

Cover Sheet for

## ENVIRONMENTAL CHEMISTRY METHOD

**Pesticide Name:** Paraquat

**MRID #:** 422174-03

**Matrix:** Soil

**Analysis:** Spectrophotomtr

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20 March 1970

COLLEGE OF EDUCATION AND HUMAN DEVELOPMENT

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(U) "The Nature of the Working Class in the United Kingdom" by  
John ELLIOTT, Ph.D., The University of Nottingham, Nottingham, U.K.  
This thesis is submitted in partial fulfillment of the requirements for the degree  
of Doctor of Philosophy in the Department of Sociology, The University of  
Nottingham, Nottingham, U.K. It is presented in two parts. Part I is a detailed  
and systematic analysis of the working class in Great Britain. Part II is a  
qualitative study of the working class in Great Britain. Both parts are based on  
the author's extensive research in the field of Sociology and Economics. The  
work is divided into three main sections: Part I, Part II, and Part III. The  
author has made significant contributions to the field of Sociology and Economics  
in his work on the working class in Great Britain. The author has also made  
significant contributions to the field of Sociology and Economics in his work on  
the working class in Great Britain. The author has also made significant  
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class in Great Britain.

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**MRID**

**NUMBER**

**428174.3**

VOLUME 3

422174-Φ3

BB

Study Title

The Determiniation of Residues of Paraquat in Soil  
A Spectrophotometric Method

Data Requirement

Guideline 171-4(C)  
158.125 Residue Chemistry

Author

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Study Completed On

January 23, 1986

Performing Laboratory

Imperial Chemical Industries PLC  
Plant Protection Division  
Jealott's Hill Research Station  
Bracknell Berkshire  
RG12 6EY

Laboratory Project ID

Plant Protection Division Residue  
Analytical Method No. 2B

*B3*

### STATEMENT OF NO DATA CONFIDENTIALITY

No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA § 10(d) (1) (A), (B) or (C).

Company: ICI AMERICAS INC.

Company Agent: M. E. Sherman

Sr. Pesticide Regulatory Specialist  
(TITLE)

M. E. Sherman  
(Signature)

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This document is not subject to the requirements of 40 CFR Part 160.

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2/20/92

Date

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Research Chemist  
Imperial Chemical Industries

Date

Study Director M. G. Sherman  
Ian Laws <sup>Ranking up to 65</sup>  
Study Director <sup>TC company</sup>  
Imperial Chemical Industries

2/20/92

Date

This method cancels and replaces PPRAN/2A dated November 1960.

## 1. SCOPE

The analytical procedures described are suitable for the determination of residues of paraquat (I, 1,1'-dimethyl-4,4'-bipyridinium ion) in soil.



The limit of determination of the method is 0.05 mg kg<sup>-1</sup>.

## 2. METHOD SUMMARY

The sample is boiled in 6M sulphuric acid solution. The filtered digest is percolated through a column of cation-exchange resin which retains the paraquat and some of the natural soil constituents. The column is washed with dilute hydrochloric acid, 2.5% ammonium chloride solution and water; the paraquat is eluted with saturated ammonium chloride solution. A portion of the column eluent is treated with sodium dichlorite in alkali. This reduces paraquat to a free radical the light absorption of which is measured with a spectrophotometer.

## 3. REAGENTS

- (a) Sodium chloride solution - saturated
- (b) Ammonium chloride solution - 2.5% (~%) and saturated
- (c) Sulphuric acid - concentrated (13M)
- (d) Hydrochloric acid solution (2M)
- (e) Cation-exchange resin: Dualite C225 (SRC 14) chromatographic grade resin, 52-100 mesh, 0.68-0.85 water regain, sodium form.
- (f) Standard paraquat solutions:

- (1) Stock solution (250ug/ml of paraquat)

Dissolve 0.0864 g 1,1'-paraquat dichloride,  $C_{14}H_{14}N_2Cl_2$  (mol.wt., 257.2; 72.4% cation), in saturated ammonium chloride solution and make up to 250 ml with saturated ammonium chloride solution. Paraquat salts are hygroscopic; they should be dried at 100°C for 5 hours and cooled in a desiccator before use.

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卷之三

the next edition will be ready early December 1st. I hope you will be able to get it before Christmas.



... But the best way to do this is to make sure that the data is well-organized and easy to understand.

卷之三

12. The following items shall be included in the bill of lading and  
the bill of exchange shall be signed by a responsible representative of the  
agent. The bill of exchange shall be signed by a responsible representative  
of the agent and shall be countersigned by a responsible representative  
of the shipper. The bill of exchange shall be countersigned by a responsible  
representative of the shipper and shall be countersigned by a responsible  
representative of the agent.

卷之三

**REFERENCES AND NOTES**

<sup>127</sup> See also the section on "The 'New' or post-World War II period" below.

(cont.) *Indeterminate - like Mittelst.* 421

第三章 中国の歴史と文化 その歴史と文化 (3)

123

ANSWER TO REPORTS OF THE INSPECTOR OF MINE SAFETY (1)

...and the local government, which is responsible for maintaining public health and safety, and the state government, which is responsible for maintaining public health and safety.

卷之三

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### (ii) Working solutions

Make dilutions of the stock solution to give a range of working solutions. Concentrations of these working solutions will vary depending on the level of residues in the samples analysed.

These solutions are stable under normal laboratory conditions provided that they are not exposed to sunlight for long periods.

- (g) Sodium dichromate solution, 0.2% (w/v) in 0.3M sodium hydroxide. This solution should, if possible be used immediately, and must not be used more than half an hour after preparation. When preparing this solution do not shake vigorously.

Solid sodium dichromate is unstable in the presence of moisture, and should therefore be stored in a tightly sealed plastic container.

- (h) Cetan-2-ol

## 4.

### SAFETY CONSIDERS

The following information is included as an indication to the analyst of the nature and hazards of the reagents used in this procedure. If in doubt, consult the appropriate safety manual (eg ICI Laboratory Safety Manual) containing recommendations and procedures for handling chemicals, and a monograph such as 'Hazards in the Chemical Laboratory', edited by G D Muir, The Chemical Society, London.

#### (a) HYDROCHLORIC ACID

Irritant vapour  
Corrosive - causes burns  
Avoid breathing vapour.  
Prevent contact with eyes and skin  
(TLV 7 mg m<sup>-3</sup> as HCl).

#### (b) SULPHURIC ACID - concentrated

Corrosive - causes burns  
Prevent contact with skin and eyes  
Do not put water into container  
(TLV 1 mg m<sup>-3</sup>)

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The following table

gives the values of  $\frac{d}{dx} \ln \left( \frac{dy}{dx} \right)$  at the points where the curves

$y = f(x)$  and  $y = g(x)$  intersect.

It is evident that if  $f'(x) = g'(x)$ , then  $\frac{dy}{dx} = 1$  at the point of intersection.

It is also evident that if  $f'(x) > g'(x)$ , then  $\frac{dy}{dx} < 1$  at the point of intersection.

It is also evident that if  $f'(x) < g'(x)$ , then  $\frac{dy}{dx} > 1$  at the point of intersection.

It is also evident that if  $f'(x) < g'(x)$ , then  $\frac{dy}{dx} < 1$  at the point of intersection.

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It is also evident that if  $f'(x) < g'(x)$ , then  $\frac{dy}{dx} > 1$  at the point of intersection.

It is also evident that if  $f'(x) > g'(x)$ , then  $\frac{dy}{dx} < 1$  at the point of intersection.

It is also evident that if  $f'(x) < g'(x)$ , then  $\frac{dy}{dx} > 1$  at the point of intersection.

(c)

### PARACETAMOL

Toxic by ingestion.

Harmful dust.

Avoid contact with eyes, skin and mouth. Avoid breathing dust. Wash hands and exposed skin before meals and after work.

Ingestion of paracetamol should be regarded as a dire emergency and action taken immediately. Details of remedial action/antidotes should be available in the laboratory.

(d)

### OCTAN-2-OL

Harmful vapour.

Harmful if taken internally.

Highly flammable.

Avoid breathing vapour or contact with skin and eyes.  
(TLV 2.60 mg m<sup>-3</sup>)

5.

### APPARATUS

- (a) Equipment which can be used for the initial preparation of samples i.e. metal trays for drying soils.
- (b) Heating mantles for the extraction procedure (e.g. Electrothermal Heating Unit available from Electrothermal Engineering Ltd, London E7 UK).
- (c) Boiling flasks - 500 ml round bottom flasks with 214 necks fitted with water cooled reflux condensers.
- (d) Glass columns for chromatography of 1.0 cm i.d. and 50 cm long. (25 ml burettes are suitable).
- (e) Scanning Spectrophotometer e.g. Perkin Elmer Lambda 5 UV/VIS Spectrophotometer.
- (f) Sieve, 2-3 mm mesh size.

6.

### PROCEDURE

6.1

#### Extraction and Chromatographic Separation

- (a) Thoroughly mix the soil sample and weigh about 100 g into a shallow metal tray or glass petri dish. Dry the soil sample at room temperature for several days.
- (b) Grind the dry soil sample to pass through a 2-3 mm sieve. Weigh an aliquot (25 g) of the ground soil into a 500 ml round bottomed flask and add water (65 ml) followed by 10 ml sulphuric acid (35 ml).

Note: **CAUTION!** The sulphuric acid must be added to the aqueous solution with care.

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On the 2nd of May, 1865, he was buried at the foot of the hill on which his house stood.

For the first time in history, we have the opportunity to end poverty.

10. The following table shows the number of hours worked by each employee in a company.

19. *Leucosia* *leucostoma* (Fabricius) *leucostoma* (Fabricius)

10. The following table shows the number of hours worked by each employee.

*Journal of Health Politics, Policy and Law*, Vol. 35, No. 4, December 2010  
DOI 10.1215/03616878-35-4 © 2010 by The University of Chicago

10. The following table gives the number of cases of smallpox reported in each State during the year 1800.

10. The following table gives the number of hours worked by each of the 100 workers.

1. *Chlorophytum comosum* (L.) Willd. (Asparagaceae) (Fig. 1)

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19. *Leucosia* *leucostoma* *leucostoma* *leucostoma* *leucostoma* *leucostoma*

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1. *Leucosia* *leucostoma* *leucostoma* *leucostoma* *leucostoma*

10. The following table gives the number of hours worked by each of the 100 workers.

10. The following table gives the number of hours worked by each of the 1000 workers.

1995-05-05

1. *Leucosia* *leucostoma* (Fabricius) *leucostoma* (Fabricius)

- (c) After adding anti-bumping granules and octan-1-ol (1 ml) which acts as an anti-foaming agent, place the 500 ml flask containing the sample on a heating mantle. Attach a water-cooled reflux condenser and heat to boiling. Swirl the flask contents occasionally to minimise local overheating and charring until the solution is boiling steadily.
- It is important to avoid local overheating and charring and this can be done by ensuring that only the bottom quarter of the flask makes contact with the heating mantle (which should be oversized).
- (d) Boil under reflux for 5 hours and allow to cool. The solution can be left overnight at this stage.
- (e) While the samples are being refluxed the ion-exchange columns are prepared as follows: Wash 5.0 g of resin with water into a burette (25 ml) containing a glass wool plug placed near the stopcock. Pass successively through the column at the rate of 5 ml/min. saturated sodium chloride solution (20 ml) and water (50 ml). Prepare a separate column for each sample.
- (f) Wash the reflux condenser attached to the boiling flask with water (50 ml) into the cooled contents of the 500 ml round-bottomed flasks from 5.1 (d) above. Dilute the flask contents to near 500 ml by the addition of water and filter the solution by suction through 2 Whatman No.3 filter papers. Suck the filter pad dry and wash the filter twice with water (100 ml), allowing the first portion to be sucked through before adding the second.
- (g) Transfer the filtrate to a 1 litre separating funnel. Allow the solution to percolate through a prepared resin column from 5.1 (e) above at a flow rate of 5-10 ml/min.
- (h) Remove the funnel and wash the column at a flow rate of 3-4 ml/min successively with water (25 ml), 2N-hydrochloric acid (100 ml), water (25 ml), 2.5% (v/v) ammonium chloride solution (50 ml) and water (25 ml). (The process can be left overnight provided the resin column has been covered with water).
- (i) Elute the paraquat from the column with saturated ammonium chloride solution at a flow rate of about 7 ml/min. Collect the first 50 ml of the eluent in a 50 ml volumetric flask and mix.

**N.B.** The recovery of the paraquat from the resin column will be adversely affected if the flow rate of the eluent exceeds 1.0 ml/min.

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1. *Leucosia* *leucostoma* (L.)  
2. *Leucosia* *leucostoma* (L.)

3. *Leucosia* *leucostoma* (L.)

4. *Leucosia* *leucostoma* (L.)

5. *Leucosia* *leucostoma* (L.)

6. *Leucosia* *leucostoma* (L.)

7. *Leucosia* *leucostoma* (L.)

8. *Leucosia* *leucostoma* (L.)

9. *Leucosia* *leucostoma* (L.)

10. *Leucosia* *leucostoma* (L.)

11. *Leucosia* *leucostoma* (L.)

12. *Leucosia* *leucostoma* (L.)

13. *Leucosia* *leucostoma* (L.)

14. *Leucosia* *leucostoma* (L.)

15. *Leucosia* *leucostoma* (L.)

16. *Leucosia* *leucostoma* (L.)

17. *Leucosia* *leucostoma* (L.)

18. *Leucosia* *leucostoma* (L.)

**Determination**

- (a) Pipette an aliquot (10.0 ml) of the eluent into a 15 ml glass-stoppered test-tube. Add by pipette 0.2% (v/v) sodium dithionite solution (2.0 ml) and mix by gently inverting the tube once.
- (b) Within 5 minutes of adding the sodium dithionite, use a recording spectrophotometer to record the spectrum of the solution in a 4 cm path length cell over the range 360-430 nm, against a reference solution prepared from saturated ammonium chloride (10.0 ml) and sodium dithionite (2.0 ml).
- (c) Draw a baseline as a tangent to the curve from the valley in the region of 390 nm. Measure the height of the peak above the baseline at 396 nm.
- (d) Draw a calibration curve relating the peak height at 396 nm (nm above the baseline) to the concentration of paraquat in ug/ml.

N.B When using a spectrophotometer with a derivative function, operation in the 2nd derivative mode will give an enhanced response to paraquat. See Appendix 1 for comparison of spectra and methods of measuring peak heights.

## 7.

**CALCULATION**

Read off from the prepared calibration curve, using the peak height measured at 396 nm, the concentration (ug/ml) of paraquat in the eluent.

N.B It has been found useful to use the linear regression function on an electronic calculator to produce the calibration curve.

Then paraquat concentration in sample (mg/kg)

Volume of eluent, ml from column I    Concentration in eluent (mg/ml)  
Weight of sample, (g)

To correct the paraquat concentration for the experimental recovery multiply by 100 and divide by the % of recovery figure.

## 8.

**RECOVERY AND LIMIT OF DETERMINATION**

Recovery experiments should be carried out by adding known amounts of paraquat to untreated samples prior to the acid digestion stage. The amount added should be similar to the amounts that are expected in the treated samples.

In these laboratories using this procedure recoveries of between 80% and 95% of the added paraquat are expected with a limit of determination of 0.05 mg/kg of the compound (25 g sample).

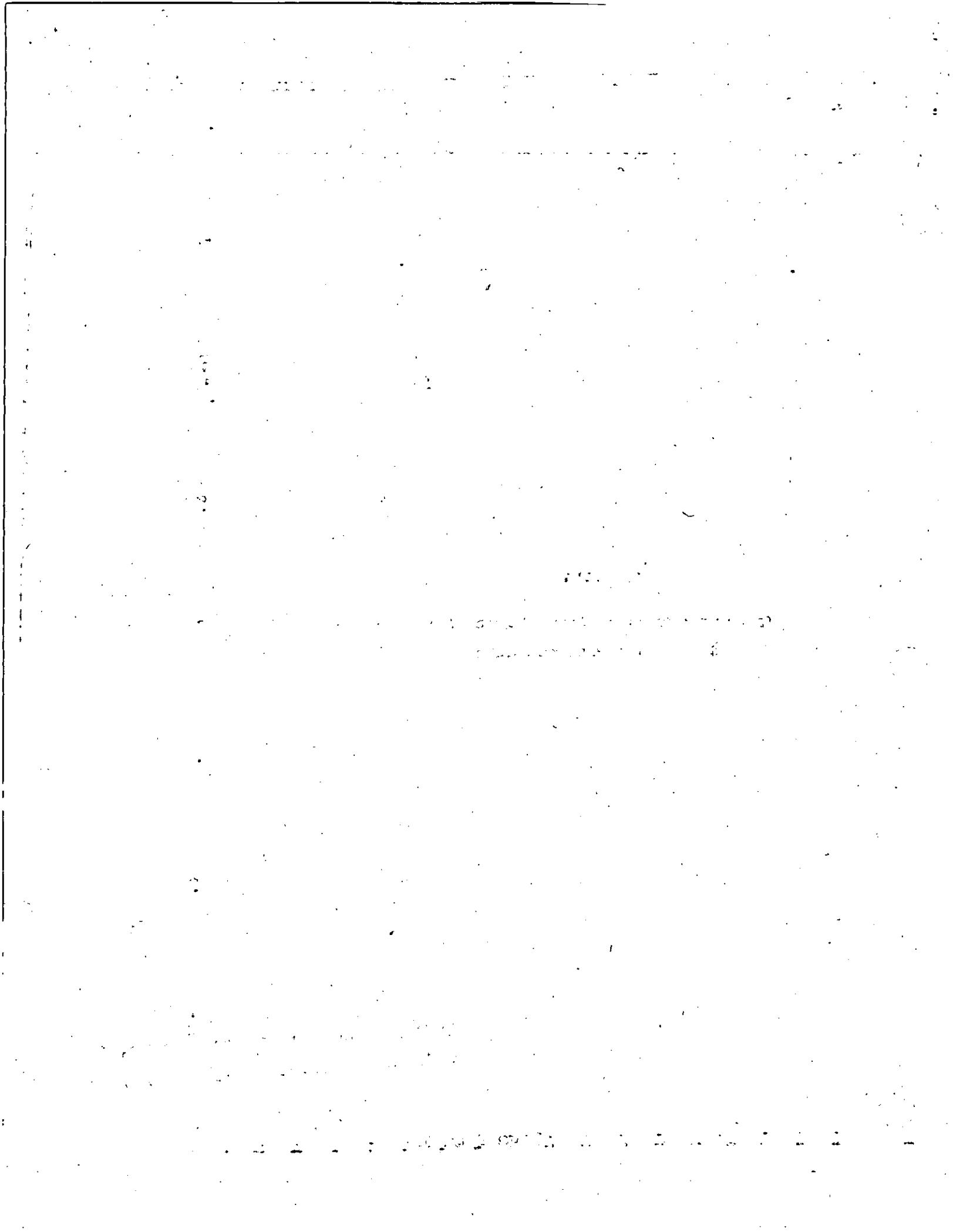
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**APPENDIX 1**

Spectrophotometer conditions and spectra for  
absorbance and derivative modes

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ABSORBANCE MODE

PERKIN-ELMER  
LAMBDA 5 UV/VIS SPECTROPHOTOMETER

SAMPLE ID .....	
OPERATOR .....	
METHOD .....	SCAN/MANUAL
01 ORDINATE MODE .....	ABS
02 SLIT .....	2 MM
03 SCAN SPEED .....	120 NM/MIN
04 RESPONSE .....	2 S
05 LAMP .....	332.8 NM
06 CYCLES/TIME .....	1 / 0.85 MIN
07 PEAK THRESHOLD .....	0.02 A
08 RECORDER .....	SERIAL / DASH 1
09 ORD MIN/MAX .....	-0.050 / 0.250
10 ABSC MIN/MAX .....	360.8 / 430.6
11 ABSCISSA FORMAT .....	10 NM/CM
12 PRINTER .....	GRID/SCALE

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DERIVATIVE MODE

PERKIN-ELMER  
LAMBDA 5 UV/VIS SPECTROPHOTOMETER

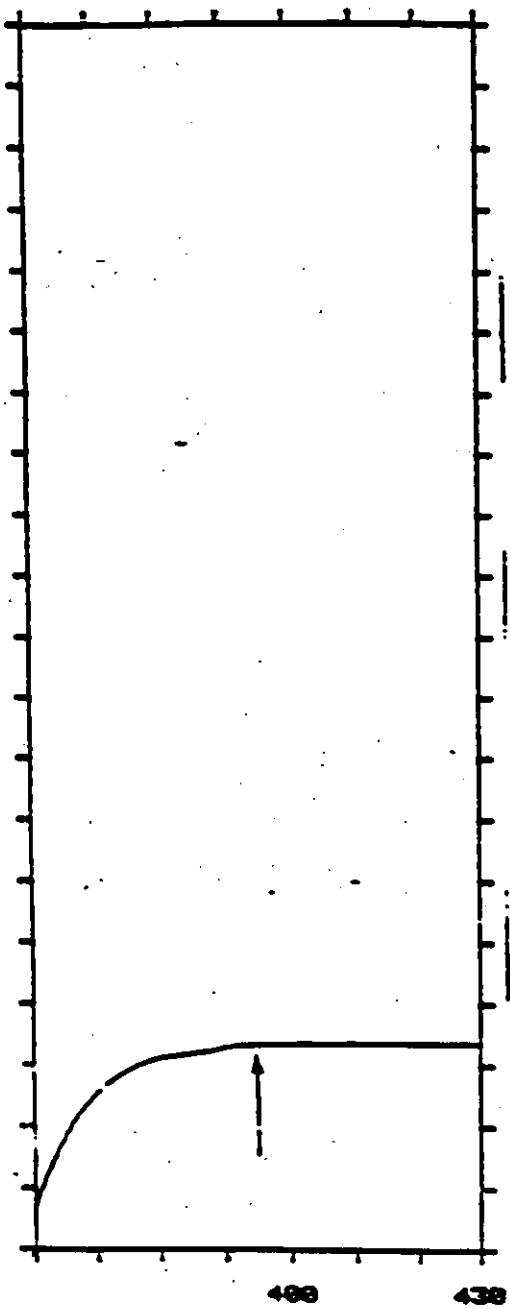
SAMPLE ID .....  
OPERATOR .....  
METHOD SCAN/MANUAL

01 ORDINATE MODE D2  
02 SLIT 2 NM  
03 SCAN SPEED 120 NM/MIN  
04 RESPONSE 2 S  
05 LAMP 332.8 NM  
06 CYCLES/TIME 1 / 0.05 MIN  
07 DELTA WAVELENGTH 2 NM  
08 PEAK THRESHOLD 0.2 D2  
09 RECORDER SERIAL / DASH 1  
10 ORD MIN/MAX -2.298 / 1.998  
11 ABSC MIN/MAX 360.0 / 430.0  
12 ABSISSA FORMAT 10 NM/CH  
13 PRINTER GRID/SCALE /

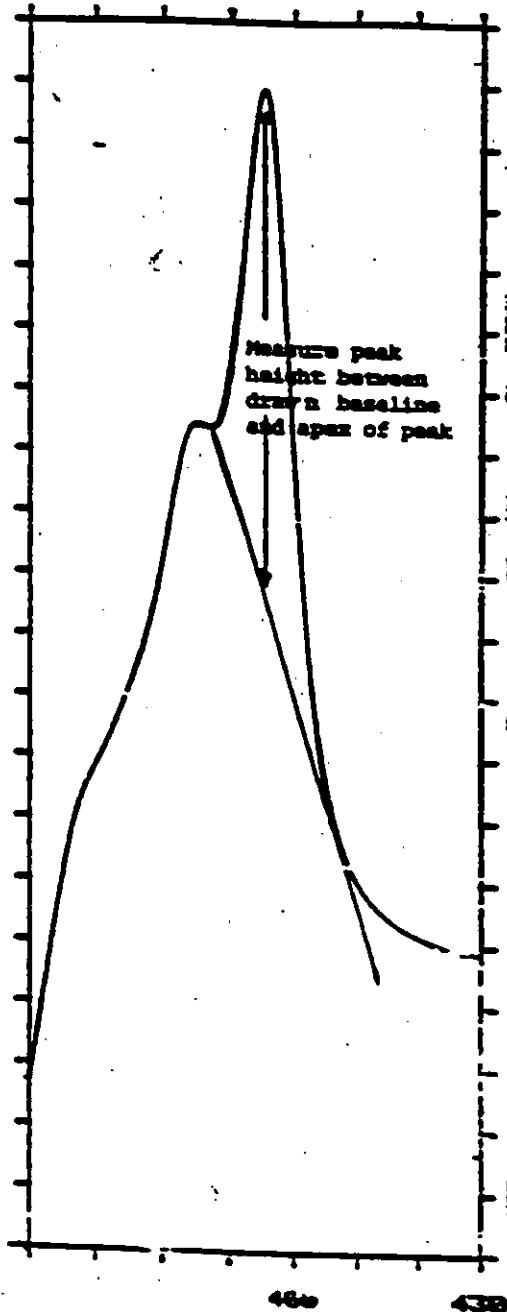
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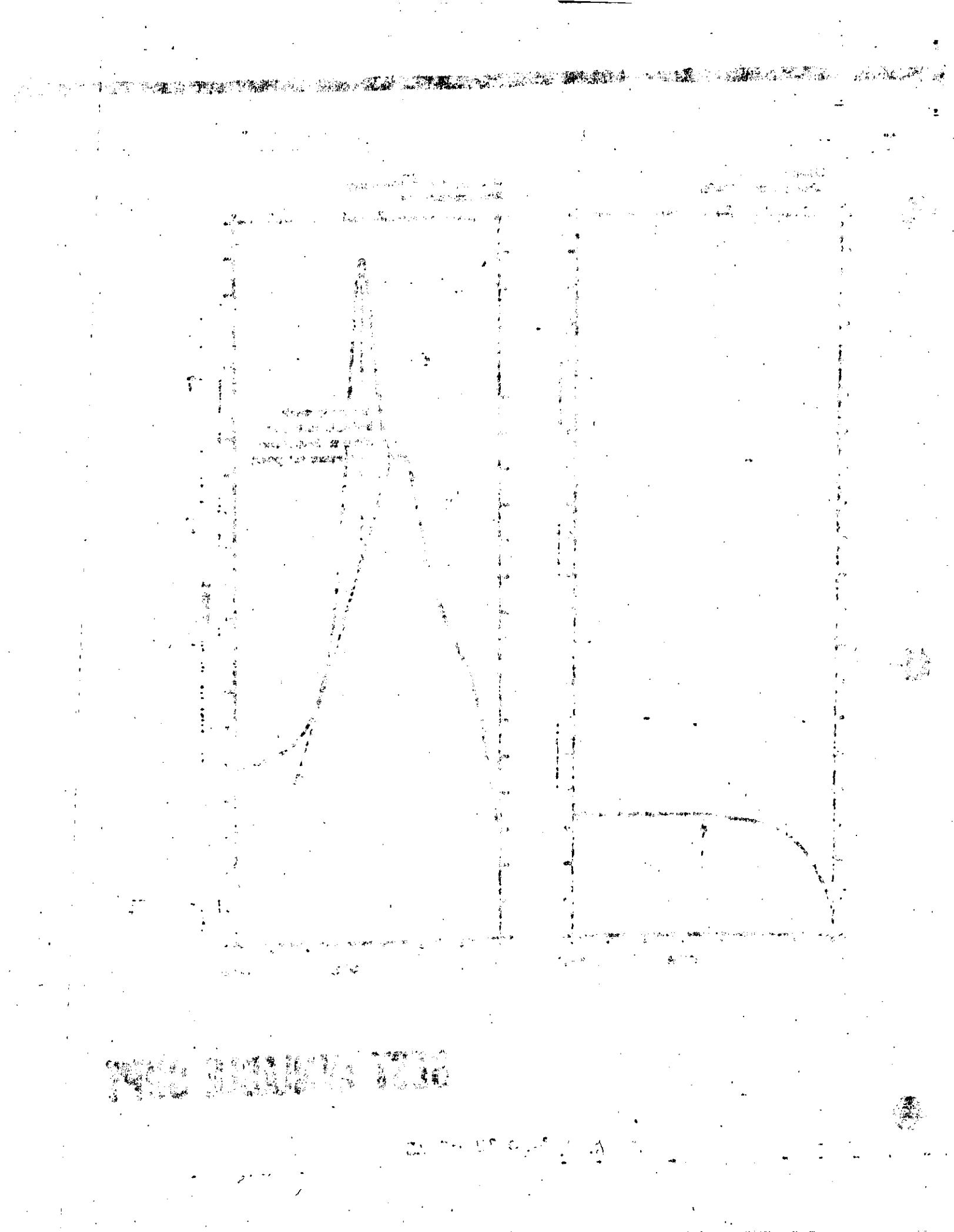
Blank  
Absorbance Mode



0.3  $\mu\text{g cm}^{-3}$  Americaine  
Absorbance Mode

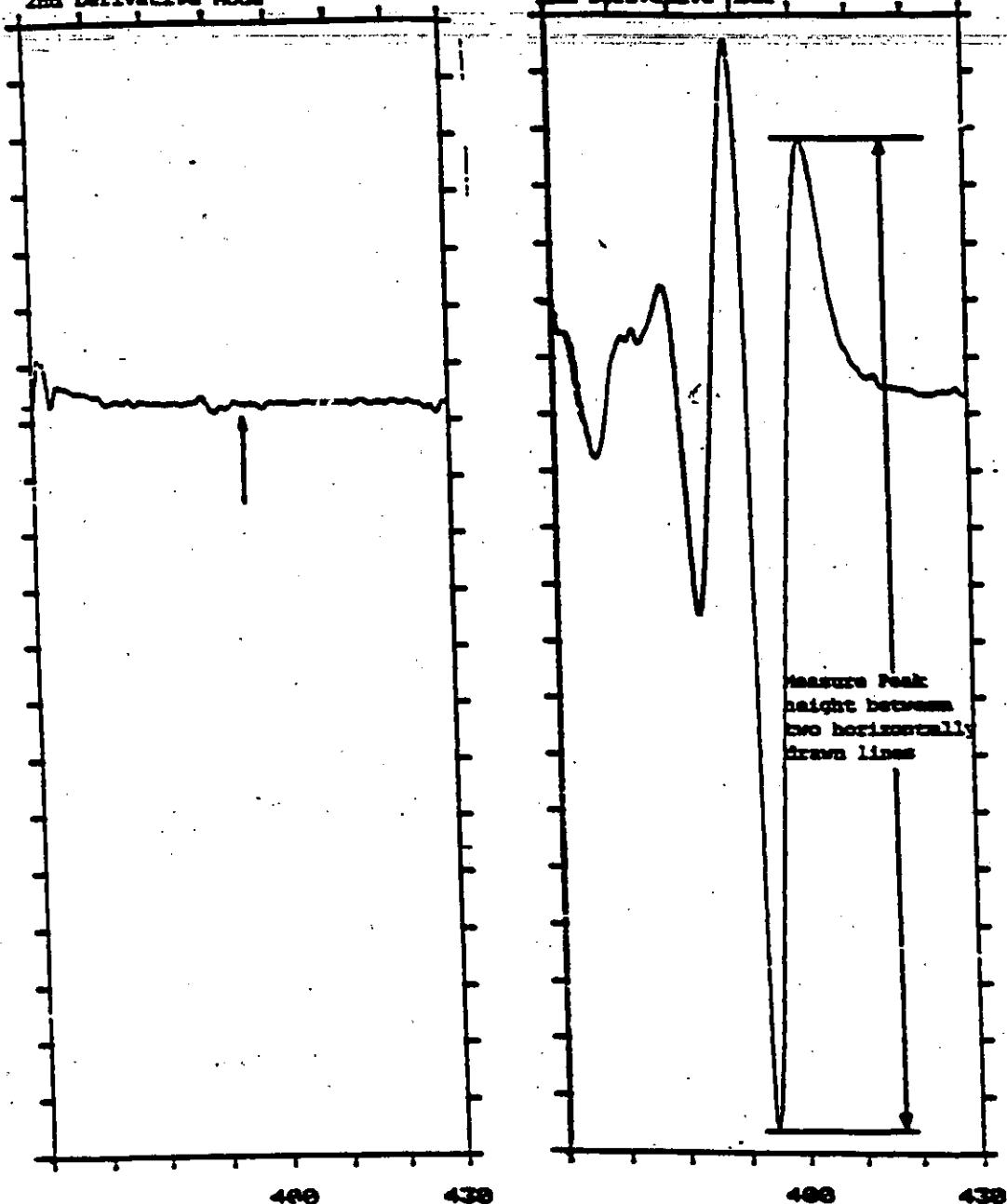


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Blank  
2nd Derivative Mode

0.3  $\mu\text{g cm}^{-3}$  Paraquat  
2nd Derivative Mode



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