAc)_3$

o = 27.00°C
x = 25.00°C

$\frac{\alpha}{f^2} \times 10^{16}$

Figure 6

Plot of $\dfrac{\alpha}{f^2}$ versus $\log(f \times 10^{-6})$

$Cu(DEDTC)_2$

Figure 6

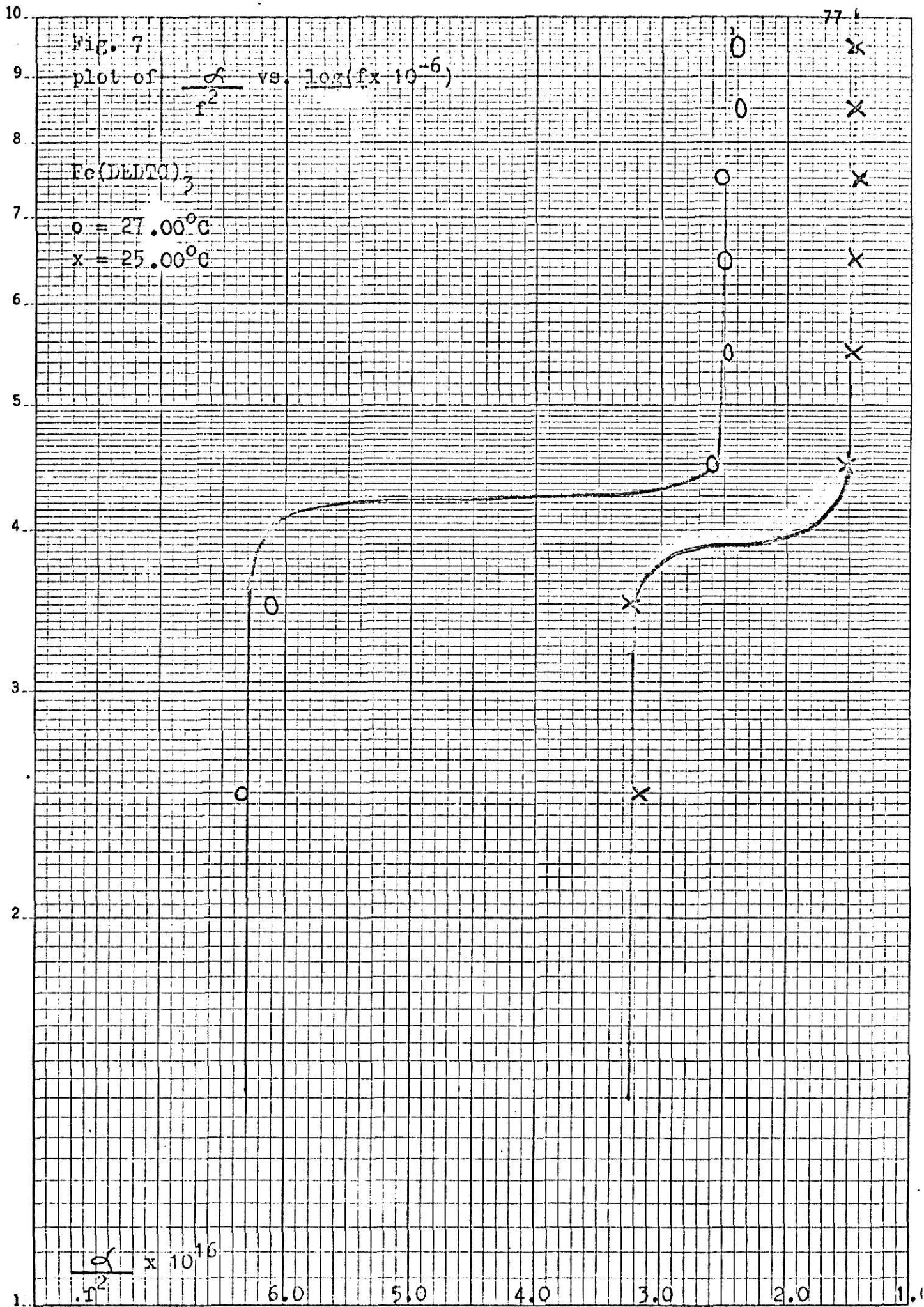plot of $\frac{\alpha}{f^2}$ vs. $\log(f \times 10^{-6})$

$Cu(DEDTC)_2$

o = 27.00°C
x = 25.00°C
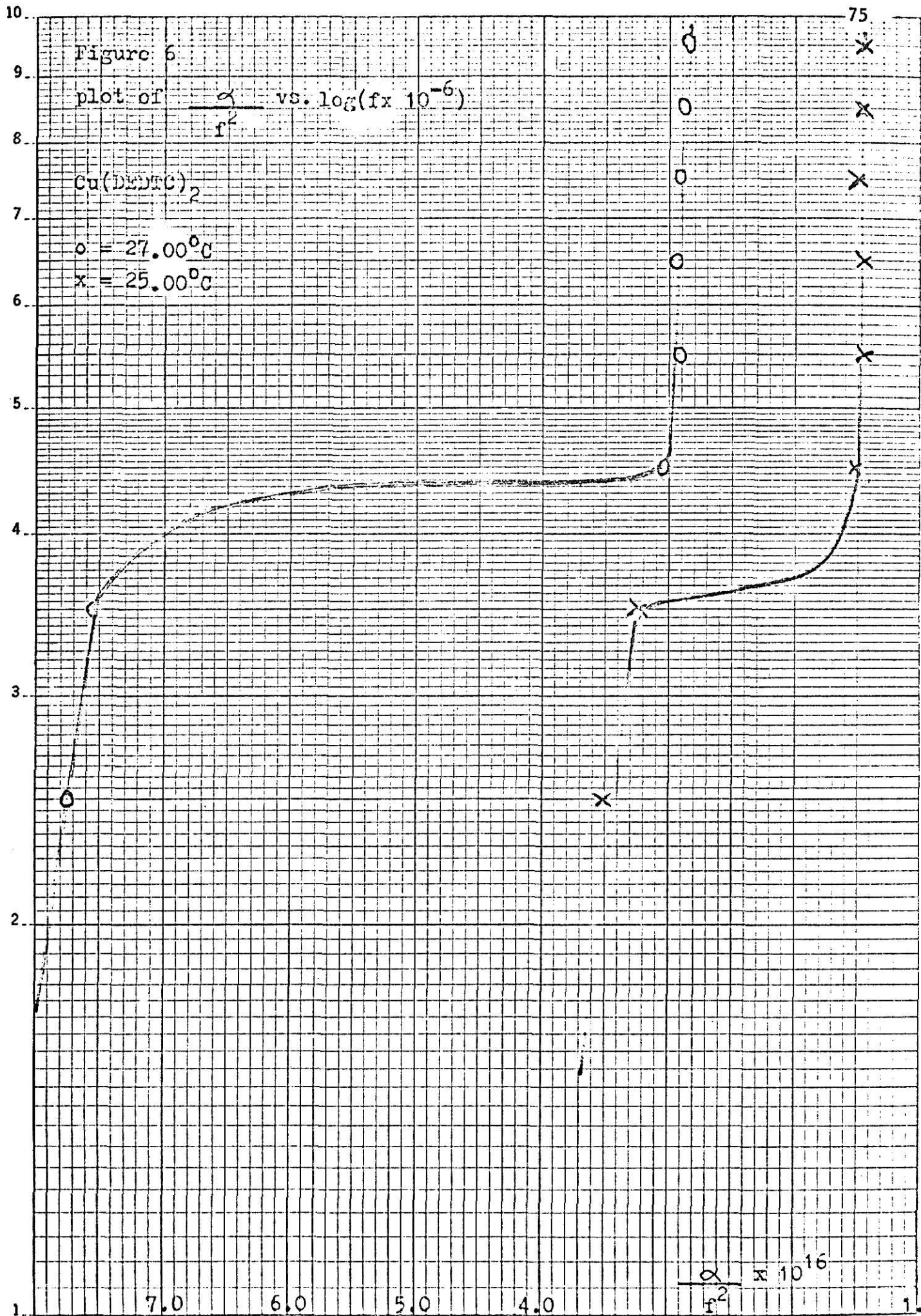
$\frac{\alpha}{f^2} \times 10^{16}$

Figure 7

Plot of $\dfrac{\alpha}{f^2}$ versus log $(f \times 10^{-6})$

$Fe(DEDTC)_3$

Fig. 7
plot of $\frac{\alpha}{f^2}$ vs. log(f x 10⁻⁶)

Fe(DETC)₃

o = 27.00°C
x = 25.00°C

$\frac{\alpha}{f^2}$ x 10¹⁶

Figure 8

Plot of $\dfrac{\alpha}{f^2}$ versus log $(fx10^{-6})$

$Fe(Bz)_3$

Fig. 8

plot of $\frac{\alpha}{f^2}$ vs. $\log(f \times 10^{-6})$

Fe(Bz)$_2$

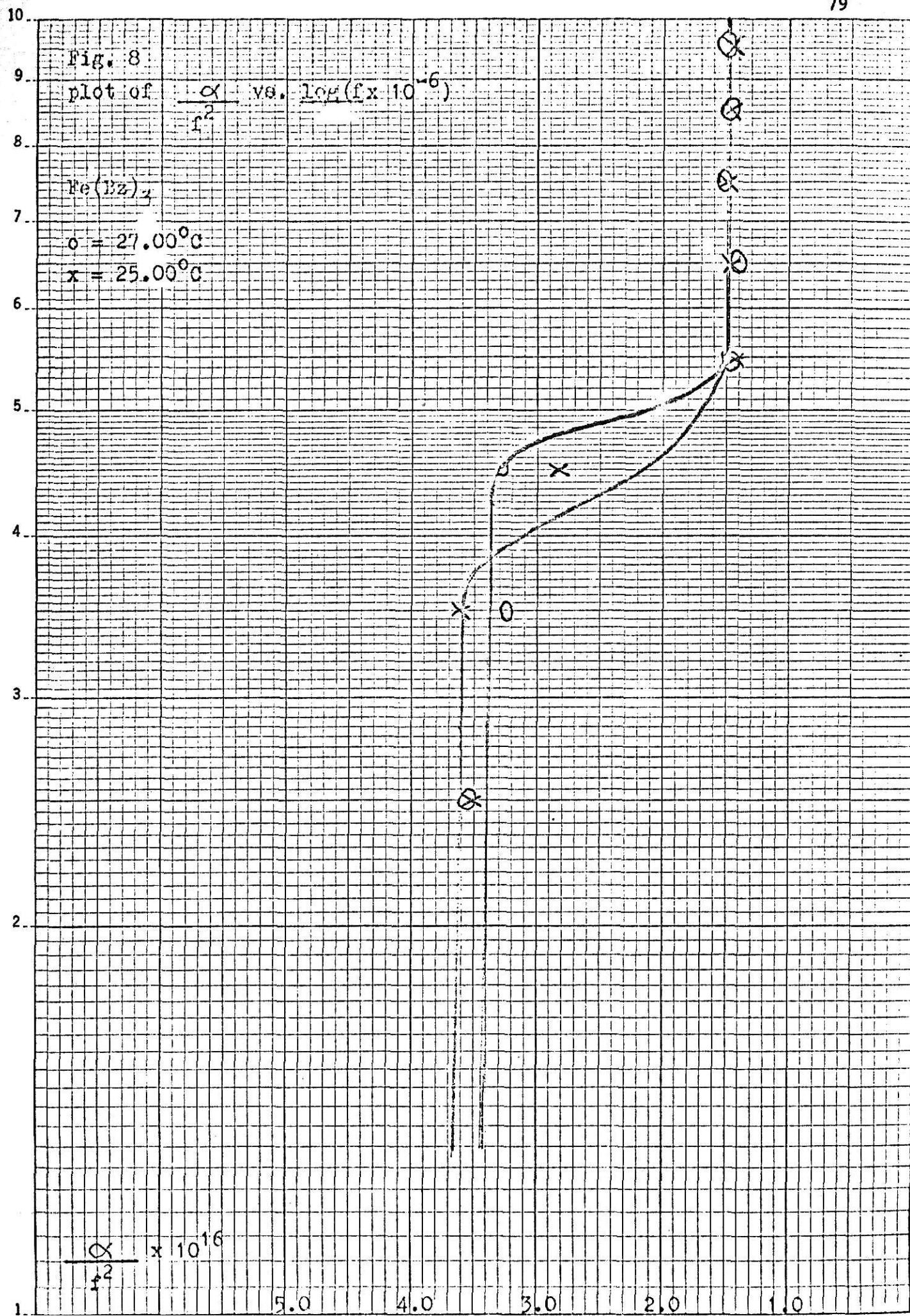o = 27.00°C
x = 25.00°C

$\frac{\alpha}{f^2} \times 10^{16}$

Figure 9

Plot of $\frac{\alpha}{f^2}$ versus log $(fx10^{-6})$

$VO(Bz)_2$

Fig. 9

plot of $\frac{\alpha}{r^2}$ vs. $\log(f \times 10^{-6})$

$VC(Bz)_2$

o = 30.50°C
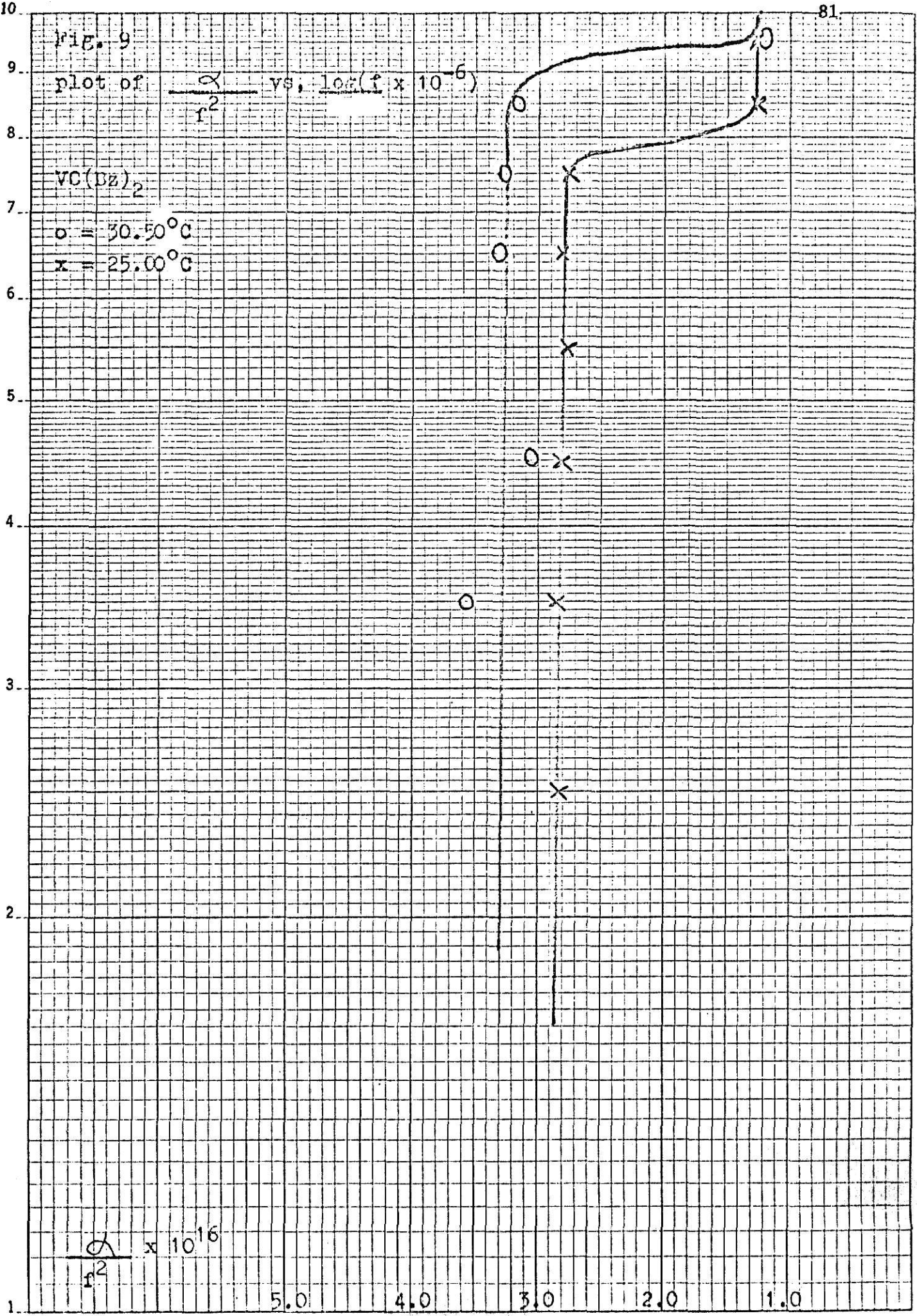x = 25.00°C

$\frac{\alpha}{r^2} \times 10^{16}$

5.0   4.0   3.0   2.0   1.0

Figure 10

Plot of $\dfrac{\propto}{f^2}$ versus log $(fx10^{-6})$

$UO_2(Bz)_2$

Fig. 10

plot of $\dfrac{\alpha}{f^2}$ vs. $\log(f \times 10^{-6})$

$UO_2(Bz)_2$

o = 27.00°C

x = 25.00°C

$\dfrac{\alpha}{f^2} \times 10^{16}$

Figure 11

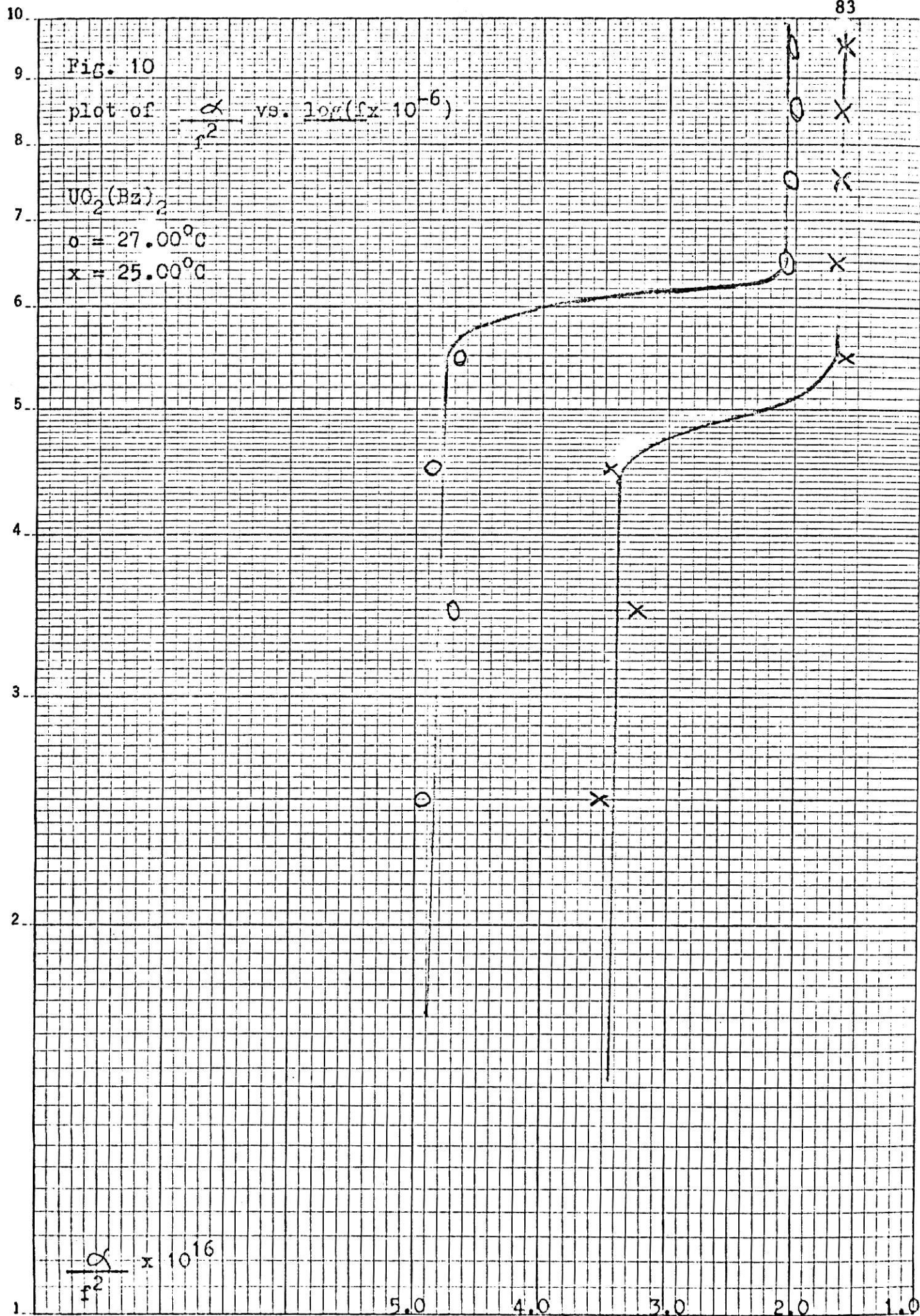Plot of $\frac{\alpha}{f^2}$ versus log $(fx10^{-6})$

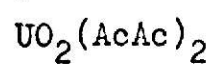$UO_2(AcAc)_2$

Fig. 11

plot of $\frac{\alpha}{f^2}$ vs. $\log(f \times 10^{-6})$

$UO_2(AcAc)_2$

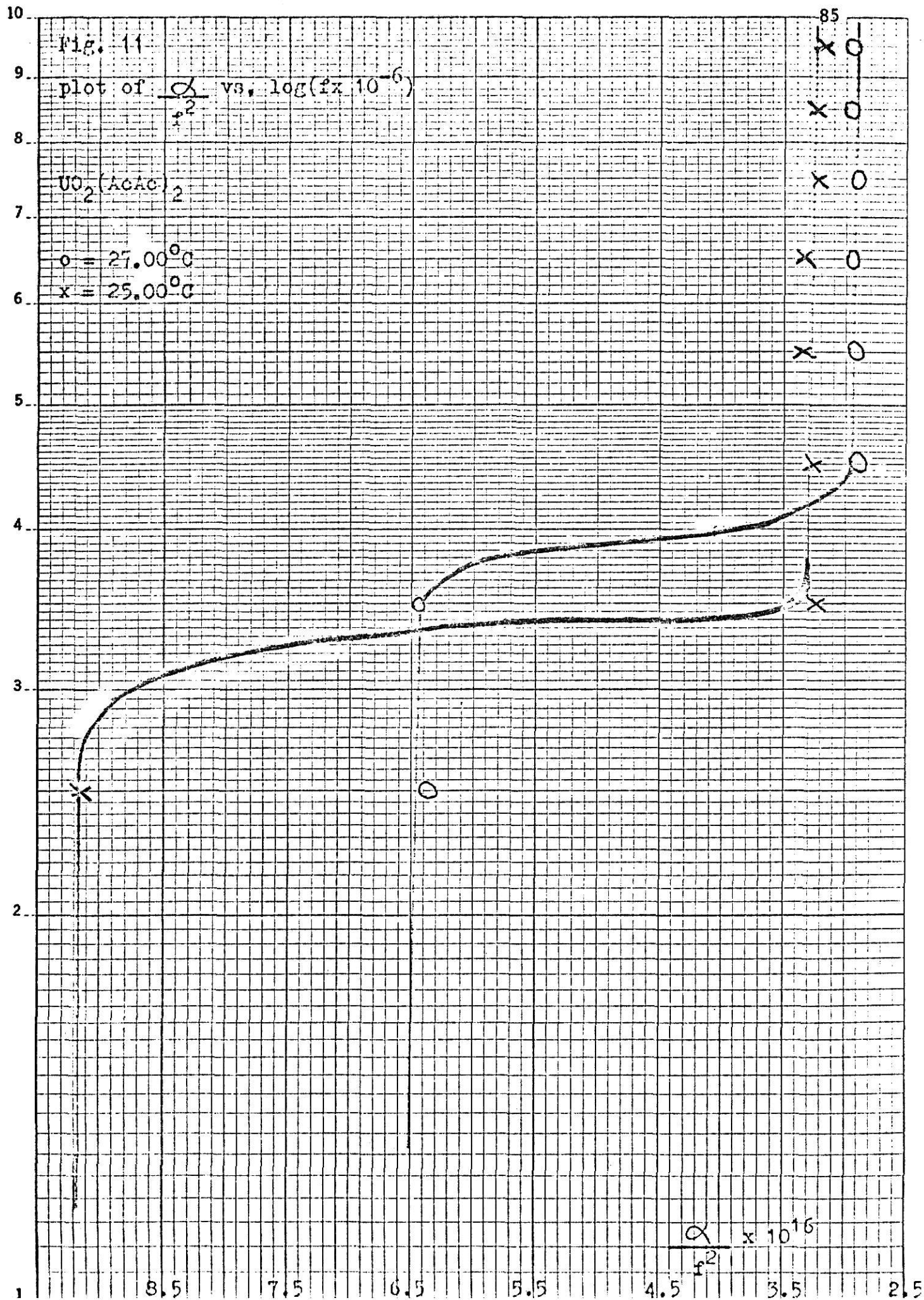o = 27.00°C
x = 25.00°C

$\frac{\alpha}{f^2} \times 10^{16}$

Figure 12

Plot of $\frac{\alpha}{f^2}$ versus log $(fx10^{-6})$

$VO(AcAc)_2$.

Fig. 12

plot of $\frac{\alpha}{r^2}$ vs. log $(fx10^{-6})$

VO(AcAc)$_2$

o = 27.20 °C

x = 25.00 °C
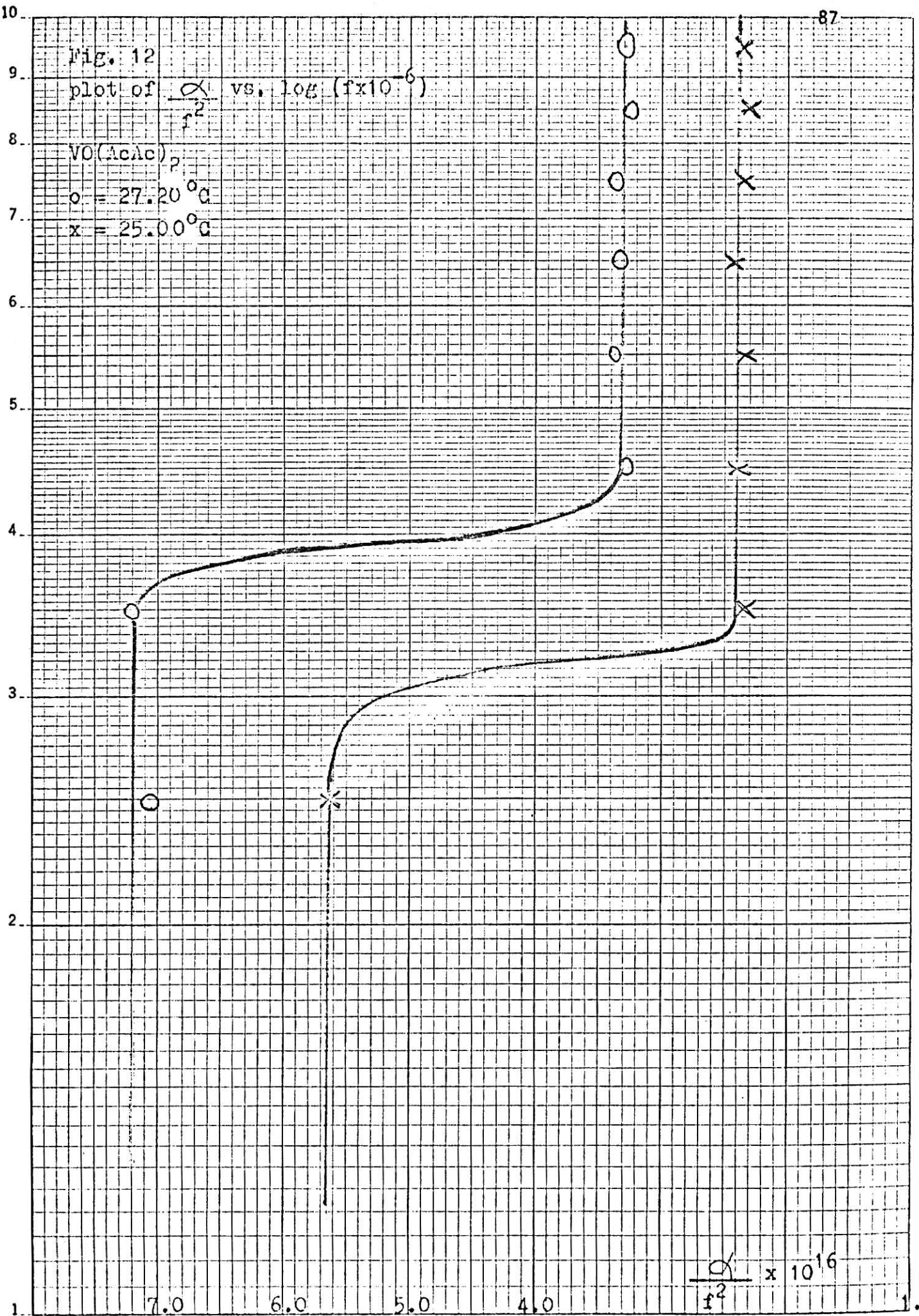
$\frac{\alpha}{f^2}$ x 10^{16}

Figure 13

Plot of $\dfrac{\propto}{f^2}$ versus $\log(fx10^{-6})$

$UO_2(DEDTC)_2$

Fig. 13

plot of $\dfrac{\alpha}{f^2}$ vs. log $(f \times 10^{-6})$

$UO_2(DEDTC)_2$

$o = 27.20^\circ C$

$x = 25.40^\circ C$

$\dfrac{\alpha}{f^2} \times 10^{16}$
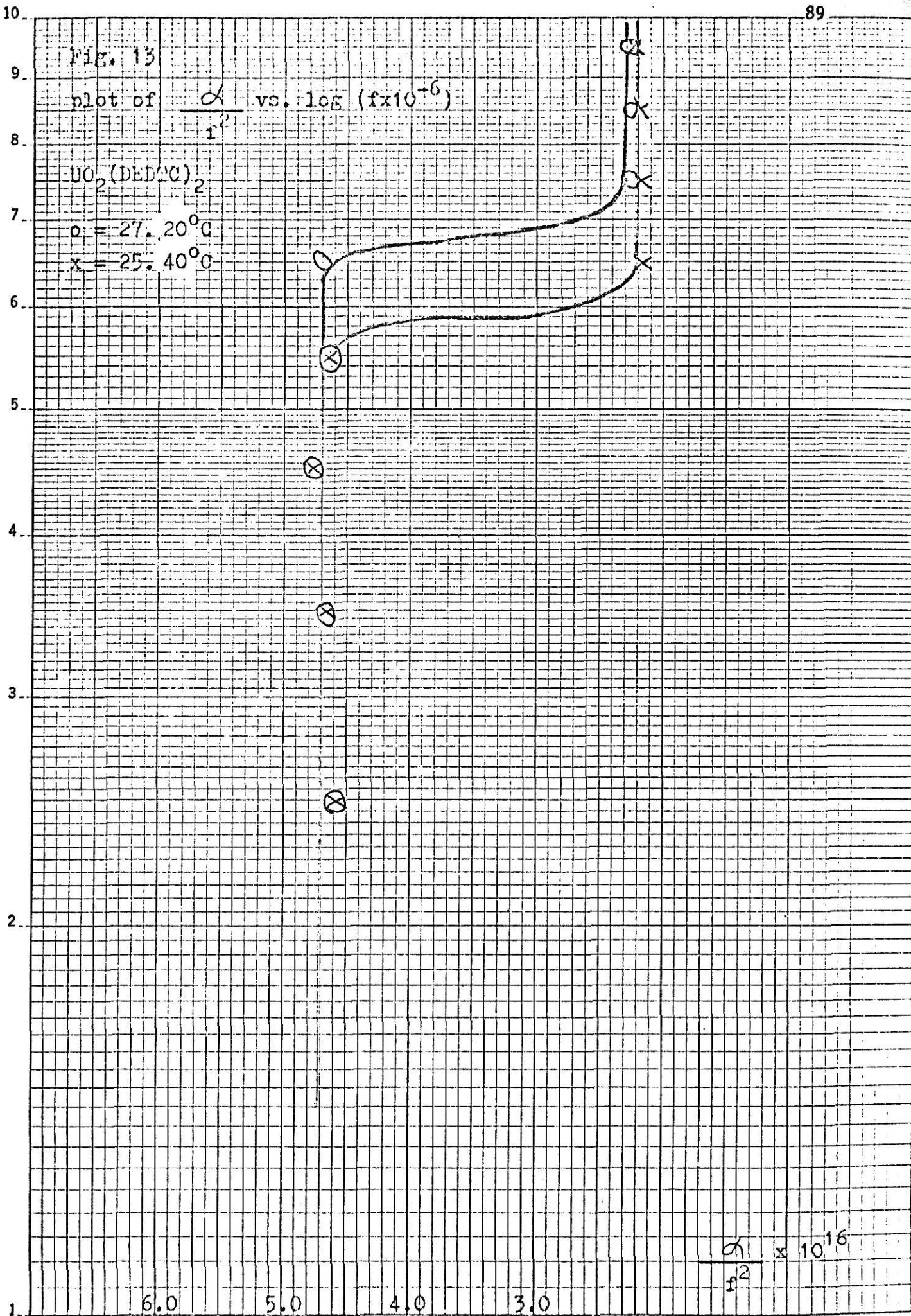
Figure 14

Plot of $\dfrac{\propto}{f^2}$ versus log $(fx10^{-6})$

VO(DEDTC)$_2$

Fig. 14
plot of $\frac{\alpha}{f^2}$ vs. log (fx10^{-6})

VO(DEDTC)$_2$

o = 27.20°C
x = 25.00°C

$\frac{\alpha}{f^2}$ x 10^{16}
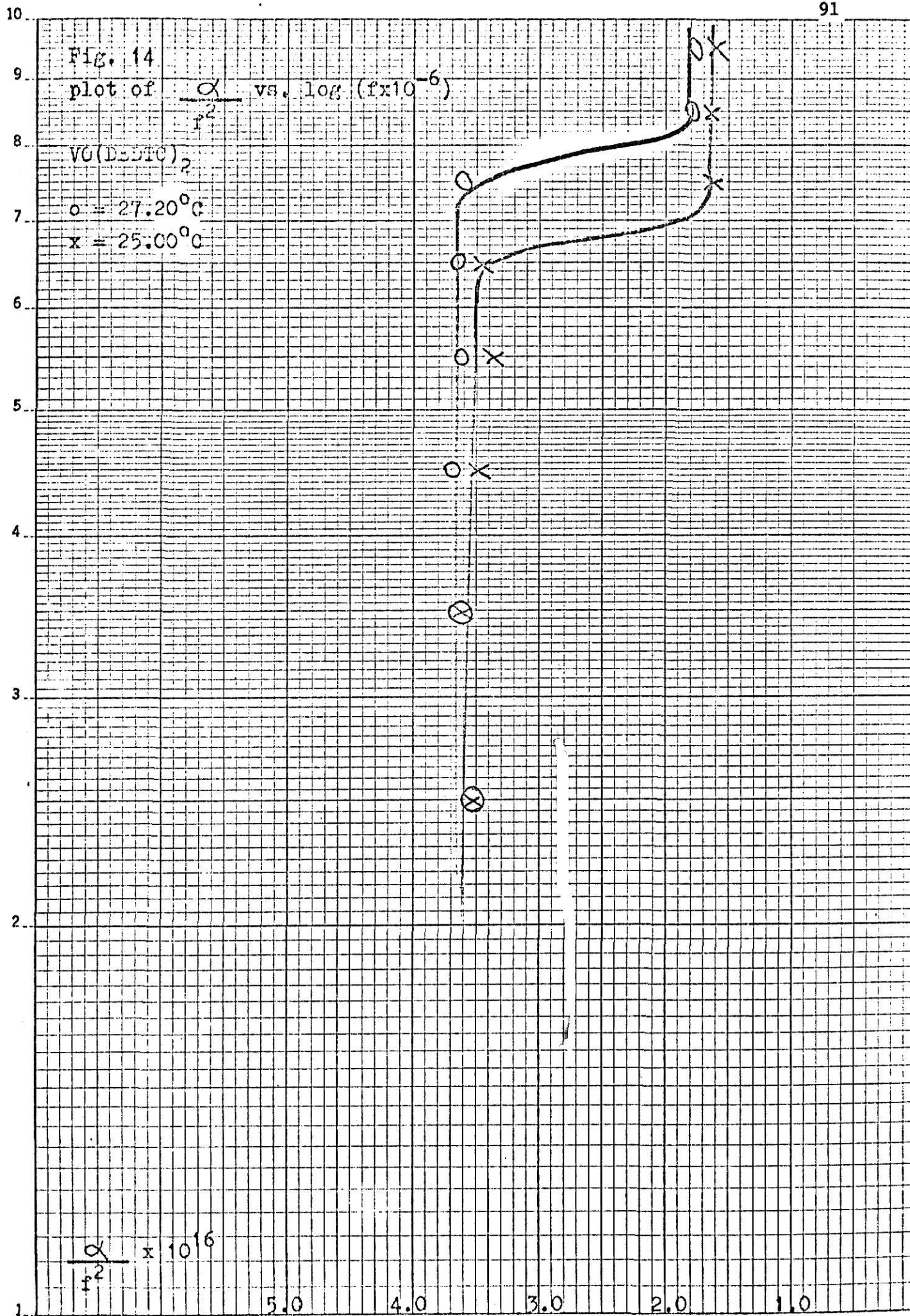
not lend itself to a good statistical treatment of the thermo-
dynamic activation parameters. The values in Table 4 seem to be
large in comparison with values obtained from inorganic compounds
which have entropies of activation in the range of 2 - 20 eu.[6,33]
An analysis of the activation parameters over a large temperature
range with a statistical error treatment should give a better
confirmation of these values.

The ability of metal chelates to hold adducts appears to be
dependent upon the coordination sphere of the metal and the
polarity of the ligand. The concept of coordinate saturation
presented by Zolotov[32] tends to favor metals that are coordinately
unsaturated to have the strongest holding power of associated
adducts. The type of solvent has an effect upon the ability of the
metal chelate to hold adducts. A polar water molecule could be
pulled from some metal chelates more easily with an alcohol as
the solvent than with a less polar solvent such as chloroform,
and vice versa. This is readily seen in the chelates of uranyl
and vanadyl ions in both chloroform and n-butanol.

A complete analysis of the factors involved in adduct
association cannot be done at this time. Other information
needed for a complete analysis include the number of water and
solvent molecules associated with each metal chelate. A mechanism
for the abstraction of adducts might then be developed.

SUGGESTIONS FOR CONTINUED RESEARCH

To be an effective instrument, the range of frequencies that
can be used must be expanded. This might be accomplished by
replacing the system of coils used presently with a voltage to
frequency converter. With this converter and a good frequency
meter, a calibration could be performed that would allow the user

to synthesize a specific frequency by applying the correct voltage across the converter. A converter of this type would be stable and lend itself to adaptation to a microprocessor that would facilitate a continuous scan over the useable frequency range.

The present instrument suffers from interference from outside sources. This is due, in part, to the total amount of exposed coaxial cable and to the lack of effective shielding in some parts of the instrument. The present instrument could be easily condensed into one cabinet. This would eliminate the large number of cables and with proper shielding there would be no cross talk within the cabinet.

When the frequency capabilities of the instrument are expanded, it will be necessary to change the dynamics of the sample cell. At very high frequencies (100 MHz) absorption of the acoustic pulse is complete within a few millimeters and at low frequencies (1 KHz) absorption of the acoustic pulse may not be seen after several meters.[6] The distance between the two crystals now should be made variable and a different sample cell built to accomodate the expected frequency region.

In order to facilitate the continuous scan characteristic of the instrument, a set of crystals with a fundamental frequency much lower than the present 0.5 MHz would be needed. The difficulty in this is that the fundamental frequency is inversely dependent upon the thickness of the crystal. A crystal with a fundamental frequency of 50 KHz would be ten times as thick as a crystal with a fundamental frequency of 500 KHz. As an alternative, another crystal other than quartz, such as barium titanate, might lend itself to lower fundamental frequencies with less thickness than quartz has.

As a final note, a microprocessor control of an instrument with expanded frequency capabilities would facilitate data collection by measuring a large amount of data over a large frequency range in a short amount of time. The data could also be analyzed and the curve fitting applied to give the instrument a greater versatility than is presently available.

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ACKNOWLEDGEMENT

PART 1

THE USE OF A COULTER COUNTER TO QUANTITATIVELY

DETERMINE MOLD IN CARBONATED SOFT DRINKS

PART 2

THE INVESTIGATION OF DIMERIC HALOGEN

ADDITION TO PIASELENOLE

PART 3

ULTRASONIC ATTENUATION OF METAL CHELATES

by

JOHN JOSEPH BLAHA

B. S., Iowa State University, 1974

AN ABSTRACT OF A MASTER'S THESIS

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1976

ABSTRACT

This thesis is in three parts:

Part 1.

A method for the rapid, quantitative screening of carbonated soft drinks for mold at levels well below what is normally detected by candling and which is quantitatively more reliable than counting mold clumps is proposed. It involves the use of a Coulter Counter and can detect as few as 10 mold filaments per milliliter of the original soft drink. Soft drinks containing pulp present a problem that is only partially solved. Dead mold in the soft drink is completely separated by a density gradient salt solution, but live mold uses the pulp as a growth base and is not separated.

Part 2.

The affinity of 2,1,3 benzoselenadiazole (piaselenole) for dimeric chlorine and bromine has been investigated. A 1:1 adduct is formed between piaselenole and both Cl_2 and Br_2. The adduct, upon reaction with water or gentle heating, liberates the chlorine or bromine dimer, however, the yields are too low to make the adduct an effective solid halogenation reagent. At slow flow rates, piaselenole quantitatively removes halogens from contaminated air streams. In addition, the Raman spectral assignments for dimeric chlorine and bromine in an associated molecular form have been found.

Part 3.

Reaction rates and activation parameters for the removal of adducts from several metal chelates in organic solvents has been determined by ultrasonic absorption. The ability of the metal

chelates to hold onto adducts appears to be dependent upon the coordination sphere of the metal and the polarity of the ligand. The type of solvent used also has an effect. A complete analysis of the factors involved in adduct association is not possible yet as the number of associated adducts remain unknown at this time.