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IMPROVED TRACE OIL ANALYSIS TECHNIQUE USING THE LIQUID CHROMATO--ETC(U)
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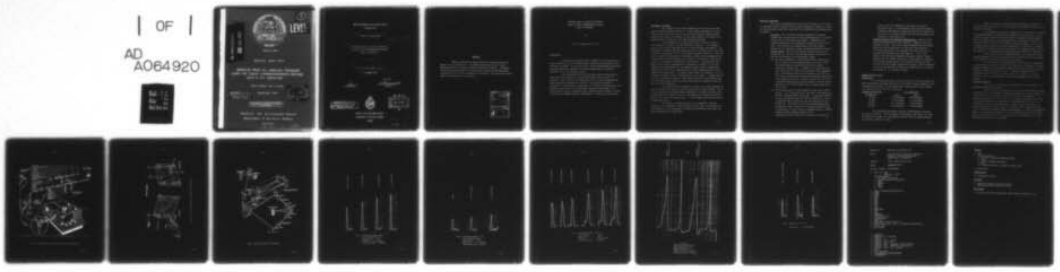

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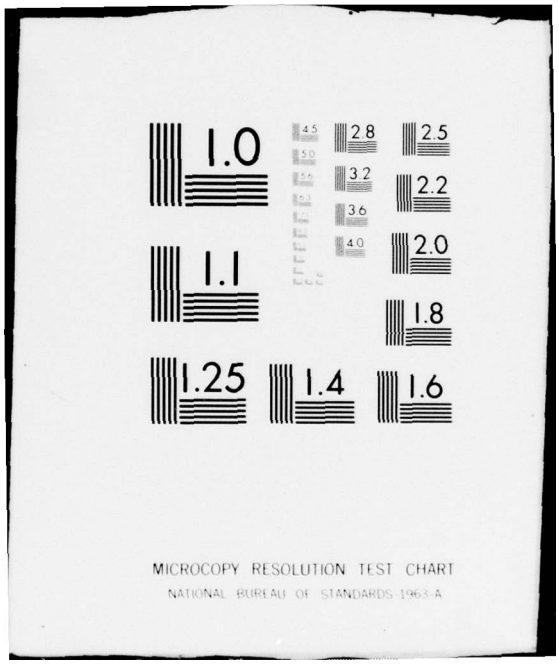
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Materials Report 78-A

IMPROVED TRACE OIL ANALYSIS TECHNIQUE USING THE LIQUID CHROMATOGRAPHIC METHOD WITH A UV DETECTOR

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September 1978

Research and Development Branch
Department of National Defence
Canada

DEFENCE RESEARCH ESTABLISHMENT PACIFIC
VICTORIA, B.C.

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(12) 22 p.

Approved

Section Head

Chief

RESEARCH AND DEVELOPMENT BRANCH
DEPARTMENT OF NATIONAL DEFENCE
CANADA

ABSTRACT

DREP has developed an improved method for measuring the trace amounts of oil in diver's air. The method includes the use of a Liquid Chromatograph with a variable wavelength ultra violet detector. The sample size for air can be reduced to 10 litres from 30 litres and the high degree of sensitivity of 0.2 of a microgram can be achieved. This method can also be used for the analysis of oil in water.

IMPROVED TRACE OIL ANALYSIS TECHNIQUE USING THE LIQUID CHROMATOGRAPHIC METHOD WITH A UV DETECTOR

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INTRODUCTION

A continuing requirement exists at DREP for the determination of minute amounts of oil in respiratory gases, particularly those gases used by the divers in FDU(P). In the recent past a liquid chromatographic method was developed[1] which made possible the reliable determination of microgram quantities of oil in respiratory gases.

It has been known for a long time that certain constituents of lubricating oils fluoresce at specific wavelengths when excited by UV radiation. Use of this fact in combination with the liquid chromotographic method previously described has resulted in a significant increase in sensitivity. This increase in sensitivity is of value in allowing analytical methods to stay ahead of the increasingly stringent requirements in the specifications covering respiratory gases, which have been changed in recent years from the maximum allowable concentration of 0.005 mg/ℓ to 0.001 mg/ℓ.

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EQUIPMENT & PROCEDURE

The equipment used in these experiments is the Pye Unicam LCM2 which has been described previously.[1] In the present experiments, an ultra-violet detector takes the place of the previous moving wire detector which picked up the eluted oil, oxidized it into carbon dioxide, and reduced it to methane which was detected by the flame ionization detector.

The arrangement of the analytical system is shown in Figure 1, the UV detector in Figure 2 and the flow cell in Figure 3. An air sample, usually from a diver's aqualung bottle, is passed through a gas bubbler. The gas bubbler is packed with fine pyrex glass wool in the inlet side of the tube to the level covered by 75 ml of pure solvent, heptane or Freon 113. The flow rate is regulated continuously by adjusting the valve on the aqualung bottle to deliver two litres per minute, for a period of five minutes. When oil is present, it is trapped and dissolved in the solvent. If the solvent used is Freon 113 and the oil contamination is suspected to be high, 25 µl of the sample can be used directly for oil analysis without further concentration. Otherwise, the solvent is transferred into a 100 ml beaker and evaporated to dryness under medium heat. The residue, when cooled, is dissolved in 0.75 ml of Freon to obtain a 100 to 1 concentration of oil content. A sample size of 25 to 35µl is used for analysis. This aliquot portion is then injected into the 25 cm SiO_2 packed column from whence the separated components (Freon and oil) enter the UV detector.

The output from the UV detector is 100 mv so a 20 dB attenuator is used to connect it to the 10 mv input Pye Unicam AR25 linear recorder. The UV detector includes the visible range, consequently, two lamps are used in the optical system (see Figure 4) and the wave length can be selected from 200 to 900 nm, for a particular organic group. In this instance 292 nm is chosen for optimum sensitivity.

The height of the peak from the oil is compared to the peak heights of known standards. With the sample size of 25µl, the sensitivity of the UV detector is 0.2 microgram. The analysis described in this report was done by employing the single beam.

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OPERATING PARAMETERS

The liquid chromatographic unit with the UV detector can be ready for operation within 15 minutes from the time the machine is turned on. There are three important areas that would affect the sensitivity and reproducibility of results.

1. Flow rate - This is the most difficult parameter to maintain because with continuous use the SiO_2 packing material in the glass column tends to pack tighter and tighter. Consequently, the pumping pressure has to be increased to maintain a constant flow rate. This variation in packing density with time requires extreme care in operation in order to ensure reproducible results.

2. Solvent system - There are two solvents involved, one for dissolving the oil, the other (the eluting solvent) carries the oil and Freon mix through the chromatographic column.

   (a) Any peaks belonging to a solvent selected for dissolution of the oil should be quite distinguishable from the oil peak; the solvent must be reasonably non-toxic and readily available at nominal cost. A number of the common solvents were tested and the choice was restricted to the halogenated ones. Chloroform was found to be reasonably good, but at a very dilute concentration the base line responded erratically, in the negative direction. Finally, a Freon 113 (1-1-2 trichlorotrifluoroethane) was selected because it has the overall suitability as a "safe" solvent and it contains less than 0.2 ppm of "oil".

   (b) The eluting solvent for many analyses of this type is ethyl alcohol. It is relatively pure, "non-toxic" and consequently does not adversely affect the analyst. It was also established that it separates Freon 113 from oil effectively. Purity is important when a solvent is used for trapping oil from divers' air. The Freon 113 (1-1-2 trichlorotrifluoroethane) contained 0.2 ppm or less oil; if its high evaporation rate is acceptable, it can be used as a trapping solvent. Heptane, another suitable trapping solvent, often contains more than 0.2 ppm of oil and must be distilled in

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glass so that the background contribution is within an acceptable level. A more expensive glass-distilled heptane supplied by BDH Chemicals containing less than 0.2 ppm of oil, was found to be suitable without any further distillation for trapping oil from divers' air.

3. Bandwidth Control and Absorbance Range Selector - There are four spectral bandwidths which can be selected. Normally, the 16 nm bandwidth is used. This is the largest bandwidth with the highest sensitivity and a good signal to noise ratio (See Figure 5). At a lower concentration, the bandwidth at 8 nm can be used to determine the detection limit (See Figure 6). It is to be expected that the smaller bandwidth does give a better "linear" response, but the overall sensitivity or peak height is decreased. The absorbance range selector on the detector was used to make sure that the peak height response was on scale. This was especially true for the analysis of higher oil concentrations in solvents, (See Figure 7), i.e. 250 ppm or higher.

ANALYSIS OF OIL IN AIR

Calculations

Oil standards were made from 200 to 500 ppm at 50 ppm increment for high concentration technique and from 10 to 150 ppm at 10 ppm increment for low concentration technique. The following table indicates some of the standard oil concentration per 25 or 35 µl injection.

Standard oil dissolved in Freon 113	Oil content per 25 µl	Oil content per 35 µl
10 ppm	0.25 microgram	0.35 microgram
50 ppm	1.25 microgram	1.75 microgram
200 ppm	5.0 microgram	7.00 microgram
500 ppm	12.50 microgram	17.50 microgram

The glass-distilled heptane supplied by BDH Chemicals contained less than 0.2 ppm oil. For the purpose of calculation, the value of 0.2 ppm, (0.2 mg/litre) is used. Oil contribution from the 75 ml of trapping solvent is 0.015 mg. (75/1000 x 0.2 mg).

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When the solvent is evaporated and the residue is dissolved in 0.75 ml (750 µl) of Freon 113, the 25 µl aliquot would contain 0.0005 mg of oil (25/750 x 0.015 mg).

If the sample size taken for analysis is 10 litres and it contains the maximum allowable concentration of airborne oil, or 0.001 mg/l, the oil in the 10 litres of air is 0.01 mg which will be trapped in the gas bubbler. After the evaporation of the trapping solvent, the residue is dissolved in 0.75 ml of Freon 113 and a 25 µl aliquot is used for analysis. The oil contribution from the maximum allowable concentration per injection is 0.00033 mg, (25/750 x 0.01 mg). The total oil content from trapping solvent and from the airborne oil is 0.00083 mg or 0.83 microgram, (0.0005 mg + 0.00033 mg).

The 0.2 ppm oil in the trapping solvent can be looked upon as an internal standard, its exact concentration can be subtracted from the sample once a blank is run and its concentration calculated.

In oil analysis two standards, one at 40.0 ppm (25 µl containing 1.0 microgram of oil) and the other at 30.0 ppm (25 µl containing 0.75 microgram), are commonly used to establish whether the diver's air meets the International Standard of 0.001 mg/l or not. The exact concentration can be determined by the selection of either a 25 or 35 µl sample, or a proper dilution to bring the peak height to within the measurable region of the recorder.

Analytical Examples

To appreciate the rapidity and sensitivity of this method, a few analytical examples are included.

Figures 5 and 6 illustrate the fact that the selection of a narrow bandwidth can bring the highest sensitivity in sharpness of peak heights, but it has its limits in its useable region for accuracy and reliability. For example, with the slit set at 16 nm., oil concentrations between the 1.6 and 3.12 microgram region can be calculated by observing that there is a 0.25 microgram per square on the graph paper. Figure 6 shows the results of a change in bandwidth from 16 to 8 nm. This change gave a lower sensitivity, but an increase in the linear response; consequently, at a lower concentration, there is a concentration change of 0.275 microgram per square on the graph paper. Notice that the blank is less than the 0.50 microgram and is close to the detection limit of 0.2 microgram.

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Figure 7 is an example of a high concentration technique. At a higher concentration, the absorbence setting is increased to decrease the signal response and the sample size should be increased a little to compensate for the decrease in the signal intensity.

Figure 8 is an example of an air analysis in which the sample was diluted 10 to 1 to bring it down to the approximate peak height of the 10.0 microgram standard. The sample was above the acceptable level of 0.001 mg of oil per litre of air.

Figure 9 is an example of an unknown air analysis that was below the 0.001 mg/l level. The oil content was calculated to be less than 0.125 microgram, (0.625-0.5), or about a third of the maximum acceptable level of 0.001 mg/l.

Discussion

Throughout the development of this improved method, it was found that the preparation of standard airborne oil for calibration purposes is very difficult because of the tendency for the oil to form into droplets and deposit out. That is why the trapment of oil in solvent was used.

To maximize the trapping efficiency, the inlet side of the gas bubbler column was packed with fine Pyrex glass wool to a level which was covered by 75 ml of solvent. The packing material used is a fine mesh silica with a particle size range between 32-63 microns. This type of material certainly cannot separate the oil into its homologues.

At lower concentrations, the "memory effect" does play an important part in determining the detection limit. One of the procedures to minimize this effect is to inject a standard alternately with a blank.

There is also some concern about the equilibrium of airborne oil and oil residue that may be found on the inside wall of aqualung bottles. Experience has been that if the oil particles are large enough, they will be deposited onto the wall very quickly and the aerosol type(s) that remain airborne are the ones that will be significant toxicologically. The proportion remaining as aerosol can be ascertained by simply analyzing the oil content in air every 24 hours.

With the variable wavelength UV detector and the bandwidth selector, the maximum sensitivity can always be obtained in any given concentration range. Unlike the flame ionization detector, no temperature stabilizing was necessary. The whole system is operational after 10 to 15 minutes of warming up.

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Further confirmation of the value of the present method has been obtained on many occasions. For example, air samples from HMC Ships' compressors that were not equipped with efficient filters were analyzed and found to contain as high as 0.20 mg of oil per litre -- 200 times higher than the normal samples.

With the selection of Freon 113 as an effective solvent for the dissolving of oil, coupled with the UV detector, this method is more than adequate to meet any anticipated analytical requirement for the analysis of oil in diver's air. Because of its sensitivity, the air requirement is reduced, thus the speed of analysis is also improved.

ANALYSIS OF OIL IN WATER

This method was primarily developed for the analysis of oil in air, but has another application as well; specifically, it can be used to analyze oil in bilge water (dirty water) after it has gone through the coalescer to be discharged into the open sea. Because of the presence of iron oxide and hydroxide in the water, the optical type of analyzer becomes questionable in its reliability. The typical procedure is to take 1 ml of the water sample and evaporate it to dryness. When cooled, 1 ml of Freon 113 is added and a 25µl sample of the aliquot is used for oil analysis with the liquid chromatograph. The peak height obtained can be compared with the standards and the concentration can easily be calculated.

SUMMARY AND CONCLUSIONS

The determination of oil in air or in water can now be done with the liquid chromatograph equipped with a variable wavelength UV detector. The sample size for air can be reduced to 10 litres from the 30 litres required with the previous method and still achieve a higher degree of sensitivity, that is, to 0.2 of a microgram. When this method is used for the analysis of oil in water, the water sample can be as small as 0.5 ml. The advantage of this method is the fact that it is designed to handle small amounts of oil in a given sample and it is reasonably fast and accurate. Within half an hour, an analysis of oil in air can be completed; consequently, it has become a standard method for this type of analysis.

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REFERENCE

1 Yee, L.K., Sewell, R.B.H., Determination of Trace Amount of Oil by a Liquid Chromatographic Method. DREP Materials Report 76-A January 1976.

2. Langdon, W.M., Mark, T., Wasan, D.T., Analysis of Trace Quantities of Oil in Water by Gas Chromatography. Illinois Institute of Technology, Chicago. Proceedings of the International Seminar & Exposition on Water Resources Instrumentation 1975.

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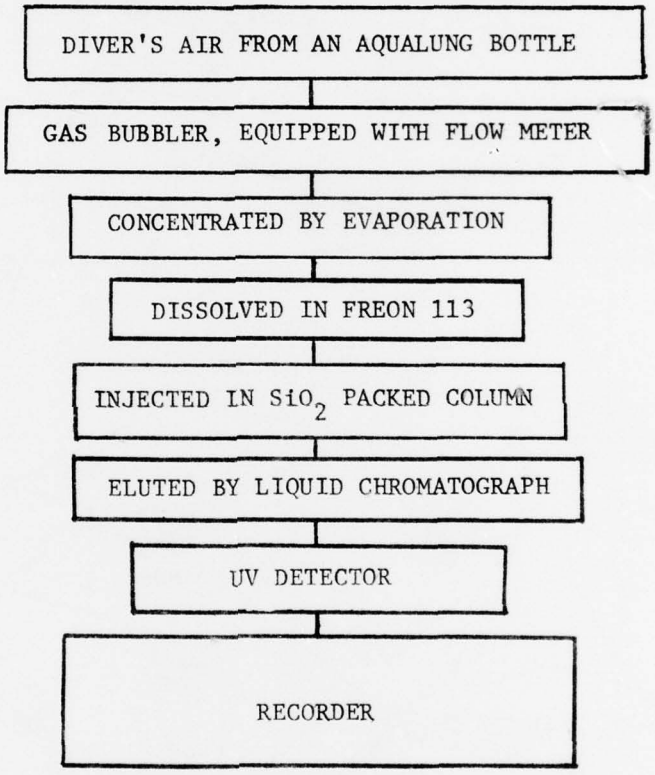
DIVER'S AIR FROM AN AQUALUNG BOTTLE
GAS BUBBLER, EQUIPPED WITH FLOW METER
CONCENTRATED BY EVAPORATION
DISSOLVED IN FREON 113
INJECTED IN SiO_2 PACKED COLUMN
ELUTED BY LIQUID CHROMATOGRAPH
UV DETECTOR
RECORDER

Fig.1

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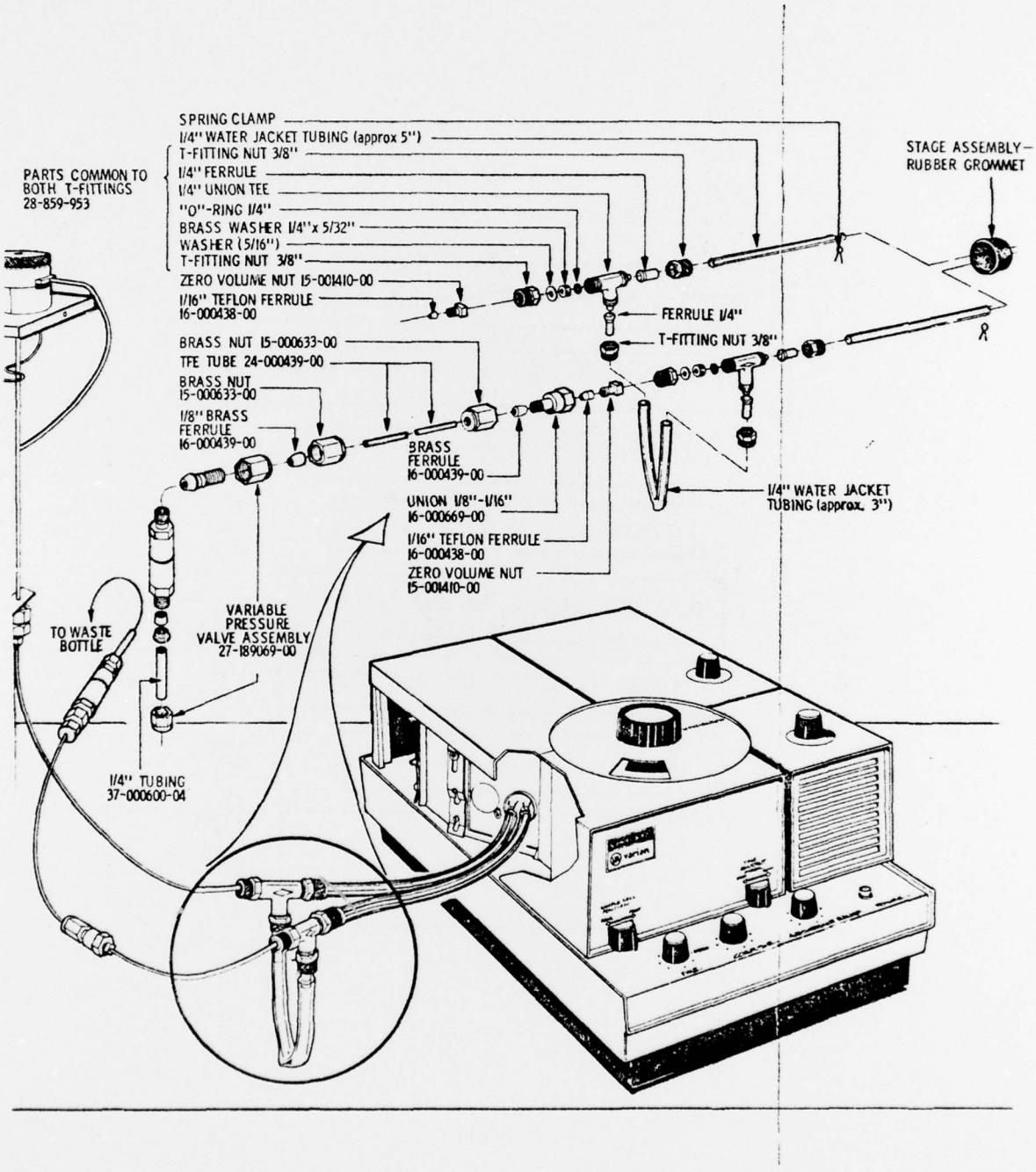

Fig.2 Installation of UV Detector with LC Pump Outlet

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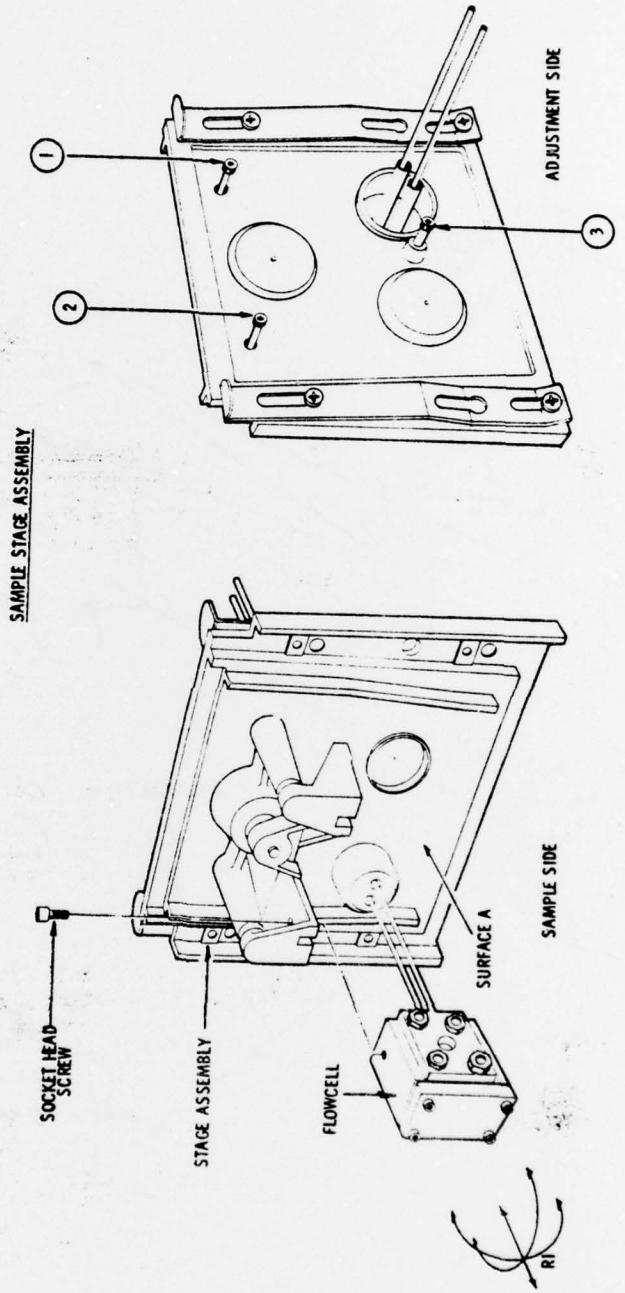

Fig.3 Flow cell assembly mounting on UV Detector

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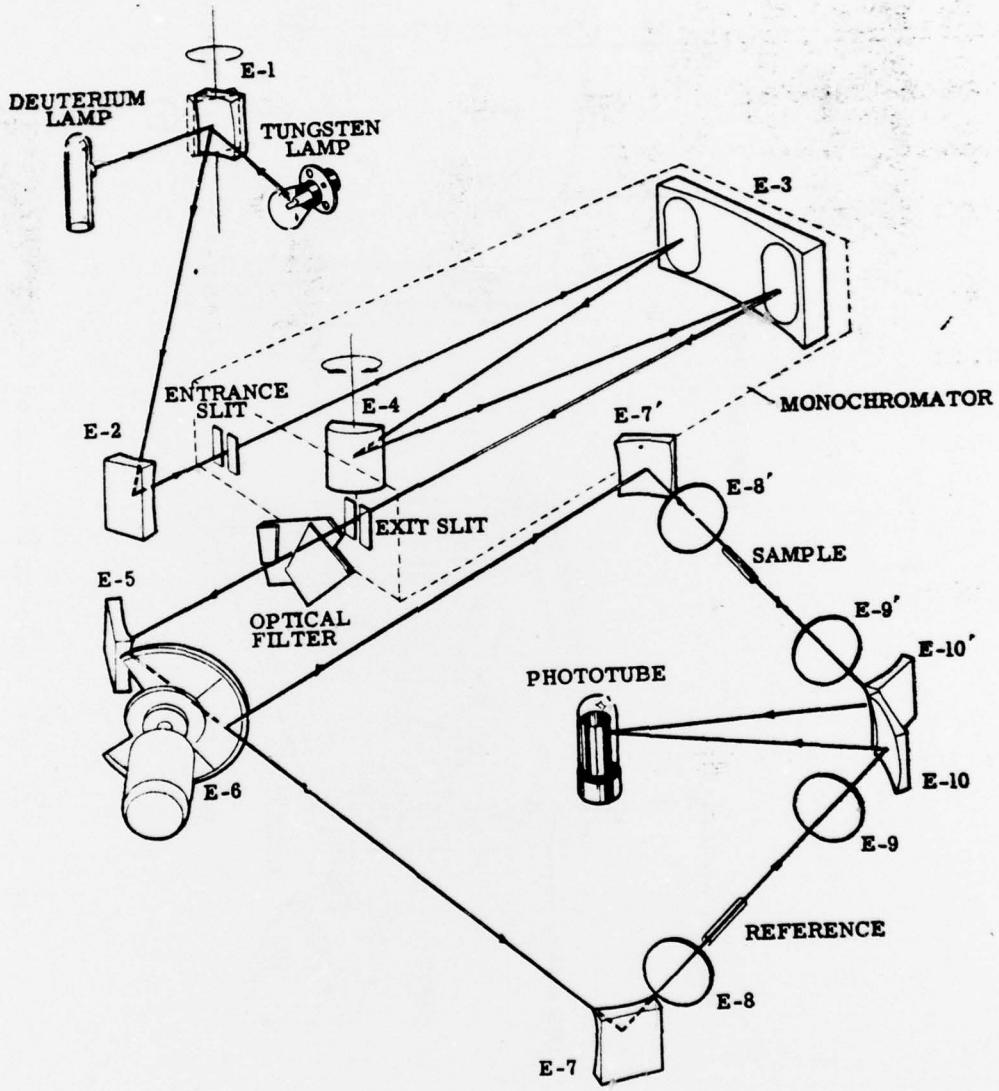

Fig.4 Optical system of UV Detector

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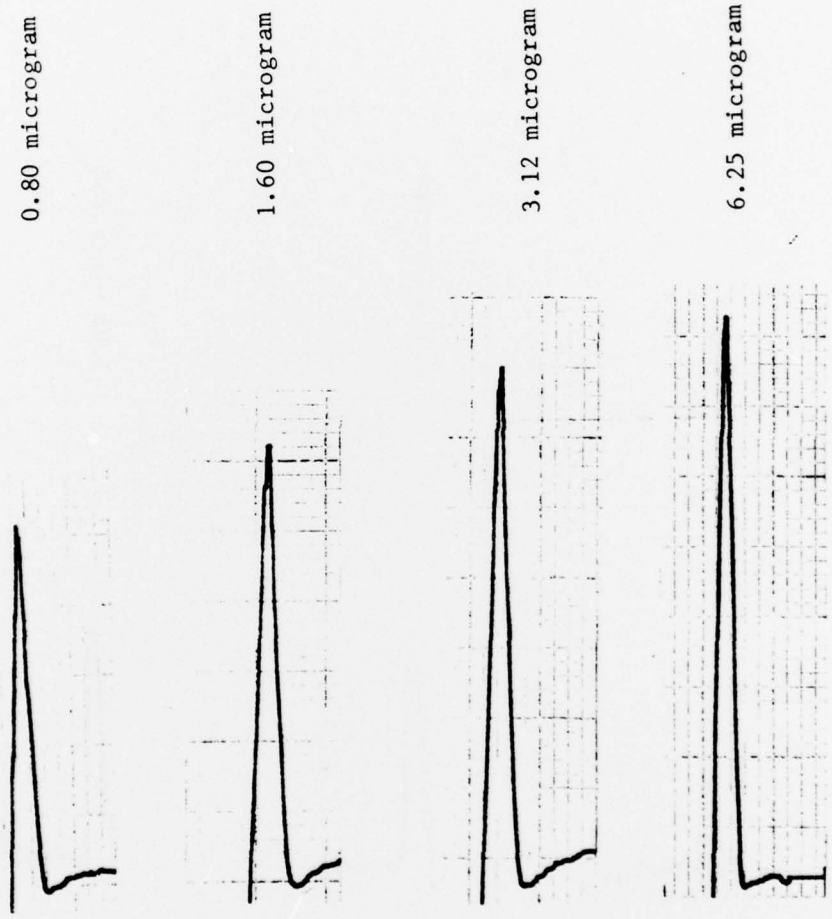

Fig.5 Absorbence Range - 0.02
Slit setting - 16 nm
Sample size - 25 µl
Flow rate - 0.5 ml/min.
Eluting solvent - ethanol

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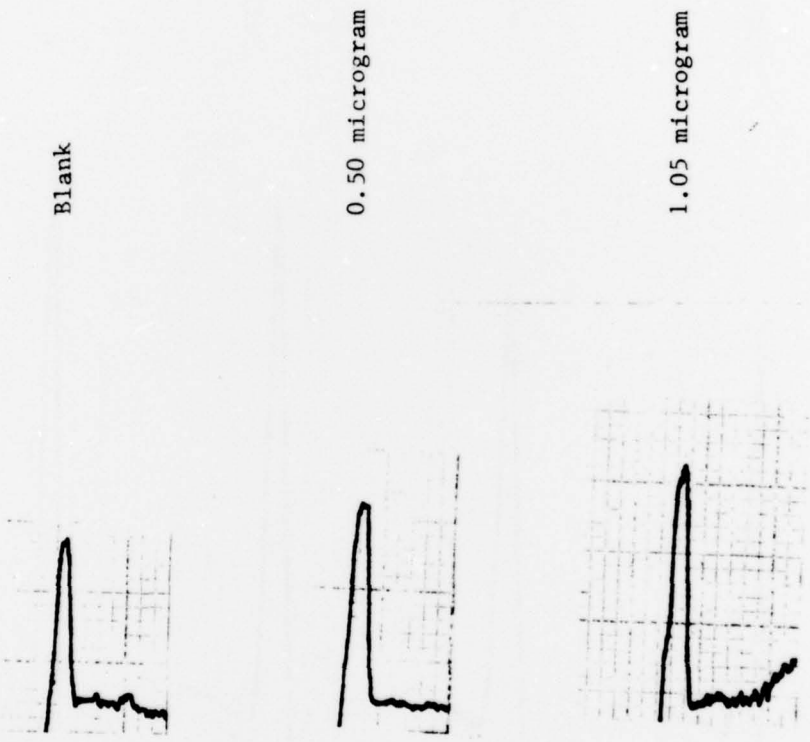

Fig.6 Absorbence Range - 0.02
Slit setting - 8 nm
Sample size - 35 µl
Flow rate - 0.5 ml/min.
Eluting Solvent - ethanol

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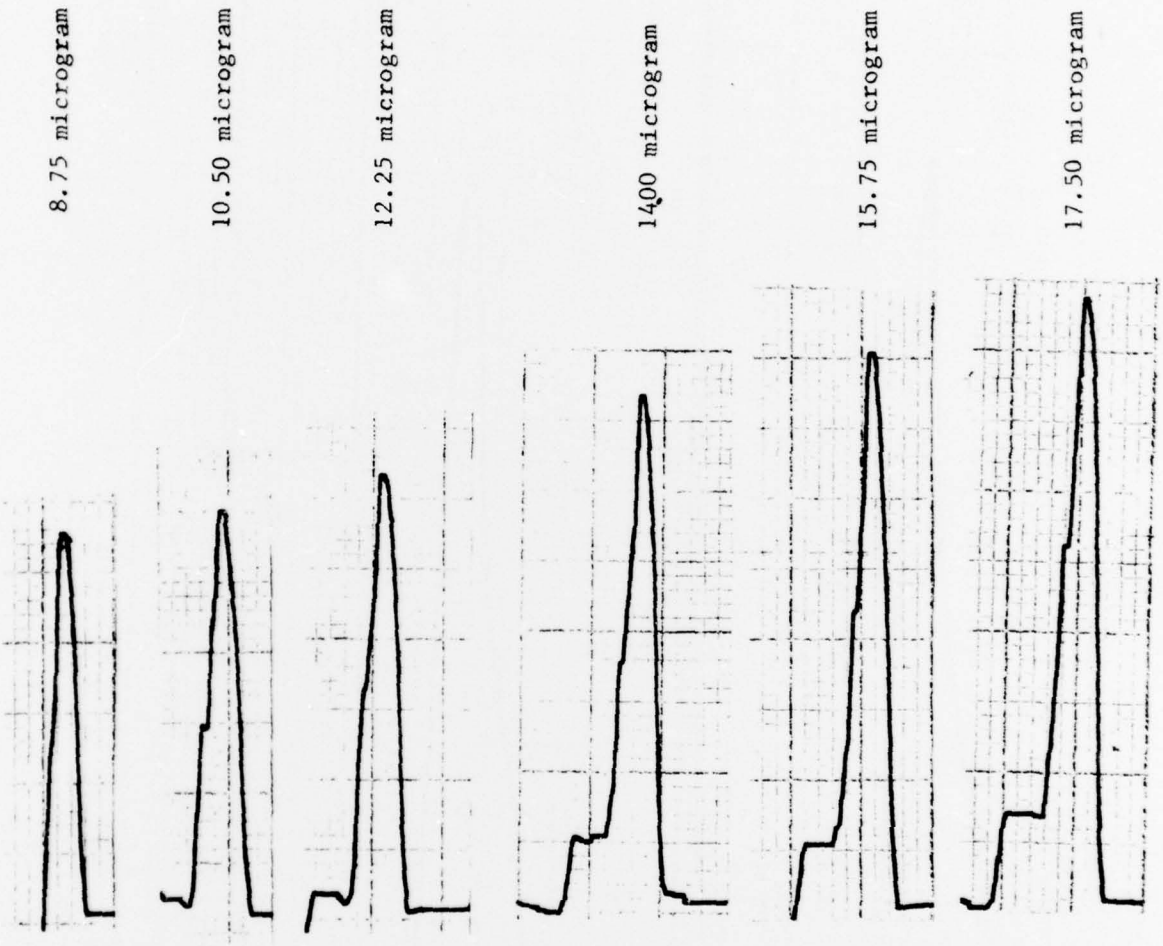

Fig.7 Absorbence Range: 0.05
Slit setting - 16 nm
Sample size - 35 µl
Flow rate - 0.5 ml/minute
Eluting solvent - ethanol

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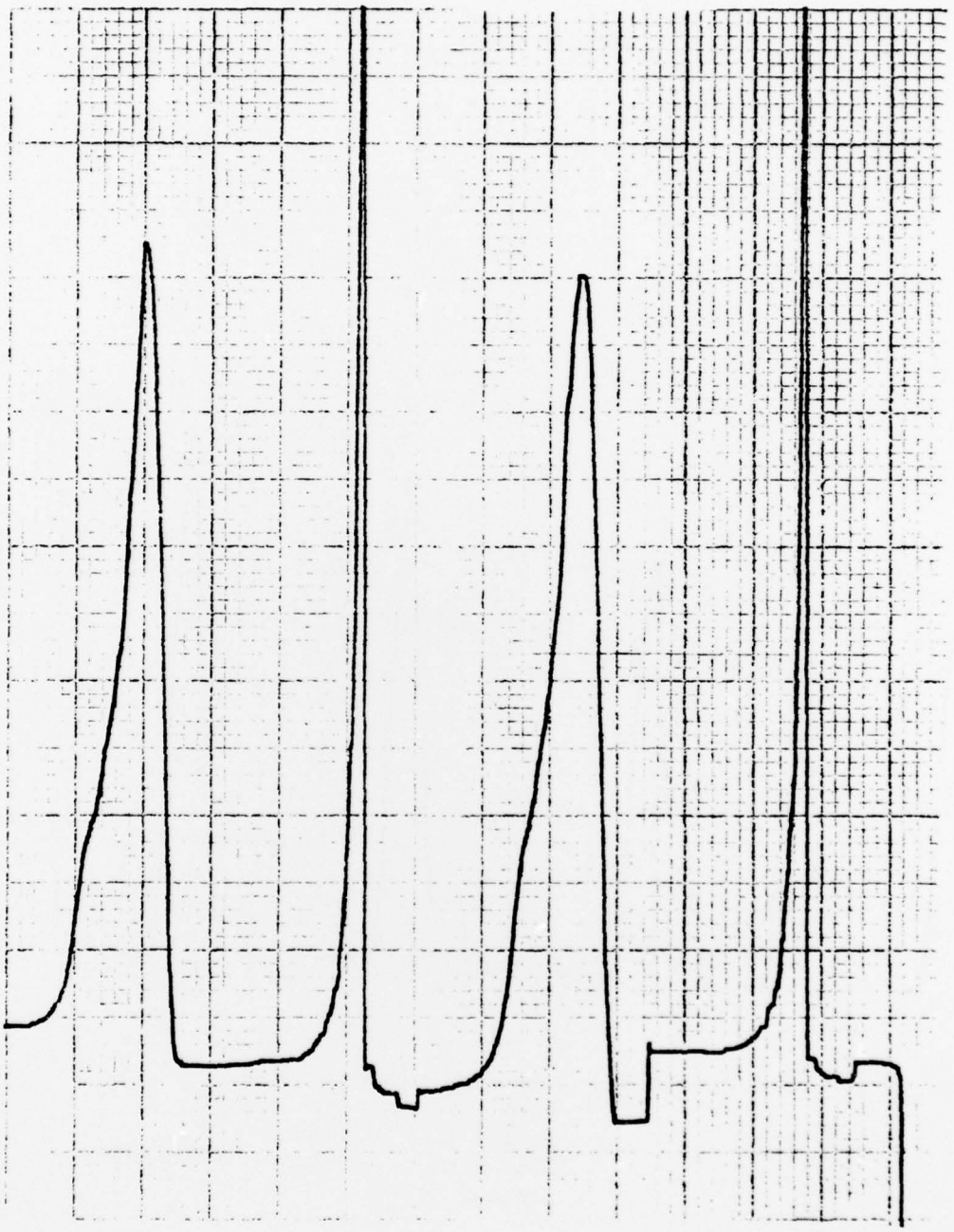

Fig.8
Absorbance Range-0.02
Slit Setting - 16 nm
Sample size-25 µl
Flow rate-0.5 ml/minute
Eluting solvent - ethanol

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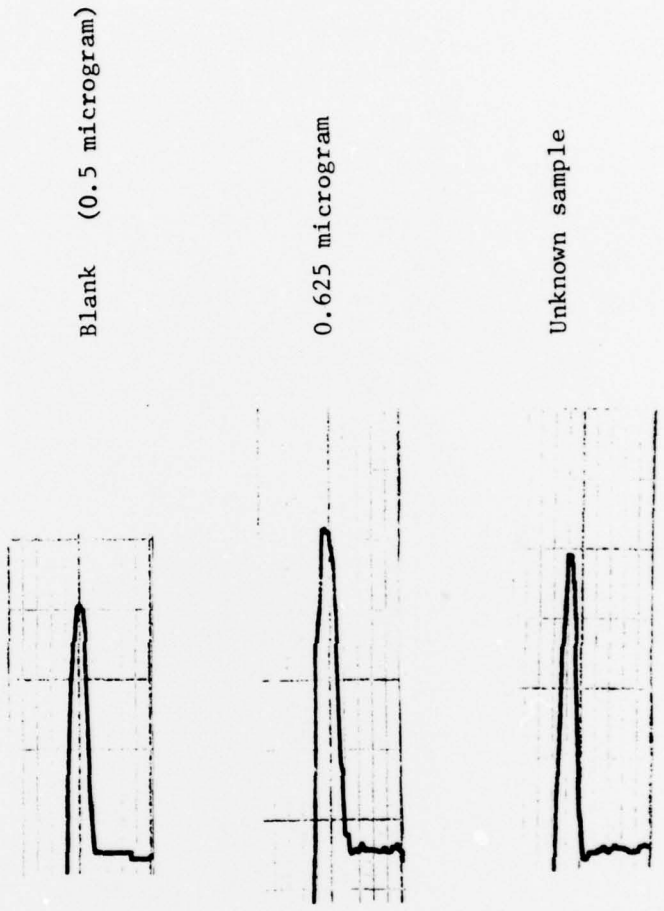

Fig.9 Sample size - 25 µl

Flow rate - 0.5 ml/minute

Report No: DREP Materials Report 78-A

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Dated: September 1978

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