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Quantitative Analysis of Phenidone and Derivatives in Photographic Developing Solutions

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QUANTITATIVE ANALYSIS OF PHENIDONE AND DERIVATIVES IN PHOTOGRAPHIC DEVELOPING SOLUTIONS.

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ABSTRACT

Spectrophotometric analysis and visual titration methods have been applied to the determination of Phenidone*, its 4-methyl and 4,4-dimethyl derivatives in photographic developers. The visual titration method is modified to allow for variation due to operator technique. Spectrophotometric methods are utilized for the identification of the Phenidone derivative in the Kodak process E-6 first developer. The derivative is believed to be Dimezome** at 0.3 g/l.

INTRODUCTION

The substitution of Phenidone for Metol in hydroquinone based developers increases the demand for a simple, rapid quantitative analysis for the determination of Phenidone concentration in developer solutions. Phenidone-hydroquinone developers are becoming more common in color developers, developer concentrates and other black and white processing solutions.

Metol can be cheaply replaced by one-tenth or less of its weight of Phenidone. Unlike Metol, Phenidone is nonallergenic. A Phenidone-hydroquinone developer is more resistant to the effects of exhaustion because bromide caused less restraint. Another attractive feature of Phenidone is that, while being a feeble developer on its own account, Phenidone is more effective than Metol in activating hydroquinone[1].

*Phenidone is a registered trademark of Ilford Ltd. for 1-phenyl-3-pyraxolidone.

** Dimezone is a registered trademark of Eastman Kodak Co. for 4,4-dimethyl-1-phenyl-3-pyrazolidone.

The activation of hydroquinone by Phenidone, superadditivity, can be partly explained by the acceleration of development rate by the James charge barrier depression effect[2] and the regeneration mechanism.[3,4] The regeneration of Phenidone is caused by the reduced form of hydroquinone reacting with the oxidized inactive form of Phenidone, the Phenidone semiquinone. The degree of superadditivity is partially dependent on the stability of the Phenidone semiquinone,[5] which is a relatively stable semiquinone.[6]

Quantitative analysis is an essential tool for the verification of reaction mechanisms as in the regeneration theory. Such analyses are also necessary for processing control and production purposes. Qualitative analyses are useful for the identification of Phenidone derivatives in a developer with an unknown formulation. A number of methods for the determination of Phenidone have been published since the introduction of Phenidone by Kendall.[7] The number of methods published reflects the difficulty encountered in obtaining accurate and consistent results.

Some analyses require the separation of Phenidone from other reducing agents in the developer. This is achieved by selective solvent extraction with chloroform. Such extractions are never 100% efficient, and their efficiency often varies significantly with very small changes in operator technique. The low concentration of Phenidone relative to other agents in the developer makes the resultant error appreciable.

Thin layer[8], paper and gas chromotography[9] are other methods of seraration that allow the different substituents in a developer to transport into well-defined areas. The separated compounds can then be analyzed by spectrophotometery.

The first published method for the determination of Phenidone, by Axford,[10] involves the oxidation of Phenidone with a known amount of iodine in acid pH. The excess iodine is then titrated with thiosulfate to a starch endpoint. This method is very dependent on the excess amount of iodine used. The elimination of sulfur dioxide and hydrolyse gelatin from used developers are also important.

Another non-instrumental method for the determination of Phenidone was introduced by Reitz and Amslem.[11] This method involves an extraction of Phenidone from the developer, with chloroform at pH 4. Phenidone in the chloroform extract is oxidized by an excess amount of ferric chloride in aqueous solution. Ferric chloride is reduced to ferrous chloride and the ferrous ions are titrated with sulfate cerate for an indirect measure of Phenidone concentration. This method of analysis was chosen for this research project because it provides a simple, non-instrumental and simultaneous analysis of Phenidone and hydroquinone in 40 minutes. However, the analysis of hydroquinone is the antithesis of the project and was not investigated. This method is also used for the determination of Phenidone B* in a monobath formulation.

* Phenidone B is a registered trademark of Ilford Ltd. for 4-methyl-1-phenyl-3-pyrazolidone.

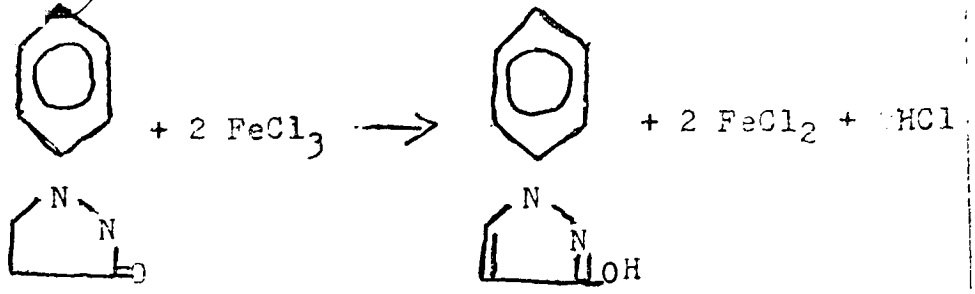
Physical methods for structure determination are essential for critical analysis of developer composition. Spectrophotometery, polagraphy, and electron spin resonance are some analytical methods for obtaining thermodynamic and kinetic properties of Phenidone oxidation.

Spectrophotometric methods are perhaps the most versatile methods available to the average photographic laboratory, providing the laboratory has a spectrophotometer working in the ultraviolet range. Such techniques involve solvent extraction with chloroform. However, these methods eliminate the preparation and standardization of reagent solutions necessary for a visual titration.

This type of analysis can be applied to quantitative as well as qualitative analysis by measuring the absorption peak of Phenidone in chloroform with a double-beam spectrophotometer from 225 to 300 nanometers. Calibration curves are constructed for the calculation of Phenidone concentration by plotting the absorption of the extract aginst the known concentration of Phenidone in the developer.

RESULTS

Quantitative analysis of Phenidone and derivatives by a visual titration technique, involves separation of Phenidone from hydroquinone and other addenda in the developer by selective solvent extraction (for a detailed extraction and titration procedure see appendix A). Mild oxidation of Phenidone by ferric chloride provides a controlled oxidation to a stable oxidation state (1-phenyl-3-hydroxypyrazolidone) without interference by hydroquinone.



Phenidone A 1-phenyl-3-hydroxypyrazolidone

The developer sample is buffered at pH 4 with glacial acetic acid and agitated with a three times volume of chloroform. Phenidone is dissolved in the chloroform while most of the hydroquinone remains in the aqueous phase. Chloroform is water washed to remove any residual hydroquinone and Phenidone is completely oxidized by thorough mixing of the chloroform extract with an excess of acidified ferric chloride. The oxidized Phenidone is removed from the aqueous ferric-ferrous solution by successive extractions with chloroform. The aqueous solution is then titrated with cerate to a ferroin endpoint.

Due to multiple extractions, losses of Phenidone and ferric chloride must be tolerated. A 7% loss of these compounds is reported by Reitz and Anslem. This loss prevents the use of stoichiometric factors for the determination of Phenidone concentration. Therefore, calibration equations were derived from data obtained by two analyst determining the Phenidone concentration of ten solutions of the Kodak process ME-4 and ECO-2 first developers. The solutions contained amounts of Phenidone varying from 0.10 to 0.50 g/l. The data was pooled and calibration curves were obtained by plotting the known concentration of Phenidone against the amount of cerate used for the titration. The calculation equation for Phenidone concentration reported by Reitz and Anslem is;

Phenidone, g/l. = (0.0757)(ml.cerate) - 0.020

To verify the results obtained by Reitz and Amslem, the author replicated* the experiment with the Kodak process ECO-2 first developer. A concentration series of Phenidone in the developer was anlayzed. The solutions contained 0.10 to 2.00 g/l Phenidone in the developer. A straight line calibration curve was obtained, (table 1.)

TABLE 1

Phenidone A concentration in grams/liter	milliliters of cerate, mean value	calculated concentration of mean value
0.100	1.78	0.092
0.201	3.21	0.201
0.300	4.38	0.292
0.404	5.73	0.397
0.500	7.10	0.504
1.000	14.30	1.063
1.500	19.50	1.470
2.000	26.28	1.994

estimated error with 95% confidence limits is ± 0.01 g/l.

Phenidone, g/l. = (0.0777)(ml cerate) - 0.048

There are many possible explainations why the authors calibration equation is not equivalent to that obtained by Reitz and Anslem. However, the author believes that the inconsistency is caused by variation in the operators technique at the extraction stage.

Reitz and Anslem state that the analysis can be applied to the determination of Phenidone B in a monobath formulation. Although they do not report any data on their analysis of Phenidone B. The analysis was performed by the author, with various concentrations of Phenidone B (K&K Lab.) in the ECO-2 developer. A straight line relationship was not evident.

* see appendix C.

The supply of Phenidone B (K&K Lab.) had depleted and another sample of Phenidone B was obtained that was manufactured by the Geigy Chemical Co. This sample did show a linear relationship, however (see table 2).

TABLE 2

Phenidone B concentration in grams/liter	milliliters of cerate, mean value	calculated concentration of mean value
0.250	3.25	0.257
0.500	5.95	0.487
0.750	9.10	0.756

estimated error with 95% confidence limits is ± 0.03 g/l.

Phenidone B, g/l. = (0.0853)(ml. cerate) - 0.020. (see fig. 1)

Dimezone was also substituted into the ECO-2 first developer at various concentrations. A stright line relation was obtained (see table 3).

TABLE 3

Dimezone concentration in grams/liter	milliliters of cerate, mean value	calculated concentration of mean value
0.250	5.10	0.246
0.500	8.43	0.508
0.750	11.45	0.746

estimated error with 95% confidance limits is 0.04

Dimezone, g/l. =(0.0787)(ml.cerate) - 0.155. (see fig. 1)

The new Kodak process E-6 first developer was analyzed with the visual titration method after results were obtained by a spectrophotometric method (see fig. 7). The assumption was made that the developing agent is Dimezone, as will be discussed later. Using the equation obtained for Dimezone, the calculated concentration of Dimezone is 0.338 ± 0.01 g/l.

Each Phenidone derivative has a different characteristic absorption peak in the ultraviolet region. This absorption peak is attributed to the vibrational stretching of the carbonyl chromophore (C=O). To determine the absorption maximum of each derivative, the absorbance of the derivative dissolved in chloroform is measured from 225 to 300 nm.(see fig. 2). A bathochromic shift is observed for Dimezone and Phenidone B (K&K Lab.) with respect to the absorption peak of Phenidone A (250 nm) The corresponding absorption peak for Phenidone B (K&K Lab.) and Dimezone respectively are 272 and 255 nm.

Phenidone derivatives are extracted from the ECO-2 first developer at pH 9 (for a detailed extraction procedure see appendix B). The absorbance is measured in a 10 mm. quartz cell, against chlforofom, with a double-beam spectrophotometer from 225 to 250 nm.[12]

The absorption spectra of extracts of the ECO-2, containing various amounts of Phenidone A, exhibited a hypsochromic shift of 10 nm. compared to the absorption spectra of Phenidone dissolved in chloroform (see fig. 2). Solvent effects on the absorption spectra of Phenidone were examined by replacing the A.C.S. chloroform, used as a reference in the spectrophotometer, with Reagent grade chloroform. The resulting absorption spectra has a maximum at 250 nm. (see fig 3). However, the effect on the Phenidone absorption by the different purity of chloroform is believed to be a coincidence.[13] Any effect on the absorption peak of Phenidone that chloroform might have would be cancelled out by the double-beam spectrophotometer. Water saturated chloroform was also used as a reference with no success.

There are numerous reasons for the absorption characteristics of a Phenidone extract to change, but the author does not have the expertise to determine the specific mechanism of the absorption shift. The concentration series did show a linear relationship. Therefore all spectrophotometric data on Phenidone A corresponds to the absorption maximum at 240 nm.

TABLE 4

Phenidone A concentration in grams/liter	% absorbance, mean value	calculated concentration of mean value
0.250	7.0	0.177
0.500	26.7	0.591
1.000	50.3	1.056
2.000	95.5	2.035

estimated error with 95% confidence limits is ± 0.10 g/l.

Phenidone A, g/l. = (0.0210)(% absorbance) + 0.030

TABLE 5

Dimezone concentration in grams/liter	% absorbance, mean value	calculated concentration of mean value
0.250	10.7	0.220
0.375	17.0	0.380
0.500	23.0	0.504
0.750	35.0	0.751

estimated error with 95% confidence limits is ± 0.01

Dimezone, g/l. = (0.0206)(% absorbance) - 0.030

The absorption spectra of an extract of Phenidone B (Geigy) from the ECO-2 first developer is similar to that of Phenidone A in the same developer. The two samples of Phenidone B are obviously different chemical species. More sensitive analyses are required for the determination of the exact chemical species of the two samples of Phenidone B (ie. elemental analysis).

The absorption spectra of an extract from the Kodak process E-6 first developer corresponds to the absorption spectra of Dimezone dissolved in chloroform (fig. 2) and that of Dimezone extracted from the ECO-2 first developer. The nature of the developing agent is still proprietary, although it is known that the developing agent is a Phenidone derivative and that it has never been analyzed before. This spectrophotometric method is not sufficient evidence for the identification of the derivative with certainty. Assuming that the derivative is Dimezone and using the calibration equation in table 5, the estimated concentration of Dimezone is 0.382 g/l. The concentration of Phenidone A in the ECO-2 first developer is 0.180 g/l. Although these two developers are not the same, a comparison can be made with the concentrations of the Phenidone derivatives. The calculated concentration of Dimezone is close to the Phenidone concentration in ECO-2.

CONCLUSIONS

For a rapid, non-instrumental analysis of Phenidone derivatives, the visual titration method by Reitz and Anslem is recomended. An attractive feature of this analysis is the capability of this method to analyze hydroquonone simultaneously. The analysis can be completed in 40 min. with glassware found in the average photographic laboratory.

To compensate for operator variation, it is recomended that each analyst derive calibration equations for their own technique. The concentration series should consist of at least three different concentrations of Phenidone in the developer formulation. Analysis of these samples must be replicated. The exact number of replicates is dependent on the operator's precision.

The spectrophotometric method is most useful for qualitative analysis of Phenidone derivatives in a developer with an unknown formulation. This analysis is applied to quantitative analysis by constructing calibration curves for the specific conditions of the analysis. That is, each analyst should derive the equations specific for the spectrophotometer and procedure he will use.

Knowledge of the chemical formulation of the developer to be analyzed, enables one to predict the effects a certain chemical might have on the analysis. For example, the presence of compounds containing the carbonyl group (oxidized form of hydroquinone for instance) will add to the absorption contributed by Phenidone. If such compounds are present, their effect can be normalized by saturating the sample and the reference with that compound. In conclusion, the precision and accuracy of the analyses studied is equivalent to quantitative analysis of Metol and other common developing agents.

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APPENDIX

A. Detailed procedure for the visual titration method.

Reagents

Chloroform, A.C.S certified, $CHCl_3$; 50 ml. tip-up pipet.

Glacial acetic acid, reagent, CH_3COOH; 4 ml. tip-up pipet.

3 N hydrochloric acid, reagent, HCl; 10 ml. tip-up pipet.

7 N sulfuric acid, reagent, H_2SO_4; 25 ml. tip-up pipet.

0.0500 N sufato cerate, analytical reagent; 50 ml. buret.

Ferrion indicator

1.8 M ferric chloride, reagent, $FeCl_3$; 2 ml. pipet.

Procedure

1. Add, from tip-up pipets, 150 ml. of chloroform and 4 ml. of glacial acetic acid to a 250 ml. separatory funnel, Funnel 1.

2. Add, from tip-up pipet, 100 ml. of distilled water to a separatory funnel, Funnel 2.

3. Add, from tip-up pipets, 2 ml. of 1.8 M ferric chloride and 10 ml. of 3 N hydrochloric acid to a separatory funnel, Funnel 3.

4. Pipet 50 ml. of sample into Funnel 1 and shake the funnel for 30 sec. After the phases separate, drain the chloroform (lower layer) into Funnel 2.

5. After the phases separate, drain the chloroform into Funnel 3 and shake for two min.

6. After phases separate, collect and remove water by adding approx. 4 gm. of sodium carbonate monohydrate to one liter of used chloroform. Distill at 60.0 to 61.0°C. and use for extractions.

7. Add, from a tip-up pipet, 50 ml. of chloroform to Funnel 3 and shake for 30 sec. After the phases separate, collect and dry the chloroform as in Step 6.

8. Repeat Step 7.

9. Add approximately 300 ml. of distilled water to a 600 ml. beaker.

10. Add, from a tip-up pipet, 25 ml. of 7 N sulfuric acid to the beaker.

11. Add 3 drops of ferrion indicator to the beaker.

12. Drain the aqueous layer from Step 8, into the beaker and rinse the funnel and stopper with distilled water from a wash bottle, allowing the water to go in the beaker.

13. Stir on a magnetic stirrer and titrate with 0.0500 N sulfato cerate to a green-yellow color. Record to the nearest 0.01 ml.

B. Detailed extraction procedure for the spectrophotometric method.

Reagents

Chloroform, A.C.S. certified, $CHCl_3$; 50 ml. tip-up pipet.

Phenolphthalin indicator.

N sulfuric acid, reagent, H_2SO_4

Procedure

1. Add 1.00 ml of developer sample to a 250 ml. separatory funnel, Funnel 1.

2. Add 90 ml. distilled water, a few drops of phenophthalin and N sulfuric acid dropwise until the solution is decolorized.

3. Add 50 ml of chloroform from tip-up pipet to Funnel 1 and shake for 30 seconds.

4. After layers separate, collect the chloroform (lower layer) in a 100 ml volumetric flask.

5. Add 40 ml. chloroform to Funnel 1 and shake for 30 seconds.

6. After the layers separate, add the chloroform (lower layer) to the volumetric flask. dilute to the mark with chloroform.

C.

An attempt was made to recycle the chloroform used, since it is the most expensive chemical involved in this analysis. Chloroform is then collected, dried with sodium carbonate monohydrate and distilled. The distilled chloroform is tested for residual Phenidone and other impurities by both the visual titration and spectrophotometric methods. There are no apperant impurities in the reclaimed chloroform that could be detected by either method. Therefore, the reclaimed chloroform was used throughout the entire experiment for the visual titration. The use of reclaimed chloroform represents a savings of 200% for the visual titration analysis. This chloroform could not be used for the spectrophotometric analysis though, because of the different absorbtion spectra of this chloroform.

figure 1.

Visual titration method
Calibration curves for Phenidone
⊙ Phenidone A
X Phenidone B
△ Phenidone C
30
20
10
0.25
0.50
0.75
1.00
1.50
idone concentration (gm/l)

Phenidone A, B and C
dissolved in chloroform
relative concentrations

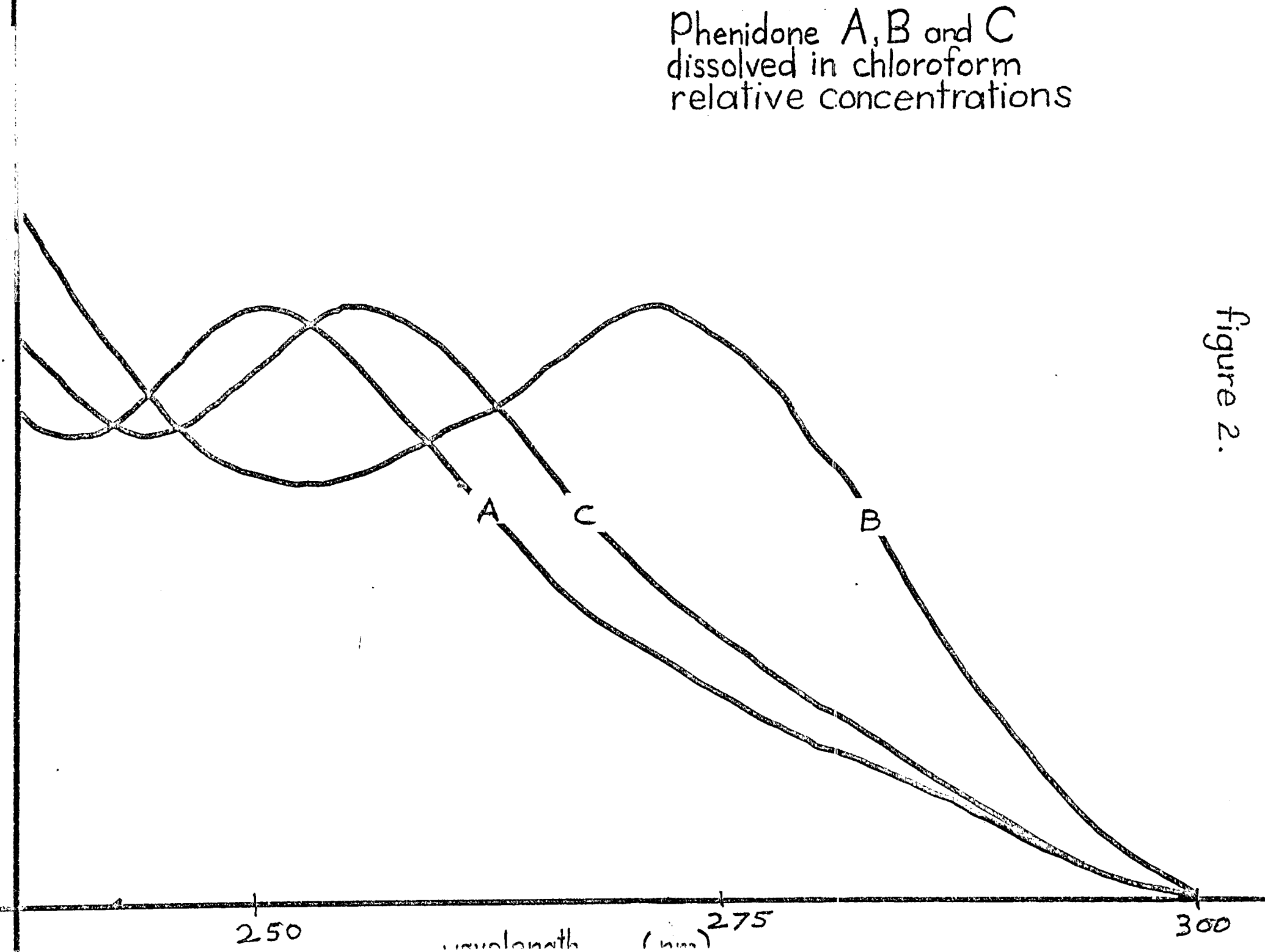

figure 2.

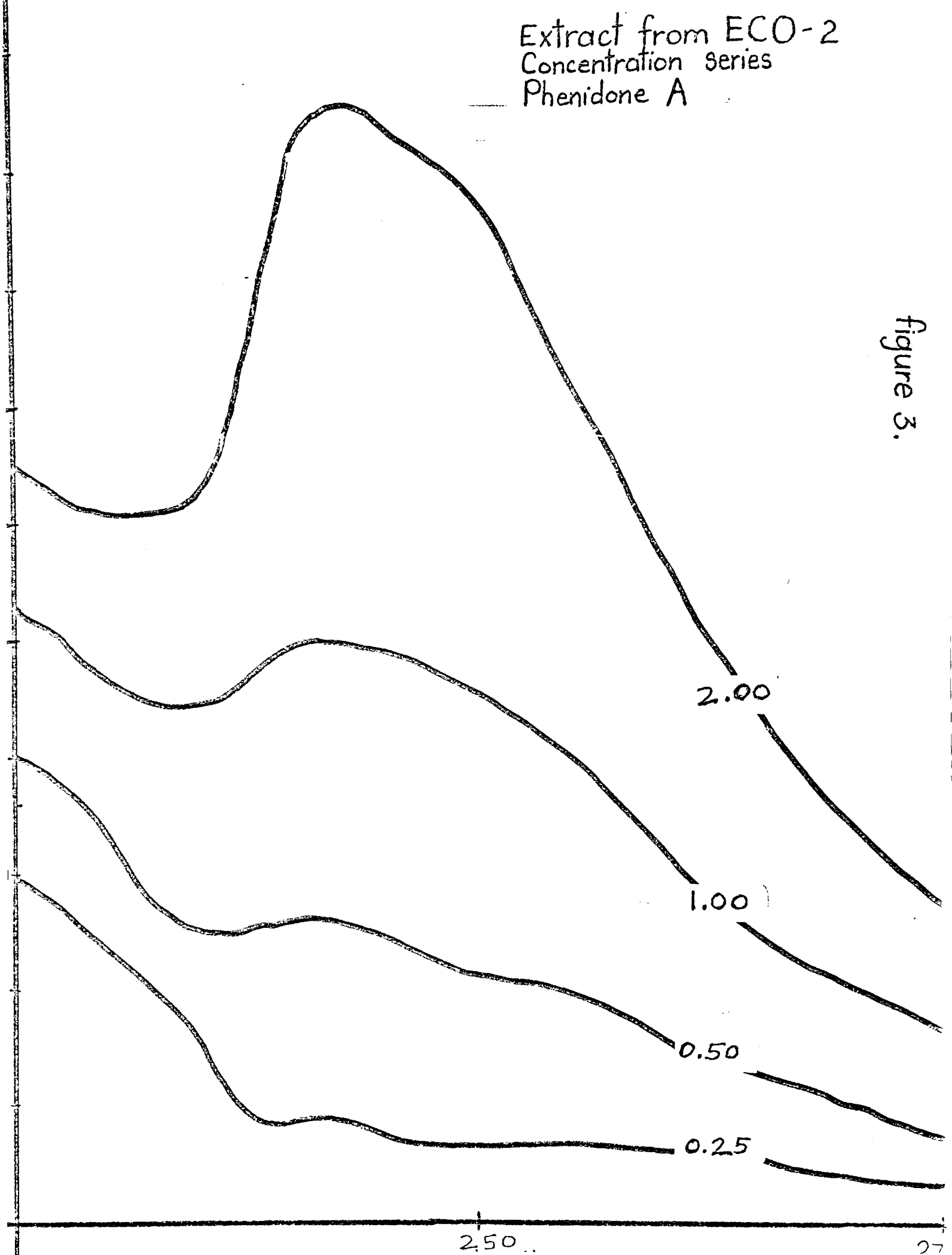
Extract from ECO-2
Concentration Series
Phenidone A
2.00
1.00
0.50
0.25
250

figure 3.

Extract from ECO 2
Concentration series
Phenidone C

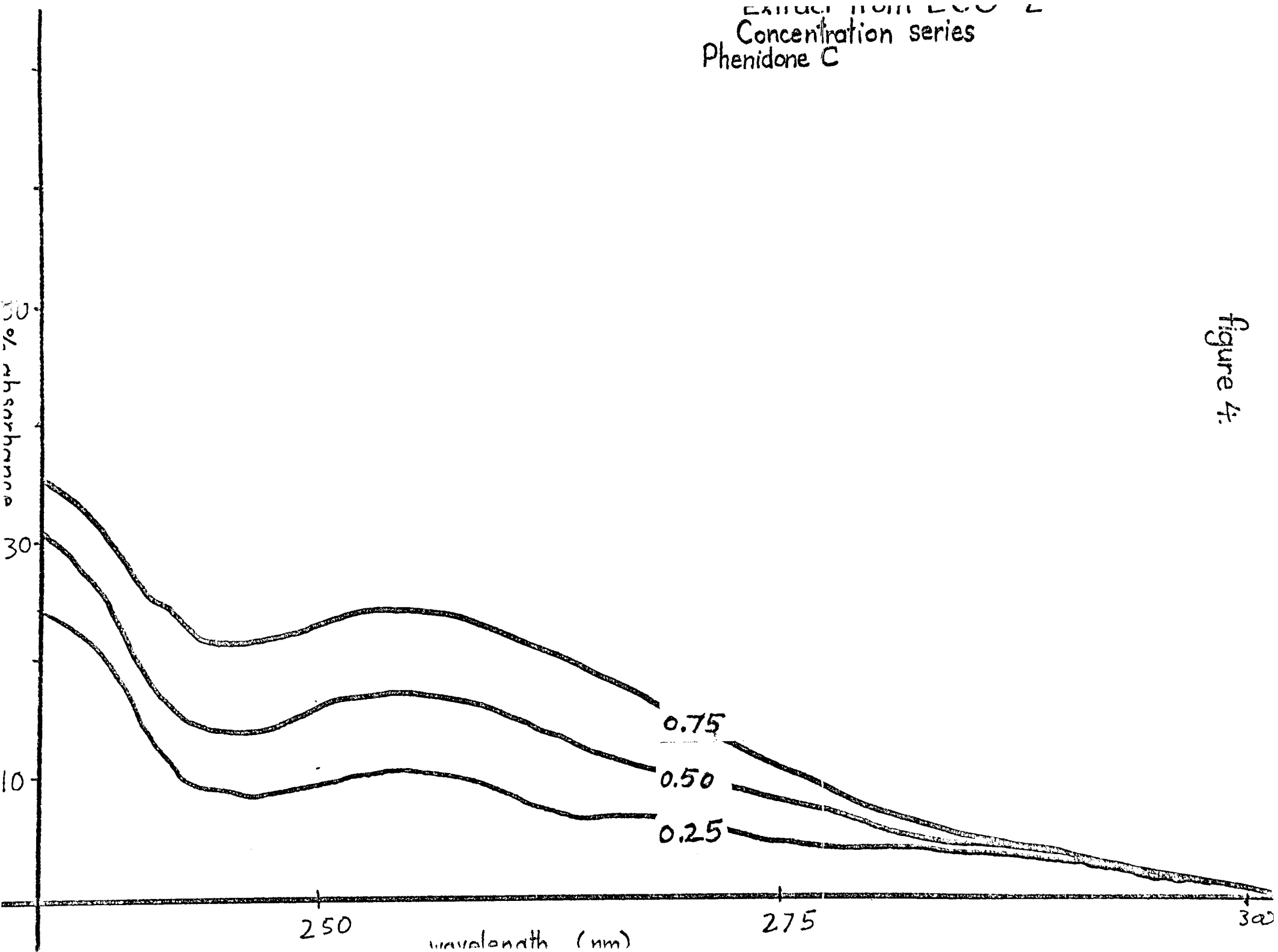

figure 4.

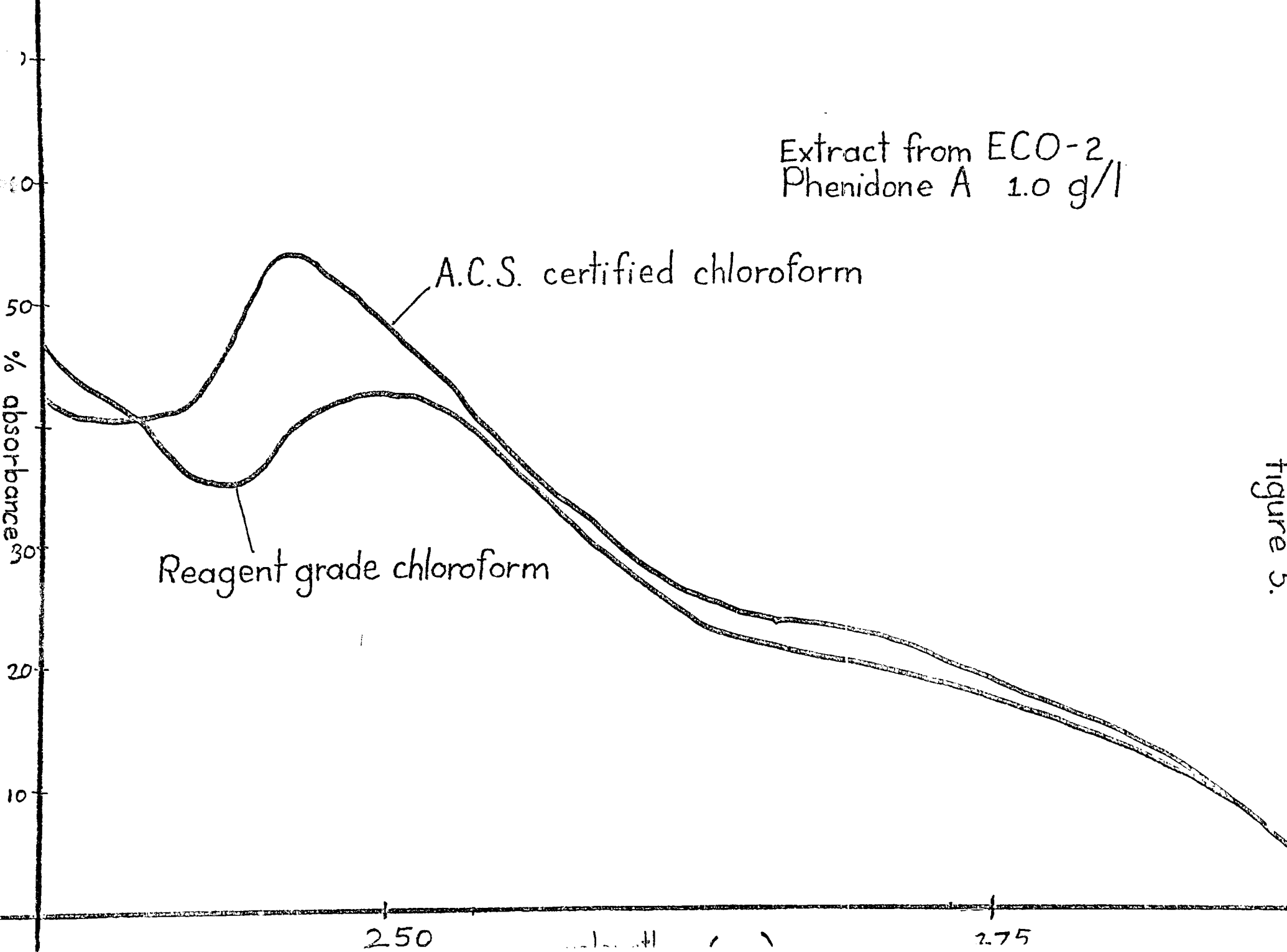
Extract from ECO-2
Phenidone A 1.0 g/l
A.C.S. certified chloroform
Reagent grade chloroform
% absorbance
50
30
20
10
250
275

figure 5.

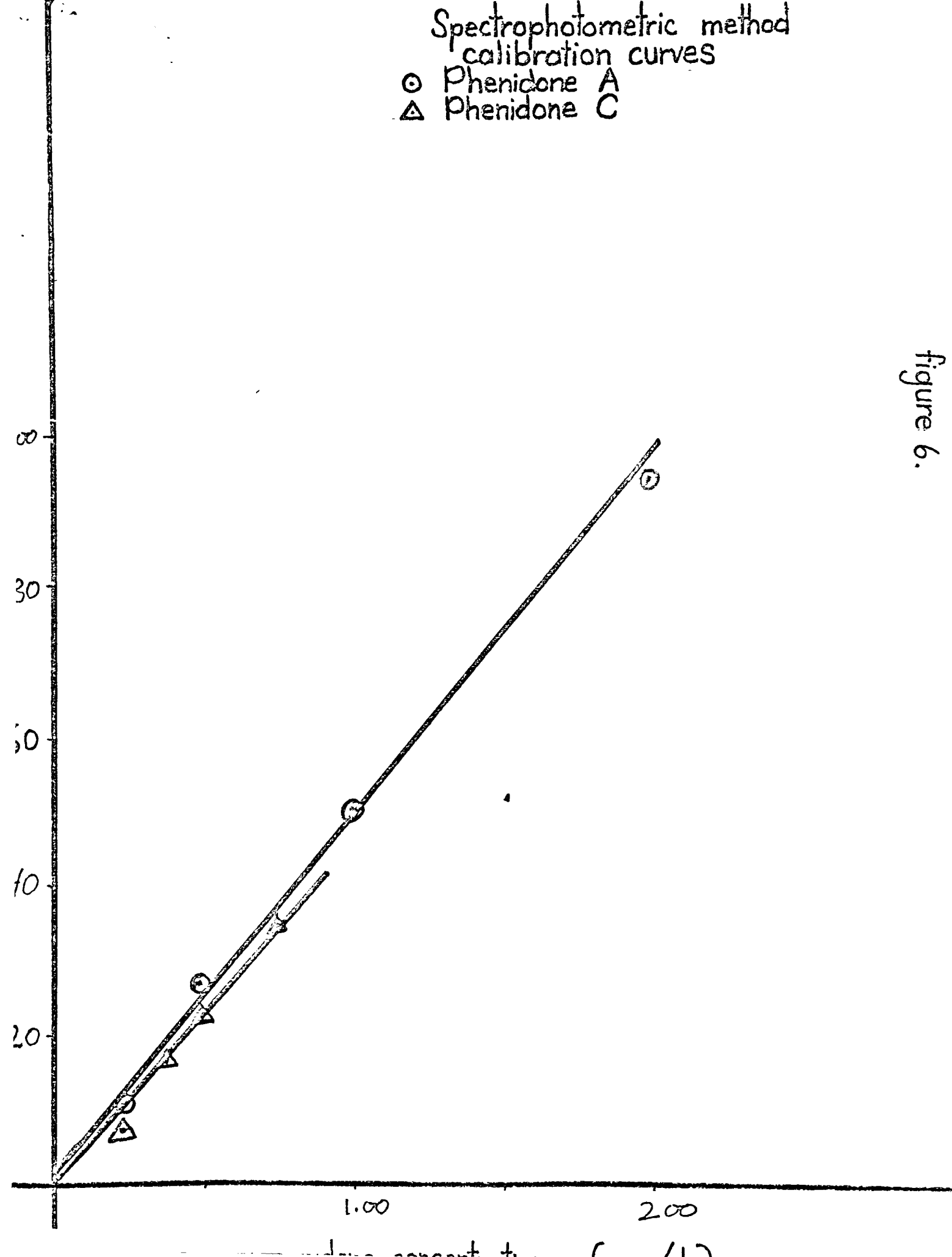
Spectrophotometric method
calibration curves
⊙ Phenidone A
△ Phenidone C
40
30
20
10
1.00
200

figure 6.

Extract from ECO-2
Comparison of Phenidone B
relative concentrations

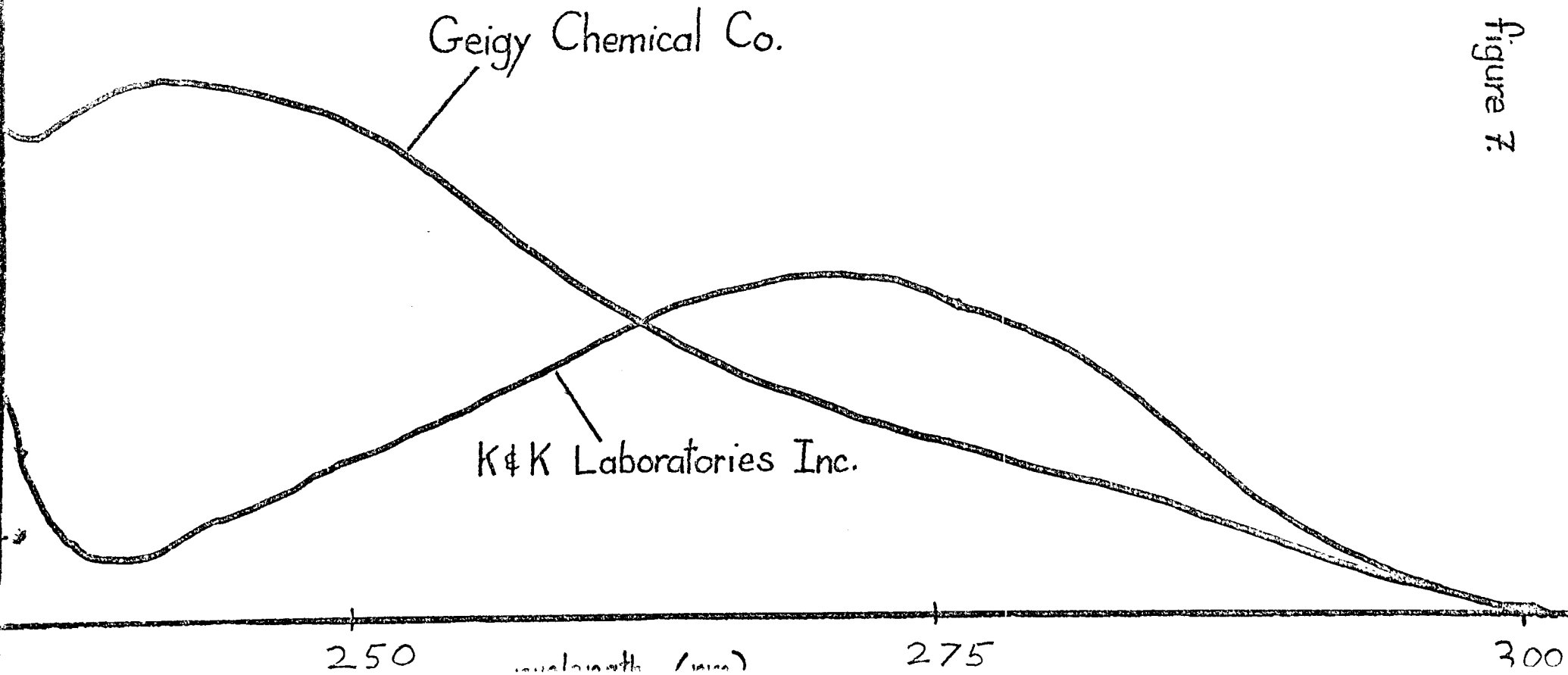

figure 7

Extract from E-6 first developer

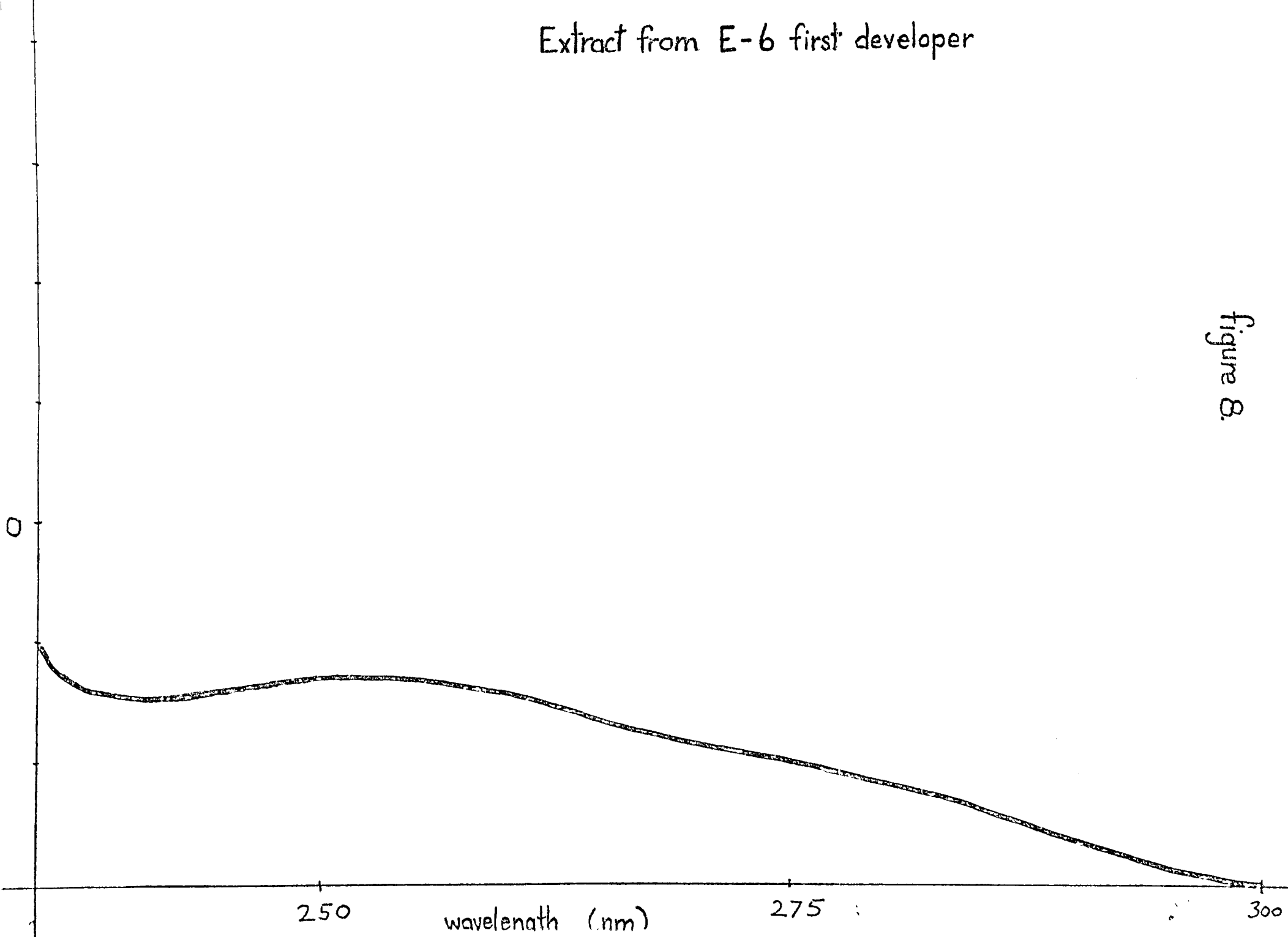

figure 8.