

Tetryl  
(2,4,6-Trinitrophenylmethylnitramine)

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Analyte:	Tetryl	Method No.:	S225
Matrix:	Air	Range:	0.882-4.51 mg/cu m
OSHA Standard:	1.5 mg/cu m - skin	Precision ( $\overline{CV}_T$ ):	0.065
Procedure:	Filter collection, colorimetric	Validation Date:	12/19/75

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1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.
- 1.2 The filters are extracted with N,N-diethylethanolamine.
- 1.3 The absorbance of the resulting reddish-brown solution is read at 420 nm as a quantitative measure of tetryl.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.882-4.51 mg/cu m at an atmospheric temperature and pressure of 23°C and 770 mm Hg. The probable range of the method is 0.15 -4.5 mg/cu m based on the range of standards used to prepare the standard curve. For samples of high concentration where the absorbance is greater than the limits of the standard curve, the samples can be diluted to extend the upper limit of the range.
- 2.2 A concentration of 0.15 mg/cu m of tetryl can be determined in a 100-liter air sample based on a 0.05 absorbance using a 1-cm cell.

3. Interferences

Other nitro aromatic compounds may interfere if they produce a color when dissolved in N,N-diethylethanolamine. A number of nitro compounds are capable of yielding a color in many organic solvents. Trinitrotoluene (TNT) gives a red-violet color in N,N-diethylethanolamine, which gradually changes to a yellow-red color (Reference No. 2). Since TNT would likely be collected on the filter if it is present in the air, it would give a positive interference and result in a high reading for tetryl.

#### 4. Precision and Accuracy

- 4.1 The Coefficient of Variation ( $\overline{CV}_T$ ) for the total analytical and sampling method in the range of 0.882-4.51 mg/cu m was 0.065. This value corresponds to a 0.098 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.
- 4.2 A collection efficiency of 0.985, standard deviation of 0.004, (essentially 1.0) was determined for the collection medium. Thus, no correction for collection efficiency is necessary, and it is assumed that no bias is introduced in the sample collection step. There is also no apparent bias in the sampling and analytical method for which an analytical method recovery correction was made. Thus,  $\overline{CV}_T$  is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

#### 5. Advantages and Disadvantages of the Method

- 5.1 The samples, collected on filters, are analyzed by means of a quick, instrumental method.
- 5.2 The color developed has the greatest absorption maximum, between 2.5 to 3.5 hours after addition of N,N-diethylethanolamine.

#### 6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of tetryl has the following components:
- 6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate polystyrene 37-mm 3-piece cassette filter holder. Do not use Tenite filter holders.
- 6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of  $\pm 5\%$  at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.
- 6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.
- 6.3 Spectrophotometer. This instrument should be capable of measuring the developed color at 420 nm.
- 6.4 Matched glass cells or cuvettes, 1-cm path length.
- 6.5 Assorted laboratory glassware -- pipets, volumetric flasks, graduated cylinders of appropriate capacities, glass screw cap bottles with Teflon-lined caps.
- 6.6 Tweezers.
- 6.7 Wrist action shaker.

## 7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Tetryl, reagent grade.

7.2 Benzene, reagent grade.

7.3 Tetryl standard solution. Weigh accurately 0.375 g of tetryl and dissolve in benzene in a 25-ml volumetric flask. Bring volume in the flask to the mark. The concentration of this solution is 15 mg/ml.

7.4 N,N-Diethylethanolamine, 99%. Caution must be taken when handling N,N-diethylethanolamine, since it is very toxic.

## 8. Procedure

8.1 Cleaning of equipment. No specialized cleaning of glassware is required.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 100 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of  $\pm 5\%$ .

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

- 8.3.7 Carefully record the sample identity and all relevant sampling data.
- 8.3.8 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.
- 8.3.9 The filter should be removed from the cassette filter holder within one hour of sampling and placed in a clean screw cap bottle. Care must be taken to handle the filter only with clean tweezers.
- 8.3.10 The screw cap bottles in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.
- 8.4 Analysis of Samples
- 8.4.1 Each sample is analyzed separately.
- 8.4.2 Pipet 10 ml of N,N-diethylethanolamine into each screw cap bottle and cap each bottle.
- 8.4.3 Shake each bottle for 10 minutes on a wrist action shaker.
- 8.4.4 Transfer the colored solution to a new screw cap bottle and allow each sample to stand for 2.5-3.5 hours.
- 8.4.5 Read each sample using a 1-cm cell at 420 nm in the spectrophotometer against a blank prepared from N,N-diethylethanolamine.
- 8.5 Determination of Analytical Method Recovery
- 8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery should be determined over the concentration range of interest.
- 8.5.2 Procedure for determining analytical method recovery. Six filters are spiked at each of the three levels with appropriate amounts of the standard solution described in Section 7.3. This corresponds to the amount of tetryl collected in a 100-liter sample at the 0.5X, 1X, and 2X levels, respectively. Allow the filters to dry and place each filter in a screw cap bottle and allow to stand overnight. The analyte is then extracted from the filter and analyzed as described in Section 8.4.

A parallel blank filter is also treated in the same manner except that no sample is added to it.

Analytical Method Recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or,

$$\text{A.M.R.} = \frac{\text{mg found}}{\text{mg added}}$$

## 9. Calibration and Standards

- 9.1 Into 5 screw cap bottles, pipet 10 ml of N,N-diethylethanolamine.
- 9.2 Carefully pipet 3, 7, 15, and 25 microliters of the standard solution (Section 7.3) into each bottle. Process one bottle as a blank.
- 9.3 Cap each bottle with a Teflon-lined cap. Shake the jars on a wrist action shaker for 10 minutes. Allow samples to stand for 2.5-3.5 hours.
- 9.4 Adjust the baseline of the spectrophotometer to zero by reading distilled water in both cells.
- 9.5 Read the blank, prepared from N,N-diethylethanolamine, and then each sample at 420 nm.
- 9.6 Construct a calibration curve by plotting absorbance against micrograms tetryl in the colored developed solution.

## 10. Calculations

- 10.1 Subtract the absorbance of the blank from the absorbance of each sample.
- 10.2 Determine from the calibration curve (Section 9.6) the  $\mu\text{g}$  of tetryl present in each sample.
- 10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain corrected  $\mu\text{g}/\text{sample}$ .

$$\text{Corrected } \mu\text{g}/\text{sample} = \frac{\mu\text{g found (Section 10.2)}}{\text{A.M.R.}}$$

- 10.4 The concentration of the analyte in the air sample can be expressed in  $\text{mg}/\text{cu m}$  ( $\mu\text{g}/\text{liter} = \text{mg}/\text{cu m}$ ).

$$\text{mg}/\text{cu m} = \frac{\text{Corr. } \mu\text{g (Section 10.3)}}{\text{Air Volume Sampled (liter)}}$$

11. References

- 11.1 Goldman, F. H. and D. E. Rushing, "The Estimation of Minute Amounts of Tetryl in the Atmosphere," Journal of Industrial Hygiene and Toxicology, 25 (5), (1943), 195.
- 11.2 Goldman, F. H., and D. E. Rushing, "Diethylaminoethanol as a Reagent for Detection and Colorimetric Determination of Small Amounts of Trinitrotoluene in Air," J. Ind. Hyg. Toxicol., 25, (1943), 164.
- 11.3 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.