

Determination of Diquat and Paraquat in River and Drinking Waters, Spectrophotometric Methods Tentive 1987

Methods for the Examination of Waters and Associated Materials

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About This Series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, short reviews of the more important analytical techniques of interest to the water and sewage industries.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in "Analysis of Raw, Potable and Waste Waters". These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as series of booklets on single or related topics; thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods and notes being issued when necessary.

The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users—the senior technical staff to decide which of these methods to use for the determination in hand. Whilst the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous

revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has 9 Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

- 1.0 General principles of sampling and accuracy of results
- 2.0 Microbiological methods
- 3.0 Empirical and physical methods
- 4.0 Metals and metalloids
- 5.0 General nonmetallic substances
- 6.0 Organic impurities
- 7.0 Biological monitoring
- 8.0 Sewage Works Control Methods
- 9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee.

The names of those associated with this method are listed inside the back cover. Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in that booklet.

L R PITTWELL
Secretary

1 July 1987

Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary.

Local Safety Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

Field Operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried.

Care should be taken against creating hazards for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use. Lone working, whether in the laboratory or field, should be discouraged.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. Hazardous reagents

and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: "Guide to Safe Practices in Chemical Laboratories" and "Hazards in the Chemical Laboratory" issued by the Royal Society of Chemistry, London; "Safety in Biological Laboratories" (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and "The Prevention of Laboratory Acquired Infection", Public Health Laboratory Service Monograph 6, HMSO, London.

It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio-chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

26.10.20

Determination of Diquat and Paraquat in River and Drinking Waters, Spectrophotometric Methods, 1987

1 Performance Characteristics of the Method

1.1 Substances determined

Diquat dibromide (9, 10-dihydro-8a, 10a-diazonia-phenanthrene dibromide, *alternative names: 1, 1' ethylene 2, 2' bipyridilium dibromide or 6, 7 dihydrodipyrido [1.2a.2.1c] pyrazidinium dibromide*) and paraquat dichloride (1, 1'-dimethyl-4, 4'-bipyridinium dichloride).

1.2 Types of Sample

River and drinking water.

1.3 Basis of method

Concentration of the determinands by ion-exchange, reduction with alkaline sodium dithionite and determination of the reduced compound by visible light spectroscopy by direct or 2nd derivate measurement.

1.4 Range of Method

Up to 10 mg/L.

1.5 Calibration Curve

The method is linear over the range 0–1 absorbance units (0–1 mg/L paraquat or diquat).

1.6 Standard Deviation

See Tables 1–3 (see also note (a) below).

1.7 Limit of Detection On a 5 litre sample (for both compounds)

Direct 0.4 $\mu\text{g/L}$
2nd Deriv 0.02 $\mu\text{g/L}$ } or better (see tables 1–3)
(see also note (a) below).

1.8 Sensitivity

Dependent upon the instrument in use.

1.9 Bias

Bias will vary with extraction efficiency.
Recoveries of external standards may be used to correct the results (see Tables 1–3).

1.10 Interference

Any component remaining after the procedure which absorbs light in the relevant region of the visible spectrum will interfere.

(a) The data quoted was obtained by ICI plc Plant Protection Division Jealott's Hill Research Station, using equipment as specified in Section 8.6. Yorkshire Water Authority, Bradford and Sheffield Laboratories have obtained similar test data, with limits of detection about one fifth the concentrations quoted, using different instruments. As performance is highly instrument dependent and can vary dependent on whether the compounds are present singly or together, analysts are advised to evaluate their own equipment prior to starting a programme of work. Even lower limits of detection could probably be obtained by using even larger samples.

2 Principle

The herbicides are removed from the solution by trapping on an ion exchange resin. This effects concentration and clean up. After elution from the resin the herbicides are reduced to coloured species that may be determined spectrophotometrically by either of the methods described.

3 Interferences

The method is normally specific for the determinands but any substance which is eluted from the column and absorbs at the appropriate wavelengths will interfere with the determination when using direct spectrophotometric measurement. The use of second derivative spectroscopy will reduce such problems and increase sensitivity.

4 Hazards

The diquat and paraquat salts are toxic; skin contact, ingestion and inhalation of dusts should be avoided. Sodium hydroxide and hydrochloric acid are corrosive.

If diquat or paraquat are accidentally ingested, call a doctor at once or take the patient to a hospital. (see Warning to Users).

5 Reagents

All reagents should be of analytical reagent quality.

Distilled or deionized water may be used for reagent preparation.

5.1 Dilute Hydrochloric Acid—Approximately 2M: Add 175 ± 5 ml of hydrochloric acid $d_{20} 1.18$ to 600 ml of distilled water with stirring and dilute to 1L with distilled water.

5.2 Ammonium Chloride 2.5% Solution w/V: Dissolve 25 ± 1 g of ammonium chloride in distilled water and make up to 1L.

5.3 Ammonium Chloride Saturated Solution: Dissolve 330 g ammonium chloride with heating in 1L of distilled water and allow to cool.

5.4 Ion Exchange Resin: Cation exchange resin, strong acid, BDH product number 55171 or equivalent. Procedural recovery tests should be made with each new batch of resin.

5.5 Sodium Hydroxide 4% w/V: Dissolve 40 ± 1 g sodium hydroxide in deionized or distilled water. Cool and dilute to 1L. Store in a plastic container and cool to 4°C before use.

5.6 Alkaline Sodium Dithionite 0.2% w/V: Dissolve 0.20 ± 0.02 g sodium dithionite in 4% sodium hydroxide (5.5) and dilute to 100 ml with the same reagent. This solution must be prepared immediately before use and discarded after 30 mins. The dithionite dissolves readily and the solution must not be shaken. This will obviate the absorption of oxygen and consequent premature deterioration of the reagent.

5.7 Sodium Chloride Saturated solution: Dissolve 1000 g of sodium chloride in 2.5 L of distilled water.

5.8 Standard Solution of the Herbicides:

5.8.1 Stock solution 10 mg/L as herbicide cation—Dissolve 18.5 mg diquat dibromide and 13.7 mg paraquat dichloride in water and dilute each to 1L with saturated ammonium chloride solution (5.3).

5.8.2 Spiking solutions are prepared by serial dilution into water. These may also be used as intermediate standards to prepare calibration standards.

5.8.3 Calibration standards—prepared by serial dilution from the stock solutions (5.8.1) using saturated ammonium chloride (5.3). Suitable ranges would be 0.05–1.0 mg/L and 0.01–0.05 mg/L.

6 Apparatus

6.1 Sample Bottles: These should all be of amber glass. A PTFE lined screw cap may be used.

6.2 Ion Exchange Columns: Glass columns 600×10 mm if fitted with a PTFE tap at the bottom (25 ml glass burettes have been found to be satisfactory and a reservoir (or a 1L separating funnel with a PTFE tap) at the top.

6.3 Spectrophotometers

a. For direct measurement a dual beam visible wavelength scanning spectrophotometer is required.

b. For the 2nd Derivative method a dual beam spectrophotometer with second derivative facilities is required. A data system with peak deconvolution or multicomponent analysis software will be advantageous.

7 Sample Storage

Diquat undergoes photo degradation in daylight. Samples should be stored at 4°C in the dark if immediate analysis is impractical.

8 Analytical Procedure

If the expected concentration is greater than 50 µg/l omit steps 8.1.1 to 8.2.4 and compare these samples with standards prepared in water.

Step	Procedure	Notes
8.1	Preparation of ion exchange column	
8.1.1	Weigh 3.5 ± 0.1 g of resin (5.4) into a beaker. Slurry with distilled water and pour into the column which has been previously plugged with glass wool (Note a.).	(a) At no time should the liquid meniscus be allowed to fall below the top level of the resin.
8.1.2	Wash the resin successively with saturated sodium chloride (5.7) 20 ± 1 ml, 2M HCl (5.1) 20 ± 1 ml and 50 ± 5 ml distilled water at a flow rate of about 5 ml per min.	
8.2	Sample Treatment	
8.2.1	Transfer the sample to the reservoir and connect the reservoir to the column. Allow 5 L of the sample to percolate through the resin at 5–10 ml/min. (Notes (b) and (c)). Record the volume of sample used (V litres).	(b) To avoid blocking the column samples containing more than about 50 mg/L suspended solids must be allowed to settle or be filtered before analysis. A Whatman No. 1 is generally adequate. The method measures only the dissolved herbicides. (c) Smaller volumes of sample may be used if the detection limits required are less stringent. A 1 L sample will give a detection limit of 0.5 µg/L by 2nd derivative measurement. 50 µg/L can be detected by direct dithionite addition and 2nd derivative measurement without resin concentration.

Step	Procedure	Notes
8.2.2	When all the sample has been entered the column, wash the reservoir with 5 to 10 ml distilled water and allow the washings to enter the resin.	
8.2.3	Wash the resin successively at 3 to 4 ml per minute with: 25 ± 1 ml of water, 100 ± 10 ml of 2M HCl (5.1), 25 ± 1 ml of water, 50 ± 5 ml of 2.5% ammonium chloride (5.2) and finally 25 ± 1 ml of water. Discard all washings.	
8.2.4	Elute the column with saturated ammonium chloride (5.3) at 1.0 ± 0.1 ml per minute and collect the first 50 ml of eluate in a volumetric flask. (note d)	(d) Use of a flow rate in excess 1 ml/min will adversely affect recovery.
8.3	Spectrophotometric Measurement	
8.3.1	The instrument must be used in accordance with the manufacturer's instructions. Mix the contents of the volumetric flask containing the eluate (8.2.4) and pipette a 10.0 ± 0.1 ml aliquot of the eluate into a 15 ml glass stoppered tube.	
8.3.2	Add 2.0 ± 0.1 ml of the freshly prepared alkaline dithionite solution (5.6) to the test tube. (Note (e)).	(e) Deterioration of the dithionite will be shown by distortion of the base line of the spectra obtained. (See Figure 5). If this occurs, fresh dithionite reagent must be prepared.
8.3.3	Immediately measure the absorption of the solution, scanning between 360 nm and 430 nm using a 4 cm path length cell. Note (f)).	(f) Each sample or standard must be reduced and measured before the next is reduced.
8.3.4	A series of appropriate calibration standards (5.8.3) and a reagent blank should be measured in the same way (Note (g)).	(g) If the concentration of herbicide exceeds the standard range the eluant may be diluted with saturated ammonium chloride (5.3). A 10.00 ± 0.01 ml aliquot of the diluted eluate must be used for reduction and measurement. An appropriate correction in the calculation of the final result must be made.
8.3.5	Procedural recovery standards and blanks must be treated in the same manner as samples to quantify the efficiency of the method.	
8.4	Calibration and Calculation of Concentrations	
8.4.1	<i>Absorbance Mode</i> In samples containing concentrations of both paraquat and diquat unresolved peaks will be observed. The determination of diquat by this method is not recommended owing to interferences to the diquat peak by other paraquat absorbances. The 2nd Derivative method is recommended in these circumstances.	
8.4.1.1	Paraquat; 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 (see Figure 1).	

Step	Procedure	Notes
	<p>Draw the calibration curve relating peak height at 396 nm (mm above baseline) to the concentration of paraquat in mg/L (Note (h)).</p> <p>Read off from the prepared calibration curve, using the peak height measured at 396 nm, the concentration (mg/L) of paraquat in the eluate (X mg/L).</p>	(h) The line of best fit may be calculated.
8.4.1.2	<p>Diquat; Draw a baseline as tangent to the curve from the valley in the region of 370 nm. Measure the height of the peak above the baseline at 379 nm. (See Figure 2).</p> <p>Draw a calibration curve relating the peak height at 379 nm (nm above baseline) to the concentration of diquat in mg/L (Note (h)).</p> <p>Read off from the prepared calibration curve, using the peak height measured at 379 nm, the concentration (mg/L) of diquat in the eluate (X mg/L).</p>	
8.4.2	<i>2nd Derivate Mode</i> (note i)	<p>(i) The use of second derivative spectroscopy removes the sloping baseline observed in normal mode spectroscopy and also enhances the signal obtained. Paraquat in the presence of diquat may be estimated without recourse to data processing.* It is possible to determine mixtures of similar amounts of paraquat and diquat by the use of commercially available peak processing software. The conditions used for performance testing are given in step 8.6.</p> <p>*The determination of diquat in the presence of large amounts of paraquat (more than 5 times) require the use of data processing or deconvolution for accurate estimation of the diquat.</p>
8.4.2.1	<p>Paraquat; Measure vertically the height of the second derivative peak at 396 nm (see Figure 3). Draw a calibration curve relating peak height (mm) at 396 nm to the concentration of paraquat in (mg/L). Read off from the calibration curve, using the peak height measured at 396 nm, the concentration (mg/L) of paraquat in the eluate (X mg/L). (note h).</p>	
8.4.2.2	<p>Diquat; Measure vertically the height of the second derivative peak at 379 nm (See figure 4). Draw a calibration curve relating peak height (mm) at 379 nm to the concentration of diquat in mg/L. Read off from the prepared calibration curve using the peak height measured at 379 nm, the concentration (mg/L) of diquat in the eluate (X mg/L) (notes h and i).</p>	

Step	Procedure	Notes
8.5	Calculation (Note j) $C_{PQ} \text{ or } C_{DQ} = \frac{0.01}{V} X \text{ mg/L}$ Where C_{PQ} = concentration of paraquat C_{DQ} = concentration of diquat V = volume of sample applied to column in L X = concentration of paraquat or diquat in the eluate.	(j) This assumes a 10 ml aliquot taken for reduction and measurement. If the eluate is diluted see 8.3.4 Note g.
8.6	Suggested Conditions (based on the Perkin Elmer Lambda 5 instrument, used to obtain the performance data)	
	Ordinate Mode	Second Derivative
	Slit Width	2 nm
	Scan Speed	120 nm min ⁻¹
	Response	2 sec
	Lamp	332.8 nm
	Cycles/time	1/0.05 min
	Wavelength	2 nm
	Peak Threshold	0.2 D2 (0.2 units in 2nd deviative mode)
	Recorder	Serial/Dash 1
	Ordinate min/max	-2.2/1.0
	Abscissa min/max	360-430
	Abscissa format	10 nm cm ⁻¹

9 Analytical Quality Control

Once the methods have been put into routine operation, many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check sources of inaccuracy should be made regularly. Many tests are possible and they should be used as appropriate. As a minimum, it is suggested that at least one sample of suitable concentration in each batch of samples be analysed at least in duplicate. Inclusion of a quality control standard of concentration unknown to the actual operator is also useful. Plots of the deviation between multiplicate samples, or of the control standard result, will facilitate detection of inadequate precision and allow the standard deviation of routine analytical results to be estimated.

Address for Correspondence

However thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. Users with information on this method are requested to write to:

The Secretary
 The Standing Committee of Analysts
 The Department of the Environment
 Romney House
 43 Marsham Street
 London SW1P 3PY

Table 1 Performance Characteristics for the Determination of Paraquat, 5L samples (Second Deviative Operation)

Sample	Found $\mu\text{g/L}$	% Recovery	Relative Standard Deviation
Tap Water	<0.1	—	}
	<0.1	—	
	<0.1	—	
0.5 $\mu\text{g/L}$ spike	0.49	98	}
	0.48	96	
	0.46	92	

No breakthrough of paraquat was observed at step 8.2.1 if a column containing paraquat was washed with 5 L of tap water.

Limit of Detection on a 5 L sample—not calculated from blank values, estimated from real sample data to be 0.02 $\mu\text{g/L}$. Performance data for a 1 L sample were similar but higher pro rata.

Table 2 Performance Characteristics for the Determination of Diquat, 1 L sample (Direct Operation)

Sample	Found $\mu\text{g/L}$	% Recovery	Relative Standard Deviation
Tap Water	<1	—	}
	<1	—	
	<1	—	
10 $\mu\text{g/L}$ spike	9.6	96	}
	9.6	96	
	9.3	93	
	9.6	96	
	9.4	94	
	9.4	94	

Table 3 Performance Characteristics for the Determination of Diquat, 1 L Sample (Second Deviative Operation)

Sample	Found $\mu\text{g/L}$	% Recovery	Relative Standard Deviation
Tap Water	<0.3	—	}
	<0.3	—	
	<0.3	—	
1 $\mu\text{g/L}$ spike	1.17	117	}
	1.14	114	
	1.04	104	
	1.07	107	
	1.11	111	
	1.11	111	

No breakthrough was observed at step 8.2.1 if a column containing diquat was washed with 5 L of tap water. Similar data pro rata was obtained for 5 L samples. Limit of Detection on a 5 L sample—not calculatable from blank data, estimated from real sample data to be ca 0.01 $\mu\text{g/L}$.

Figure 1 Absorbance mode

0.3mg/L Paraquat

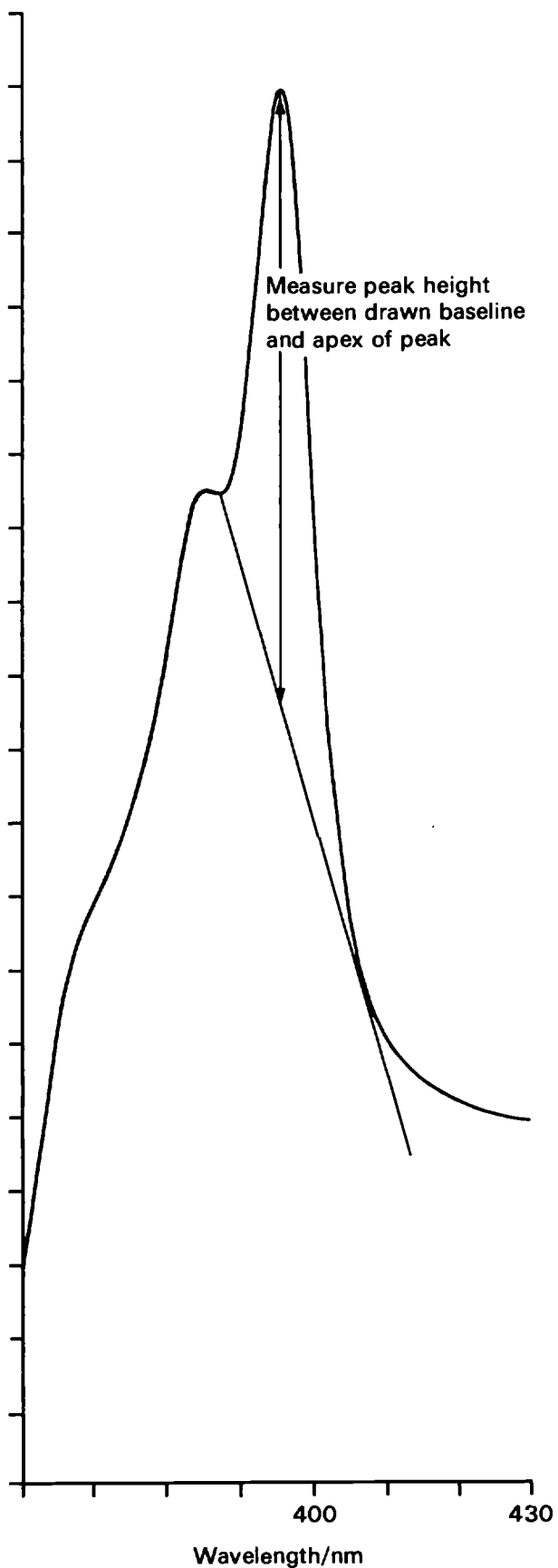


Figure 2 Absorbance mode

0.3mg/L Diquat

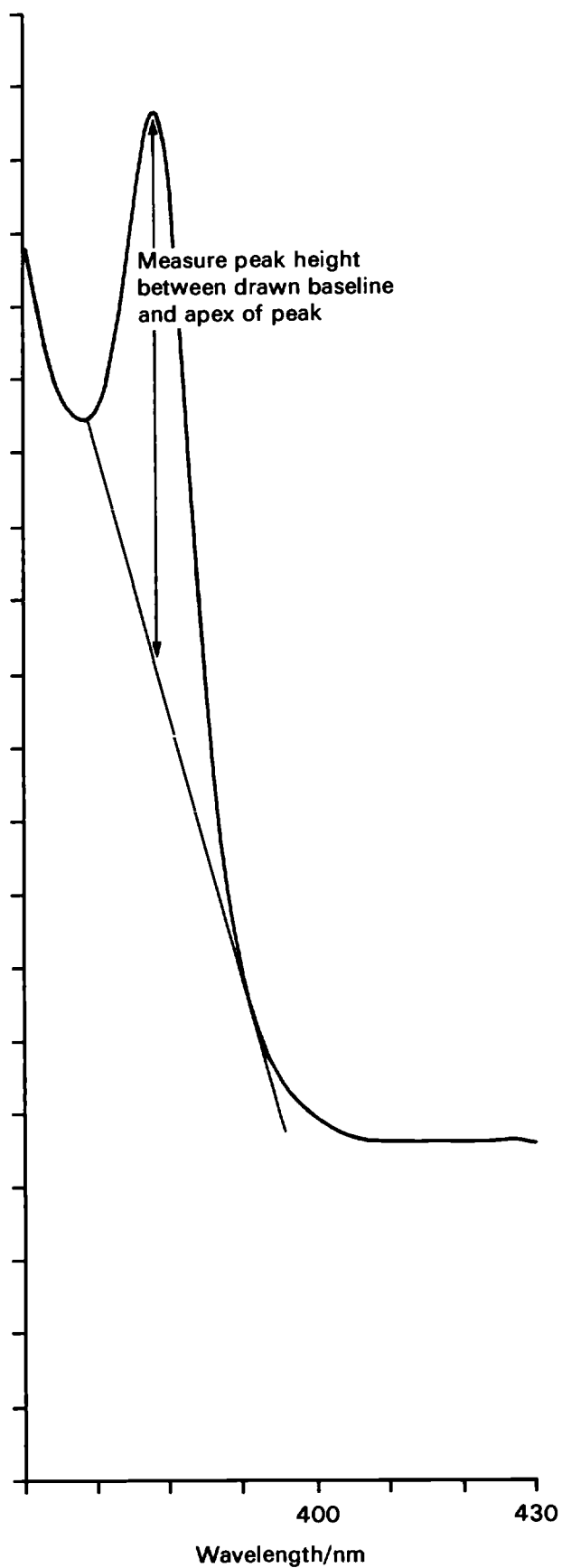


Figure 3 Second derivative mode

0.3mg/L Paraquat

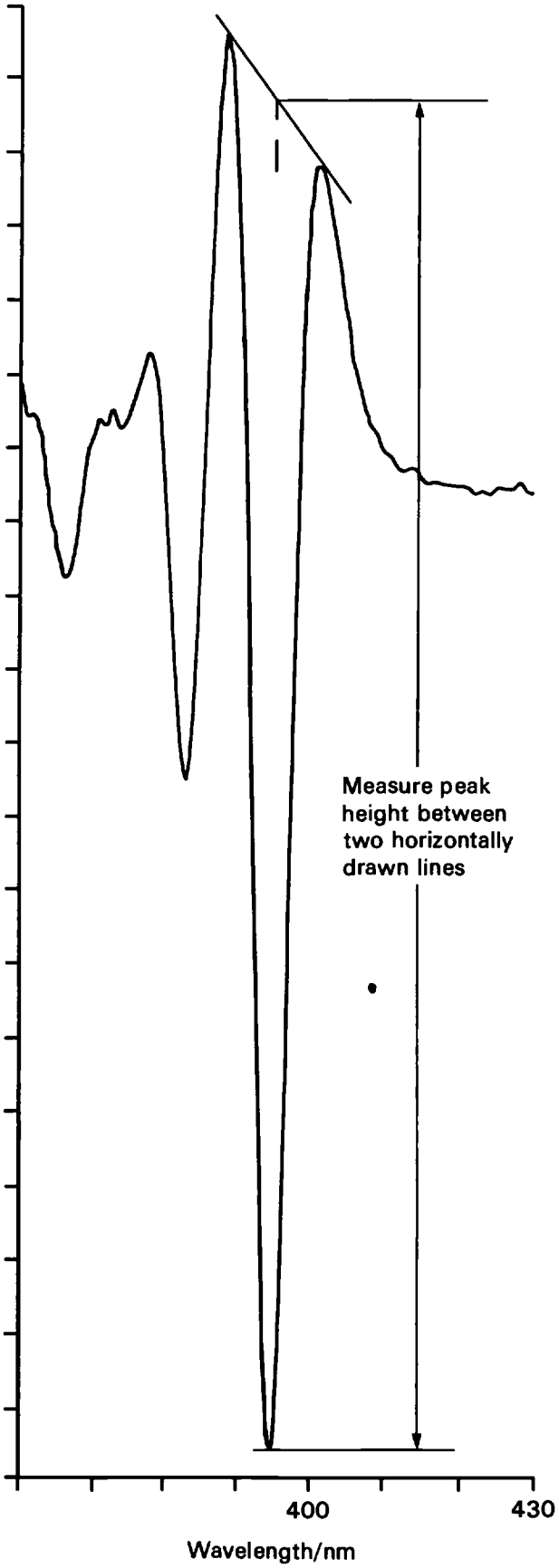


Figure 4 Second derivative mode

0.3mg/L Diquat

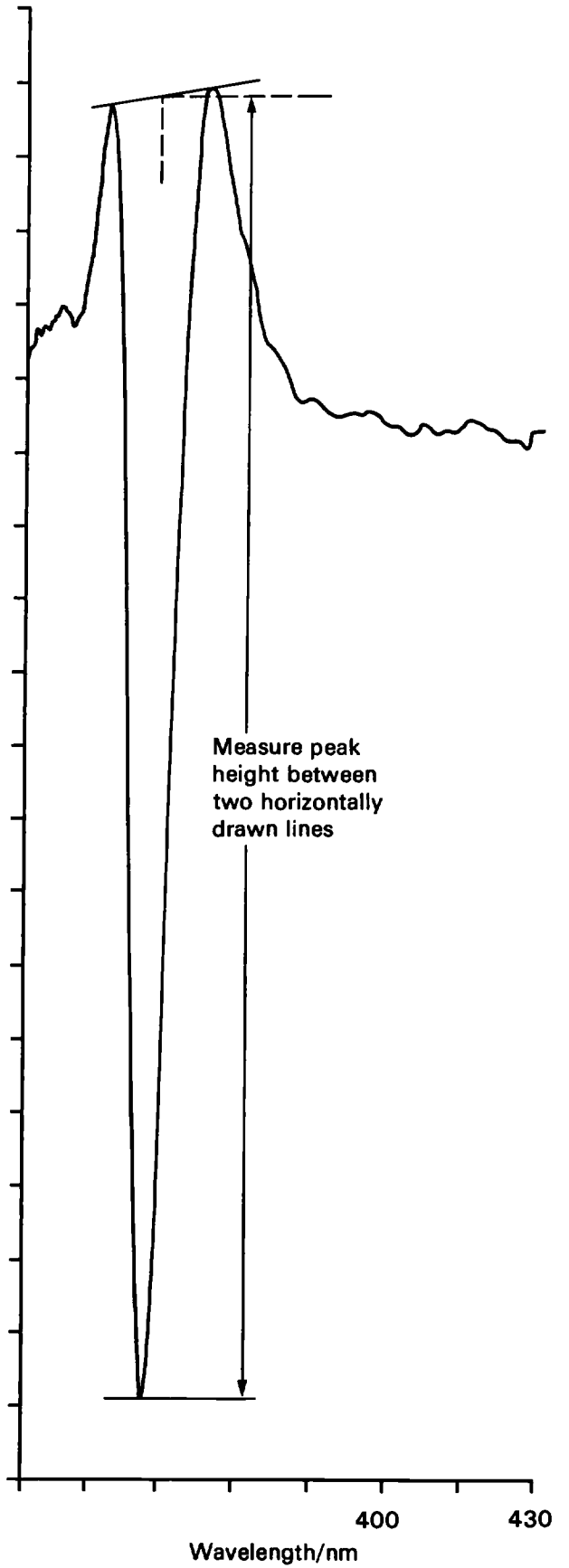
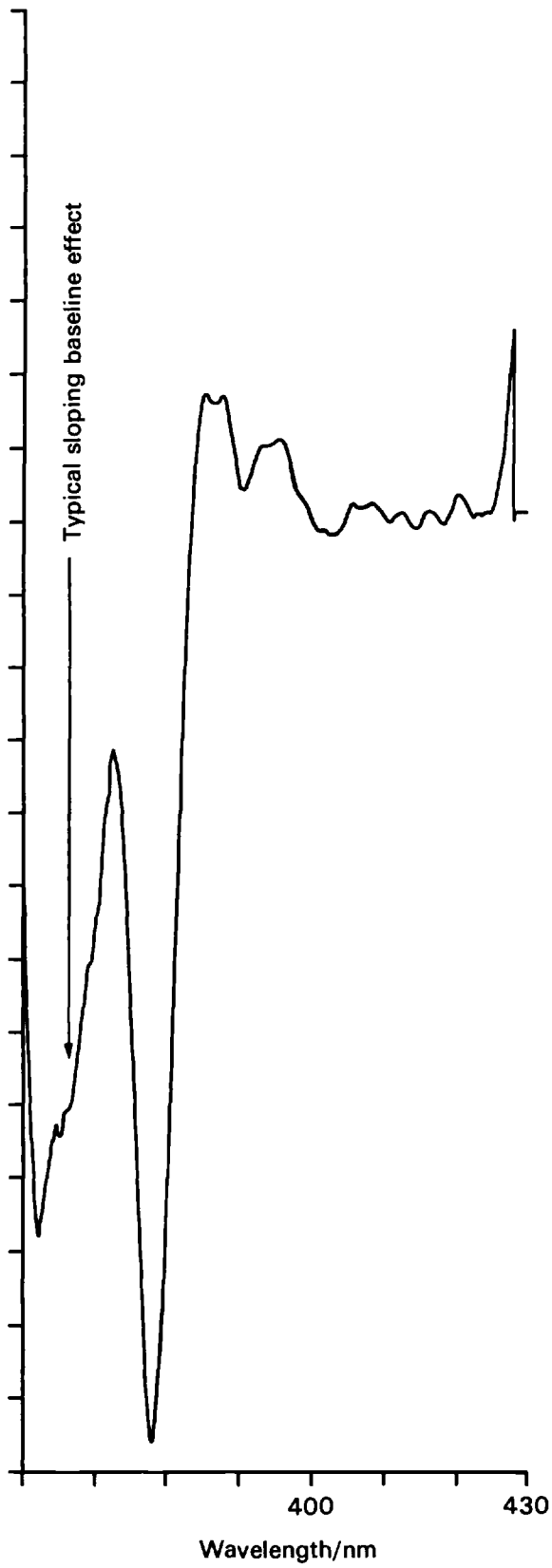


Figure 5 Effect of poor dithionite solution on spectra



Department of the Environment

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