Method no.: 43

Matrix: Air

OSHA PEL: (ceiling)

EGDN and/or NG	- 0.2 ppm (1 mg/m^3)
NG	- 0.2 ppm (2 mg/m^3) (skin notations apply)

Procedure: Samples are collected by drawing a known volume of air through large (100/50-mg sorbent beds) sampling tubes containing Tenax-GC resin. The samples are desorbed with methyl alcohol and analyzed by liquid chromatography with a Thermal Energy Analyzer or an ultraviolet HPLC detector.

Recommended air volume and sampling rate: 15 L at 1 L/min

	EGDN	NG
Reliable quantitation limits:	2.0 ppb (12 µg/m^3)	2.0 ppb (19 µg/m^3)
Standard error of estimate at the OSHA PEL: (Section 4.7)	6.9 %	8.1 %

ppb = parts per billion

Special requirement: The sampling pump must be certified by NIOSH and/or MSHA (formerly MESA) as intrinsically safe for use in coal mines.

Status of method: A sampling and analytical method that has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

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1. General discussion

1.1 Background

1.1.1 History

The purpose of this work was to evaluate air sampling and analytical procedures which permit the simultaneous determination of EGDN and NG. It is necessary to determine the analytes together because the OSHA standard regulates exposure to EGDN and/or NG.

Previously, air samples for EGDN and NG have been collected with midget impingers containing ethanol (Ref. 5.1), and with sampling tubes containing silica gel (Ref. 5.1), Chromosorb 102 porous polymer beads (Ref. 5.2), or Tenax-GC resin (Ref. 5.3). EGDN and NG have been determined by colorimetry (Ref. 5.1) and by gas chromatography (GC) using an electron capture detector (Ref. 5.3). EGDN and NG have also been analyzed by high performance liquid chromatography (HPLC) using various means of detection including electrochemical (Ref. 5.4), photoconductivity (Ref. 5.5), electron capture (Ref. 5.6), and chemiluminescence (Ref. 5.7).

Tenax-GC resin was selected for evaluation as a collection medium for EGDN and NG because of published recommendations and also because initial laboratory tests indicated that the material would perform satisfactorily. An HPLC separation procedure was chosen over GC methods because of the inherent thermal instability of the analytes (Ref. 5.7). The Thermal Energy Analyzer (TEA) detector was selected because it has been shown to have a sensitive and selective response to the analytes (Ref. 5.7.). An HPLC ultraviolet detector can be substituted for the TEA but this will result in less selectivity for the analytes.

The volatile nature of EGDN has been reported in the literature (Ref. 5.8) and it was shown, by vapor spiking experiments (Section 4.11), that the compound could be collected on Tenax-GC resin with high efficiency. NG, however, because of its low vapor pressure (Section 1.1.4), could exist as an aerosol. The collection efficiency of NG on Tenax-GC resin was investigated using a Model 3050 Bergland-Liu Vibrating Orifice Monodisperse Aerosol Generator to produce a test atmosphere which contained an aerosol component. The presence of an aerosol was indicated by a Model 3200 Thermo Systems Inc. Particle Mass Monitor.

Glass fiber filters, midget bubblers containing ethanol, small (20/10-mg sorbent beds) Tenax-GC resin tubes, and large (100/50-mg sorbent beds) Tenax-GC resin tubes were evaluated as sampling media for NG. The aerosol test atmospheres contained 1 mg/m^3 of NG. Glass fiber filters proved to be an ineffective sampling medium because of low retention efficiency for NG. The small Tenax-GC resin tubes gave slightly higher results than did the large Tenax-GC tubes when both were compared to the ethanol bubbler. (Section 4.10) The large Tenax-GC tube was selected because EGDN presented breakthrough and migration problems on the small size Tenax-GC tubes (Section 2.4). Because it is more convenient to use solid sorbents than bubblers, the Tenax-GC tubes were selected as the test sampling medium for EGDN and NG.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy).

The OSHA PEL for EGDN and/or NG is 0.2 ppm (1 mg/m^3) and the PEL for NG is 0.2 ppm (2 mg/m^3). Both of these standards are for ceiling concentrations. An EGDN footnote states that "An atmospheric concentration of not more than 0.02 ppm or personal protection may be necessary to avoid headache". (Ref. 5.9)

The effects of exposure to EGDN and NG are reported to be similar. Both compounds are potent vasodilating agents. Both chemicals are easily absorbed by inhalation and through the skin. The greatest exposure to workers who directly handle these compounds is probably through skin absorption (Ref. 5.10).

The effects of exposure to NG were first reported over 100 years ago. The most frequently reported symptoms of exposure to EGDN or NG include intense headaches, dizziness, nausea and decreases in systolic, diastolic and pulse blood pressure. These symptoms are a result of the rapid shift of blood volume from the central to the peripheral circulatory system, caused by the dilation of the blood vessels. After 2 to 4 days of occupational

exposure to NG or EGDN, most workers no longer experience symptoms because they have become tolerant to the vasodilatory effects of the compounds (Ref. 5.10).

Angina pectoris has been reported among workers who were exposed to EGDN and/or NG. In those affected, the angina usually occurred in periods away from work. Sudden deaths without any apparent cause have also been reported among these workers. The deaths, like the angina, occurred more frequently during periods away from work. In most cases, the workers who died suddenly had no symptoms other than angina during periods away from work. The deaths are thought to be related to compensatory vasoconstriction (tolerance) induced by repeated exposure to the substances. Vasoconstriction is thought to lead to spasms of the coronary arteries and then the related angina pectoris and sudden deaths (Ref. 5.10).

Historically, it has been noted that wives of dynamite workers often experienced heavy menstrual bleeding and had fewer children than did other women. It was also reported that children of dynamite workers were born prematurely and were cyanotic or were not as strong as other children (Ref. 5.10).

No evidence of teratogenic and embryotoxic effects were observed after the intraperitoneal administration of as much as 20 mg/kg NG to rats during gestation and lactation (Ref. 5.11).

The potential carcinogenicity of NG has been studied in rats and mice. In the rat study, NG was administered in a 0.03% solution as the drinking water. The investigators concluded that NG was not carcinogenic under the experimental conditions. The mice were exposed to time-weighted average concentrations of 214 mg/L in their drinking water. Increased incidence of adenomas of the pituitary gland was found in the female mice. It was concluded that NG was not carcinogenic under the experimental conditions because the tumors were benign. Even though the tumors were benign, their development indicates that exposure to NG can affect the pituitary gland (Ref. 5.10).

1.1.3. Potential workplace exposure

EGDN and NG are used with a mixture of sodium nitrate and an absorbent, often wood pulp, to produce dynamite. EGDN is added to lower the freezing point of the EGDN/NG mixture and is currently the major component. The EGDN/NG ratio is about 8/2 or 9/1. This is the only commercial use for EGDN. Because EGDN is more volatile than NG, there is usually more airborne EGDN than NG from the dynamite mixture. In 1976, about 250 million pounds of dynamite, containing 5 to 50% EGDN/NG, were produced by U.S. manufacturers (Ref. 5.10).

NG is used to make smokeless gun powder and rocket propellants. Single-base powders contain only nitrocellulose, double-base powders contain nitrocellulose and NG, and triple-base powders contain nitrocellulose, NG, and other combustible materials (Ref. 5.10).

NG is used for medical purposes, primarily to treat angina pectoris and other circulatory disorders (Ref. 5.10).

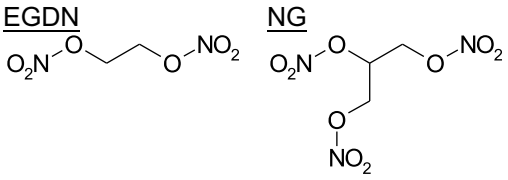
Therefore, occupations with potential exposure to EGDN and NG include chemical and explosives workers, drug makers, dynamite makers, miners, missile technicians, munitions loaders, munitions workers, NG workers, rocket fuel makers, shell fillers and smokeless-powder makers. NIOSH estimates that about 8,000 persons in the United States may be exposed to EGDN/NG mixtures or to NG alone (Ref. 5.10).

1.1.4 Physical properties (Ref. 5.10).

	EGDN	NG
CAS no.:	55-63-0	628-96-6
molecular weight:	152.06	227.09
specific gravity (20°C):	1.49	1.59
freezing point (°C):	-22.3	13.3
vapor pressure (mmHg at 20°C):	0.038 to 0.05	0.00012 to 0.011
explosion point (°C):	114	256
physical appearance:	yellowish liquid	pale yellow viscous liquid

EGDN is insoluble in water, but miscible with most organic solvents. NG is slightly soluble in water, soluble in alcohol and ether.

Structure:



A labile, rotational isomer of NG exists; however, it is converted to the stable form after 1 - 2 weeks of storage (Ref. 5.12).

Synonyms for EGDN, NG and EGDN/NG Mixtures (This data taken directly from Ref. 5.10)

Ethylene Glycol Dinitrate
1,2-Ethanediol dinitrate*; EGDN; Ethylene dinitrate; Ethylene nitrate; Glycol dinitrate; Nitroglycol.

Nitroglycerin
1,2,3-Propanetriol trinitrate*; Angibid; Anginine; Angiolingual; Angorin; Blasting gelatin; Blasting oil; Cardamist; Glondin; Glycerin trinitrate; Glycerol trinitrate; GTN; Lenitral; NG; Niglycon; Nitric acid triester of glycerol; Nitrine-TDC; Nitro-glycerin; Nitroglycerin, liquid undesensitized**; Nitroglycerine; Nitroglycerol; Nitroglyn; Nitrol; Nitrolan; Nitro-lent; Nitrolingual; Nitrolowe; Nitromel; Nitrong; Nitrorectal; Nitroretard; Nitro-Span; Nitrostat; Nitrozell retard; NTG; Nysconitrine; Perglottal; Propanetriol trinitrate; 1,2,3-Propanetriyl nitrate; S.N.G.; Soup; Trinalgon; Trinitrin; Trinitroglycerin; Trinitroglycerol; Vasoglyn.

EGDN/NG Mixtures
Nitroglycerine; Nitroglycerol; Nitroglycol; Nitroglyn; Nitrogranulogen; alpha-Nitroguanidine; beta-Nitroguanidine; 2-Nitro-2-heptene; 3-Nitro-2-heptene; 3-Nitro-3-heptene; 4-Nitro-3-heptene; 2-Nitro-2-hexene.

*International Union of Pure and Applied Chemistry (IUPAC) common name
**Department of Transportation (DOT)

1.2 Limit defining parameters (by TEA detector) (The analyte air concentrations listed throughout this method are based on an air volume of 15 L and a desorption volume of 2.0 mL).

1.2.1 Detection limits of the analytical procedure

The detection limits of the analytical procedure for EGDN and NG are 0.93 and 1.4 ng per injection respectively. These are the amounts of analytes which will give peaks whose heights are about 5 times the height of the baseline noise (Section 4.1).

1.2.2 Detection limits of the overall procedure

The detection limits of the overall procedure for EGDN and NG are 186 ng (2.0 ppb or 12 $\mu g/m^3$) and 280 ng (2.0 ppb or 19 $\mu g/m^3$) per sample respectively. These are the amounts of EGDN and NG spiked on the sampling device which allow recoveries of the analytes approximately equivalent to the detection limits of the analytical procedure (Section 4.2).

1.2.3 Reliable quantitation limits

The reliable quantitation limits for EGDN and NG are 186 ng (2.0 ppb or 12 $\mu g/m^3$) and 280 ng (2.0 ppb or 19 $\mu g/m^3$) per sample respectively. These are the smallest amounts of the analytes which can be quantitated within the requirements of a recovery of at least 75% and a precision (1.96 SD) of ±25% or better (Section 4.2).

The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

1.2.4 Sensitivity

The sensitivities of the analytical procedure over concentration ranges representing 0.5 to 2 times the OSHA PEL, based on the recommended air volume, are 16890 area units per µg/mL for EGDN and 14120 area units per µg/mL for NG. These are determined by the slope of the calibration curves (Section 4.4). The sensitivity will vary with the particular instrument used in the analysis.

1.2.5 Recovery

The recoveries of the analytes from samples used in a 17-day storage test remained above 93.1% for EGDN and 95.1% for NG when the samples were stored at ambient temperature (Section 4.7). The recovery of each analyte from the collection medium after storage must be 75% or greater.

1.2.6 Precision (analytical method only)

The pooled coefficients of variation obtained from replicate determinations of analytical standards at 0.5, 1, and 2 times the OSHA PEL were 0.068 for EGDN and 0.053 for NG (Section 4.3).

1.2.7 Precision (overall procedure)

The precisions at the 95% confidence level for samples used in the 17-day storage test were ±13.5% for EGDN and ±15.8% for NG (Section 4.7). These values each include an additional ±5% for sampling error. The overall procedure must provide results at the OSHA PEL that are ±25% or better at the 95% confidence level.

1.2.8 Reproducibility

Six vapor spiked (Section 4.11) samples and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 5 days of storage at ambient temperature. The average recoveries (corrected for desorption efficiency) were 103% for EGDN and 94.6% for NG. The standard deviations were 4.7% for EGDN and 6.1% for NG (Section 4.9).

1.3 Advantages

1.3.1 The sampling and analytical procedures are precise, reliable and convenient.

1.3.2 The air sampling device is commercially available.

1.4 Disadvantages

1.4.1 This method has not been field tested.

1.4.2 The TEA detector is quite expensive.

2. Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected by use of a personal sampling pump that can be calibrated to within ±5% of the recommended flow rate with the sampling device in line. The sampling pump must be certified by NIOSH and/or MSHA (formerly MESA) as intrinsically safe for use in coal mines.

2.1.2 Samples are collected on sampling tubes containing 35/60 mesh Tenax-GC resin. The tube has two sections of resin separated by a glass wool plug. The front (sampling) section contains 100 mg of resin and the back section 50 mg. The sections are held in place by glass wool plugs in an 8-mm o.d. × 100 mm long glass tube. SKC, Inc. Tenax-GC resin sampling tubes (catalog no. 226-35-03) were used in this evaluation.

2.2 Reagents

None required.

2.3 Technique

2.3.1 Break open both ends of the flame-sealed Tenax-GC sampling tubes so that the holes in the tube ends are at least one-half the i.d. of the sampling tube. Connect the sampling tube to the sampling pump with flexible tubing. The smaller section of the sampling tube is used as a backup and should be positioned nearest the sampling pump. Sampled air should not pass through any hose or tubing before entering the sampling tube.

2.3.2 Place the sampling tube vertically in the employee's breathing zone.

2.3.3 After sampling, seal the tubes immediately with plastic caps and wrap lengthwise with OSHA Form 21.

2.3.4 Submit at least one blank for each sample set. The blank should be handled in the same manner as samples, except no air is drawn through it.

2.3.5 Record sample volume (in liters of air) for each sample, along with any potential interferences.

2.3.6 Ship any bulk sample(s) in a separate container(s) from the air samples.

2.4 Retention efficiency

Retention efficiency studies were performed by first vapor spiking (Section 4.11) 74 µg of EGDN and 112 µg of NG on the recommended sampling device. An appropriate volume of humid air was pulled through the sampling tube and the device was analyzed. Retention efficiency was defined as the percent of an analyte remaining on the sampling section of the tube after air had been pulled through the device.

The retention efficiency for EGDN was found to be greater than 95% after 426 L of air at about 80% relative humidity and 22°C had been pulled through the vapor spiked tube. The retention efficiency for NG was determined to be 100% on the same sample (Section 4.5).

Because retention efficiencies for EGDN and NG remained high at large air volumes, the smaller size (20/10-mg sorbent beds) Tenax-GC sampling tubes were evaluated to determine analyte breakthrough. This study was performed by connecting the sampling sections of two tubes in series and then vapor spiking the first section with 37 µg of EGDN and 56 µg of NG. Humid air was pulled through the sampling train at 1 L/min, the second sample was removed at appropriate times and then subjected to analysis. The second tube was replaced with a fresh sampling tube and sampling continued. The first tube was also analyzed after the study was terminated.

Two breakthrough studies were performed using the smaller tubes and in both experiments, EGDN was observed in the second tube before 10 L of air had been sampled. The average 5% breakthrough air volume for EGDN was about 33 L. No breakthrough was observed for NG after 55 L had been sampled (Section 4.5).

About 19% of the EGDN spiked on small size Tenax-GC resin tubes was found to migrate from the sampling to the reference section after storage at ambient temperature for 7 days. No migration was observed for NG after storage at ambient temperature for 14 days (Section 4.5).

The 5% breakthrough air volume for EGDN using the small tubes was shown to be sufficiently high to permit sampling the recommended air volume; however, the rapid appearance of EGDN in the reference portion of the sampling tube indicated that the device may be subject to channeling. The migration and channeling problems were such that the small Tenax-GC resin tubes were eliminated from further consideration as sampling media for EGDN. Since it was desirable to determine EGDN and NG on the same sample, the small tubes were not evaluated for NG alone.

2.5 Desorption efficiency

The average desorption efficiencies for EGDN and NG from samples spiked at 0.5, 1 and 2 times the OSHA PEL, were 98.1% and 99.4% respectively (Section 4.6).

2.6 Recommended air volume and sampling rate

2.6.1 The recommended air volume is 15 L.

2.6.2 The recommended sampling rate is 1 L/min.

2.7 Interferences (sampling)

2.7.1 There are no known interferences to the sampling method.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precautions (sampling)

2.8.1 The air sampling pump must be certified by NIOSH and/or MSHA (formerly MESA) as intrinsically safe for use in coal mines.

2.8.2 Exercise due caution when breaking open the sampling tubes. Take measures to prevent cuts from the sharp ends of the broken glass tubes.

2.8.3 Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

2.8.4 Follow all safety practices that apply to the work area being sampled.

3. Analytical Procedure

3.1 Apparatus

3.1.1 An HPLC apparatus equipped with a TEA and/or UV detector. For this evaluation, a Waters Extended Wavelength Module/Waters Model 440 Absorbance Detector (214 nm) and a Thermo Electron Corporation Model 502 TEA (EAP) were used in series with a Waters M-6000A pump.

3.1.2 An HPLC column capable of resolving the analytes from each other and potential interferences. The column used in this work was a DuPont Zorbax CN, 4.6 mm × 25 cm.

3.1.3 An electronic integrator or other suitable means to measure peak area and record chromatograms. A Hewlett-Packard 3354 B/C Data System was used in this evaluation.

3.1.4 Vials, 4-mL, with Teflon-lined caps. Waters WISP vials were used in this evaluation.

3.1.5 Volumetric flasks, pipets and syringes for preparing standards, making dilutions and making injections.

3.1.6 Dewar flasks, for liquid nitrogen.

3.2 Reagents

3.2.1 HPLC grade methanol, isopropanol and isooctane.

3.2.2 Technical grade n-propanol or ethanol for cold traps.

3.2.3 Liquid nitrogen.

3.2.4 GC grade helium.

3.2.5 Medical grade oxygen.

3.2.6 Standard EGDN. A solution containing 1 g EGDN in 100 mL of ethanol was obtained from Atlas Powder Co., Tamqua, PA, for use in this evaluation.

3.2.7 Standard NG. A solution containing 1 g NG in 100 mL of dichloromethane was obtained from Hercules, Inc., Magna, UT, for use in this evaluation.

3.3 Standard preparation

3.3.1 Prepare stock standards by diluting known amounts of EGDN and NG with methanol.

3.3.2 Prepare an intermediate standard mixture using known volumes of the stock standard and diluting the mixture with methanol. The intermediate standard should contain 0.93 mg/mL EGDN and 1.4 mg/mL NG.

3.3.3 Prepare fresh working range standards daily by diluting the intermediate standard mixture with methanol. Standards representing the OSHA PEL were obtained by diluting the intermediate standard mixture 1 to 50 with methanol.

3.3.4 Prepare standards at concentrations other than the OSHA PEL in order to generate the calibration curve.

3.3.5 Store the standards in a freezer using well-sealed, dark containers.

3.4 Sample preparation

3.4.1 Transfer each section of the sample to separate vials. Place the front glass wool plug in the vial with the front section of the Tenax-GC tube. Discard the other glass wool plugs.

3.4.2 Add 2.0 mL of methanol to each vial.

3.4.3 Seal the vials with Teflon-lined caps and allow them to desorb for 1 h. Gently shake the vials several times during the desorption time.

3.5 Analysis

3.5.1

column:	DuPont Zorbax CN (4.6 mm × 25 cm)
solvent:	isooctane/isopropanol/methanol (90:6:4) (v/v)
flow rate:	1 mL/min
injection volume:	10 µL
retention time:	EGDN - 8.4 min
	NG - 11.5 min

3.5.2 UV detector

wavelength:	214 nm

3.5.3 TEA detector

HPLC pyrolyzer temp:	550°C
HPLC interface temp:	100°C
oxygen flow rate:	5 mL/min
helium flow rate:	30 mL/min (carrier gas)
cold trap temp:	-80°C (ethanol/water or n-propanol/water, with liquid nitrogen)

3.5.4 Chromatograms: Section 4.8

3.5.5 Detector response is measured with an electronic integrator or other suitable means.

3.5.6 Use an external standard method to prepare the calibration curve with at least three standard solutions of different concentrations. Prepare the calibration curve daily. program the integrator to report results in µg/mL.

3.5.7 Bracket sample concentrations with standards.

3.6 Interferences (analytical)

3.6.1 Any compound with the same general retention time as EGDN or NG and which also gives a detector response is a potential interference. Possible interferences should be reported to the laboratory with submitted samples by the industrial hygienist.

3.6.2 HPLC parameters (solvent composition, column, detector, etc.) may be changed to possibly circumvent interferences.

3.6.3 The only unequivocal means of structure designation is by GC/MS. It is recommended this procedure be used to confirm samples whenever possible.

3.7 Calculations

3.7.1 Results are obtained by use of a calibration curve. The detector response, for each standard, is plotted against its concentration in µg/mL and the best straight line through the data points is determined by linear regression.

3.7.2 The concentration, in µg/mL, for a particular sample is determined by comparing its detector response to the calibration curve. If any EGDN or NG is found on the backup section, it is added to the amount found on the front section. This total amount is then corrected by subtracting any interference found in the blank.

3.7.3 The EGDN and/or NG air concentration can be expressed using the following equations:

$$mg/m^3 \text{ EGDN or NG} = (A)(B)/(C)(D)$$

where A is µg/mL from Section 3.7.2
B is desorption volume (mL)
C is sample air volume (L)
D is desorption efficiency

$$ppm = (mg/m^3)(24.46)/\text{molecular weight}$$

where molecular weights = EGDN, 152.06; NG, 227.09
24.46 = molar volume of an ideal gas at 760 mmHg and 25°C

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and inhalation of all chemicals used.

3.8.2 Restrict the use of all chemicals to a fume hood whenever possible.

3.8.3 The handling of EGDN and NG, especially in more concentrated forms, may be hazardous because of the instability of the compounds.

3.8.4 Check to be sure that the TEA exhaust is connected to a fume hood.

3.8.5 Wear safety glasses and a lab coat in all laboratory areas.

4. Backup Data

4.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure was 0.93 ng for EGDN and 1.4 ng for NG. These amounts produce peaks whose heights were about 5 times the height of the baseline noise (Figure 4.1).

4.2 Detection limit of the overall procedure and reliable quantitation limit

The detection limit of the overall procedure was 186 ng/sample for EGDN and 280 ng/sample for NG. The equivalent air concentrations were 12 µg/m^3 (2.0 ppb) for EGDN and 19 µg/m^3 (2.0 ppb) for NG. The 10-µL injection size recommended in the analytical procedure was used in the determination of the detection limit of the overall procedure.

The reliable quantitation limits were determined by liquid spiking 6 large Tenax-GC resin tubes with 186 ng of EGDN and 280 ng of NG. The samples were desorbed with 2.0 mL of methanol and subjected to analysis. The 10 µL-injection volume recommended in the analytical procedure was used to determine the reliable quantitation limits.

Table 4.2
Reliable Quantitation Limit Data

sample no.	EGDN	NG
1	85.7	96.3
2	100	98.4
3	84.9	100
4	93.7	100
5	98.0	88.6
6	80.3	91.0
$\bar{x}$	90.4	95.7
SD	7.9	4.8
1.96SD	16	9.5

Since the recoveries were near 100% and also the precisions were better than ±25%, the detection limits of the overall procedure and the reliable quantitation limits were the same.

4.3 Precision (analytical method only)

The following data were obtained from multiple injections of analytical standards. The data are also presented graphically in Figures 4.3.1 and 4.3.2.

Table 4.3.1
Sensitivity and Precision Data for EGDN

× target concn µg/mL	0.5× 4.65	1.0× 9.3	2.0× 18.6
area counts	68505	161111	328323
	68152	148645	305681
	73602	142462	318531
	78557	139825	303060
	75178	132371	301729
	81354	127943	288860
$\bar{x}$	74224.7	142059.5	307697.3
SD	5300.7	11871.2	13847.9
~~CV~~	0.0714	0.0836	0.0450
CV	0.068		

Table 4.3.2
Sensitivity and Precision Data for NG

× target concn µg/mL	0.5× 7.0	1.0× 14.0	2.0× 28.0
area counts	135816	226043	405955
	126207	230653	417600
	128996	242265	419134
	122751	244586	439648
	125092	258245	428030
	117101	270668	450057
$\bar{x}$	125993.8	245410.0	426737.3
SD	6260.1	16769.8	16033.5
~~CV~~	0.0497	0.0683	0.0376
CV	0.053		

4.4 Sensitivity

The sensitivity for EGDN was 16890 area counts per µg/mL and that for NG was 14120 area counts per µg/mL. These values were determined from Figures 4.3.1 and 4.3.2.

4.5 Retention efficiency data

Retention efficiency studies were performed by vapor spiking (Section 4.11) 74 µg of EGDN and 112 µg of NG on each of several large Tenax-GC resin (100/50 mg sorbent beds) tubes. Humid air (about 80% RH and 22°C) was drawn through the tubes at 1 L/min. The tubes were then subjected to analysis and the results are presented in Table 4.5.1.

Table 4.5.1
Retention Efficiency

air volume L	EDGN recovery front sec., %	EDGN recovery back sec., %	NG recovery front sec., %	NG recovery back sec., %
171.3	100	ND	100	Trace
248.1	100	Trace	100	ND
305.0	100	Trace	100	ND
333.0	99.6	0.4	100	ND
370.0	98.6	1.4	100	ND
383.0	98.5	1.5	100	ND
397.0	98.1	1.9	100	ND
426.0	97.0	3.0	100	ND

Two breakthrough experiments were performed with small Tenax-GC resin (20/10-mg sorbent beds) tubes. The studies were conducted by connecting the sampling sections of two tubes in series and then vapor spiking the first section with 37 µg of EGDN and 56 µg of NG. Humid air (at about 80% RH and 22°C) was drawn through the sampling train at 1 L/min. The second tube was removed at appropriate intervals and subjected to analysis. The second tube was replaced with a fresh sampling tube and sampling continued. The first tube was also analyzed after the study was terminated. No breakthrough was observed for NG. The results of the two breakthrough studies are presented in Table 4.5.2.

Table 4.5.2
Breakthrough Studies

study one		study two	
air volume L	cumulative EDGN breakthrough, %	air volume L	cumulative EDGN breakthrough, %
4.5	0.7	9.2	1.4
13.6	1.7	18.4	3.2
22.7	3.1	27.6	5.3
31.8	4.3	36.8	6.3
40.9	5.1	46.0	6.9
50.0	7.8	55.2	9.2

All of the vapor spiked NG was recovered from the first tube in both studies. The EGDN recovery for the first tube in Study One was 92.2% and that for the first tube in Study Two was 90.8%.

A migration study was performed with small Tenax-GC tubes to determine if either analyte would move from the sampling to the back section of the tubes. The device was liquid spiked with 19 µg of EGDN and 28 µg of NG and then stored at ambient temperature. No migration was observed for NG; however, considerable migration and some loss was noted for EGDN

Table 4.5.3
Migration Study

day	sampling section recovery, %		back section recovery, %	
	EGDN	NG	EGDN	NG
0	100	96.3	–	–
7	68.2	99.2	19.2	–
14	57.6	93.6	19.2	--

4.6 Desorption efficiency

The following data represent the analysis of large Tenax-GC tubes liquid spiked with EGDN and NG at 0.5, 1, and 2 times the OSHA PEL.

Table 4.6
Desorption efficiency

× PEL	0.5×		1×		2×	
analyte	EGDN	NG	EGDN	NG	EGDN	NG
µg/sample	9.3	14.0	18.6	28.0	37.2	56.0
desorption	102	102	99.5	103	92.8	101
efficiency, %	105	104	97.1	98.9	97.9	103
	102	102	96.3	94.2	97.1	101
	96.9	98.9	97.7	93.7	98.4	101
	95.4	97.7	96.3	93.8	95.9	99.2
–	98.5	98.3	105	100	93.1	98.9
X	100	100	98.6	97.3	95.9	101

The average desorption efficiency for EGDN was 98.1% and that for NG was 99.4%.

4.7 Storage data

The data in Table 4.7.1 represent the effects of storage at ambient (21 to 26°C) and reduced (-20°C) temperature on large Tenax-GC tubes vapor spiked (Section 4.11) with 18.6 µg of EGDN and 28.0 µg of NG. The results are not corrected for desorption efficiency. The data are also presented graphically in Figures 4.7.1 - 4.7.4.

Table 4.7.1.
Storage Tests of EGDN

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	98.0	97.3	94.1	101	101	102
3	100	95.4	99.8	97.4	93.9	92.9
7	96.3	91.0	95.5	91.9	104	98.0
10	96.3	94.8	92.5	94.4	93.3	95.9
14	87.1	88.4	94.1	91.1	89.2	96.2
17	98.5	95.8	95.0	106	95.6	101

Table 4.7.2.
Storage Test of NG

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	99.7	95.9	95.2	103	94.0	103
3	99.9	93.0	93.3	97.1	93.1	93.7
7	96.5	92.2	97.7	89.0	106	100
10	100	95.3	96.1	93.9	93.6	99.0
14	85.9	90.0	93.4	90.1	89.3	95.7
17	101	95.5	98.6	109	92.1	106

The back sections of the samples used in the ambient temperature storage study were analyzed on days 10, 14, and 17 to determine if migration from the sampling sections had occurred. No EGDN or NG was found in the back sections.

4.8 Chromatograms

4.8.1 HPLC/UV Chromatogram

Figure 4.8.1 is a chromatogram obtained by the injection of 10 µL of a standard mixture containing the analytes. The HPLC column was 4.6 mm × 25 cm DuPont Zorbax CN. The mobile phase was 90% isooctane, 6% isopropanol, and 4% methanol. The flow rate was 1 mL/min. The UV detector wavelength was 214 nm.

4.8.2 HPLC/TEA Chromatogram

Figure 4.8.2 is a chromatogram obtained by the injection of 10 µL of a standard mixture containing the analytes. In this case, the TEA was connected in series with a UV detector. The HPLC column and mobile phase was the same as used in Figure 4.8.1.

4.9 Reproducibility study

Six vapor spiked large Tenax-GC tubes and a draft copy of this evaluation were given to a chemist unassociated with this work. The samples were analyzed after five days of storage at ambient temperature. The results of the study are presented in Table 4.9.1. The results are corrected for desorption efficiency.

Table 4.9
Reproducibility Study

amount vapor spiked, µg	EGDN 18.6	NG 28.0
recovery, %	103	97.5
	103	93.9
	100	85.4
	103	100
	98.3	89.6
$\bar{x}$	112	101
X, %	103	94.6
SD, %	4.7	6.1

4.10 Aerosol data

NG aerosols were generated by means of a Model 3050 Berland-Liu Vibrating Orifice Monodisperse Aerosol Generator. The frequency of the orifice was set at 7.5 KHz. An isopropanol solution containing 0.25 mg/mL of NG was metered into the system at 0.20 mL/min with a syringe pump. The resulting stream was diluted with air (0.05 m^3/min) to produce a 2.4-µm diameter monodisperse aerosol containing 1 mg/m^3 of NG. The aerosol was sampled by means of ports connected to a sampling chamber. Several experimental runs were performed to compare the collection efficiencies of glass fiber filters, midget bubblers containing ethanol, small Tenax-GC tubes and large Tenax-GC tubes. The air sample volumes were about 15 L and the sampling rate was 1 L/min.

NG aerosol samples were collected using small Tenax-GC tubes to determine the location of the NG in the sampling tube. All the NG was found on the front sorbent section. No NG was found on the front glass wool plug, on the center polyurethane plug, on the reference sorbent section, on the back polyurethane plug, or on the glass tubing itself.

In another experiment, 3 glass fiber filters and 3 small Tenax-GC resin tubes were used to sample the same NG aerosol. The recovery of NG from the glass fiber filters was only 38% of that recovered from the Tenax-GC tubes. A retention efficiency experiment was later performed to determine if the filters could retain NG. It was found that only 79% of the NG spiked on glass fiber filters was retained after 14 L of air had been drawn through the filter cassette. The aerosol and

retention efficiency experiments together indicate that the generated test aerosols probably have a vapor component which was not collected on the filters.

The bubbler results were taken as the generation efficiency of the aerosol apparatus because no NG was detected in backup bubblers or backup Tenax-GC tubes. The generation efficiency was 75%.

The data in Table 4.10. are the results of 15 aerosol runs. Each data point represents the average of at least two separate air samples taken using identical sampling devices. The bubblers each contained 15 mL of ethanol as the trapping solution. Corrections for bubbler volume and desorption efficiency were made in the reported results. The results for the Tenax-GC tubes are expressed as ratios relative to the bubbler results.

Table 4.10
Summary of NG Aerosol Results

run no.	bubbler, mg/m^3	(ratio) large Tenex, mg/m^3 bubbler, mg/m^3	(ratio) small Tenex, mg/m^3 bubbler, mg/m^3
1	0.77	–	0.91
2	0.77	–	1.1
3	0.78	–	0.96
4	0.78	–	0.73
5	0.81	0.79	–
6	0.78	–	1.0
7	0.79	0.99	1.0
8	0.76	0.95	0.95
9	0.80	0.82	0.92
10	0.78	0.90	0.97
11	0.74	0.99	1.1
12	0.68	0.97	1.2
13	0.81	0.93	1.1
14	0.56	0.95	0.99
15	0.69	0.92	1.0
X	0.75	0.92	1.0
SD	0.066	0.068	0.11
CV	0.087	0.074	0.11

The data in Table 4.10 indicate that the small Tenax-GC tubes give slightly higher results than do the large tubes. The significance of the difference between the ratio means of the two adsorbent tube collection methods was tested using a two-tailed Student-t distribution. This is a test of hypothesis regarding the difference between the means of two normal populations having unequal and unknown variances when the samples are small and of different size. The critical region, at the 95% confidence level, was determined to be T' greater than 2.07 and less than -2.07. The calculated t' statistic was 2.12. These computations show that a small but significant difference between the two collection methods exists. The large tubes were selected in preference to the small tubes because of their higher retention efficiency and lack of migration problems for EGDN.

4.11. Vapor spiking technique

The Tenax-GC tubes were vapor spiked with EGDN and NG by first injecting a liquid mixture of the analyte on a 1-cm plug of silanized glass wool contained in an 8-mm i.d. × 40 mm long silane treated glass tube. The spiked tube was placed in front of the Tenax-GC tube and then air, at about 80% relative humidity and 22°C, was drawn through the sampling train. The analytes were vaporized from the glass wool and collected on the Tenax-GC tube. The vaporization process was determined to be complete after 25 L of air had passed through the sampling train.

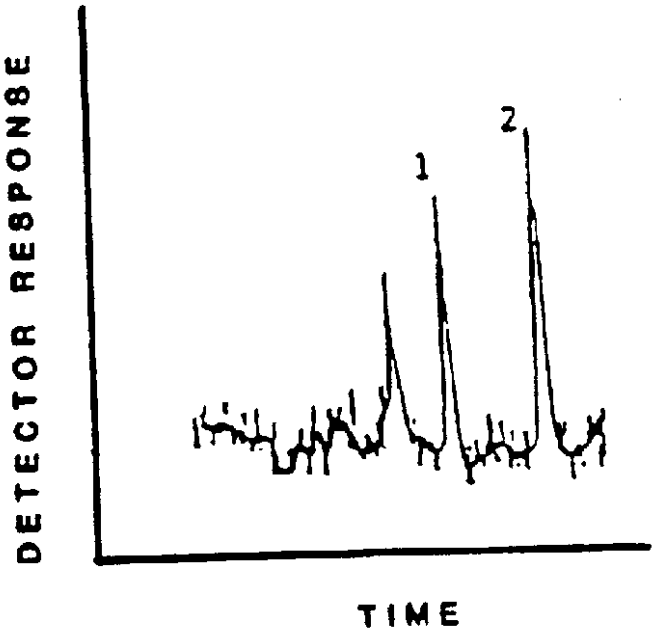


Figure 4.1. Detection limits of the analytical procedure. Peak identification was as follows: 1, EGDN; 2, NG.

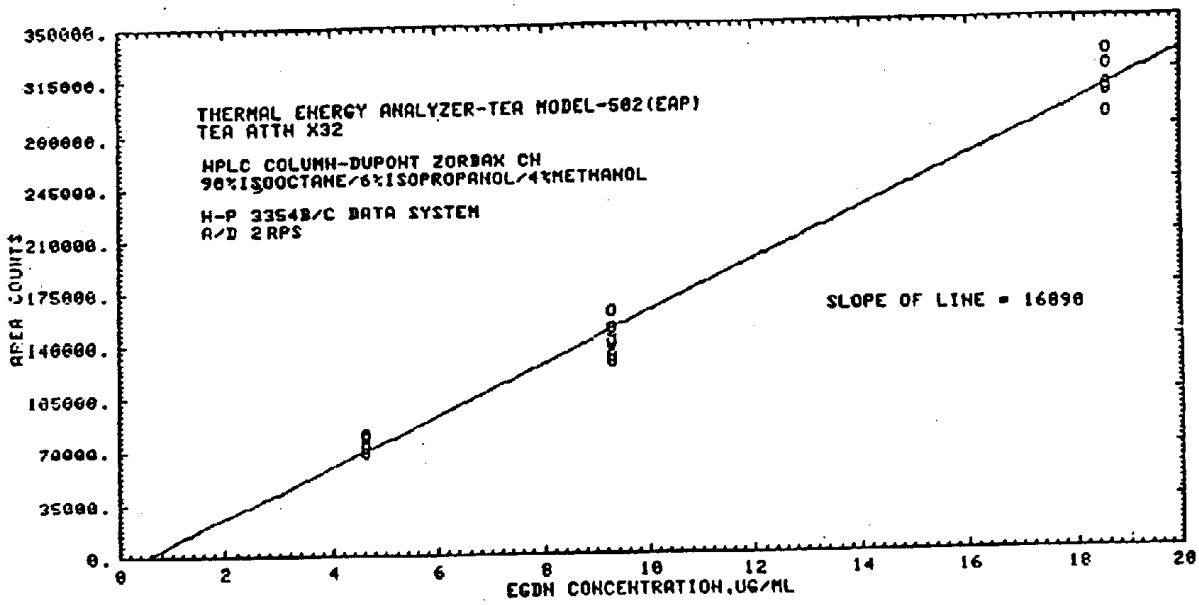


Figure 4.3.1. Calibration curve for EGDN.

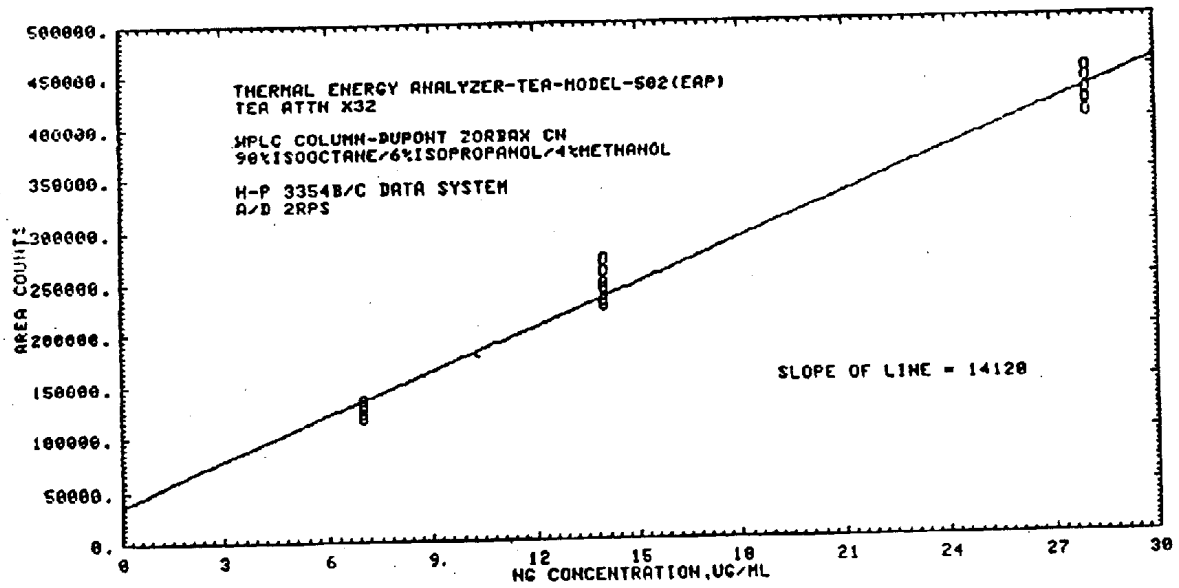


Figure 4.3.2. Calibration curve for NG.

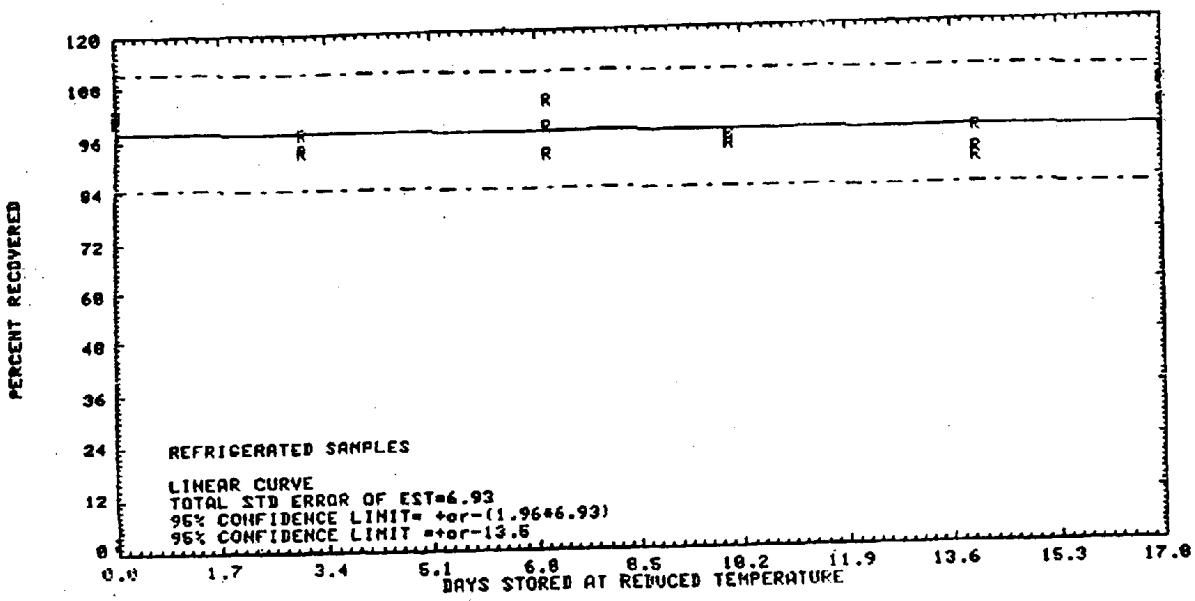


Figure 4.7.1. Refrigerated temperature storage test for EGDN.

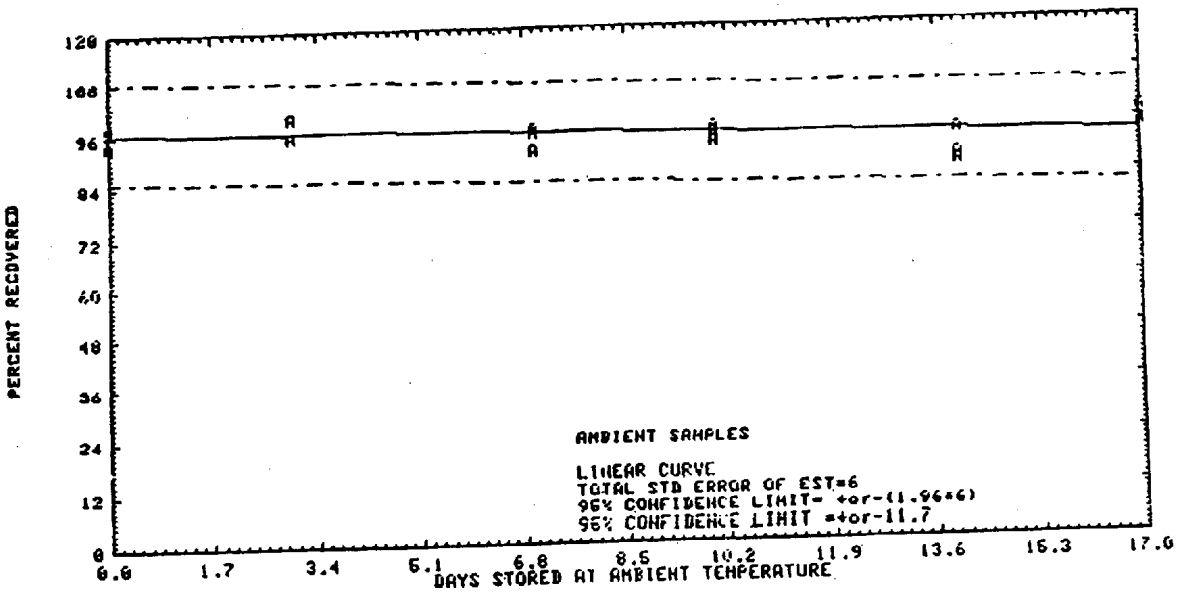


Figure 4.7.2. Ambient temperature storage test for EGDN.

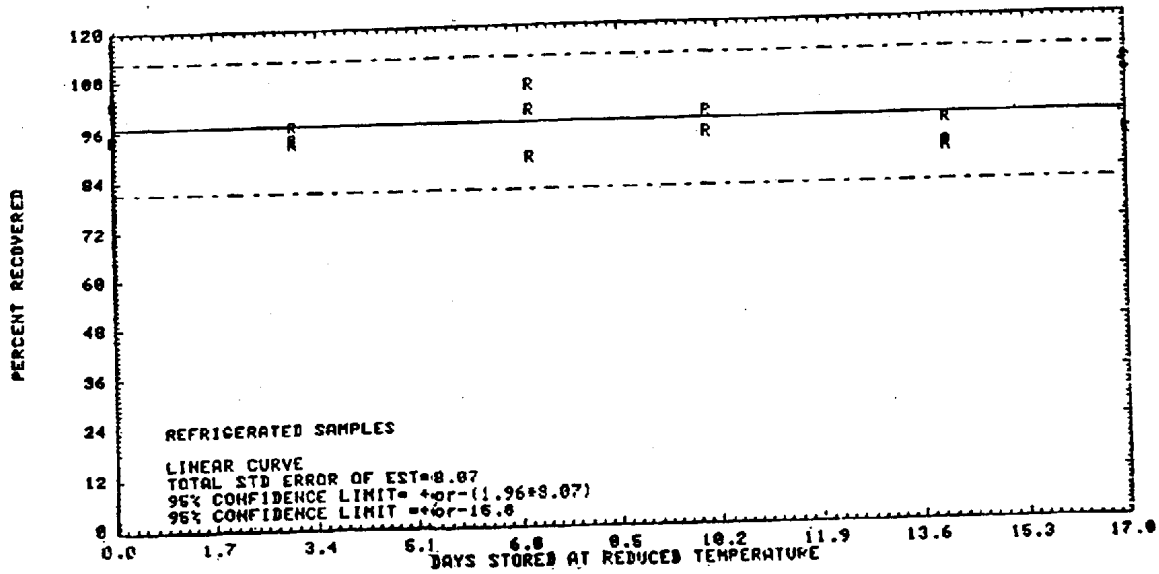


Figure 4.7.3. Refrigerated temperature storage test for NG.

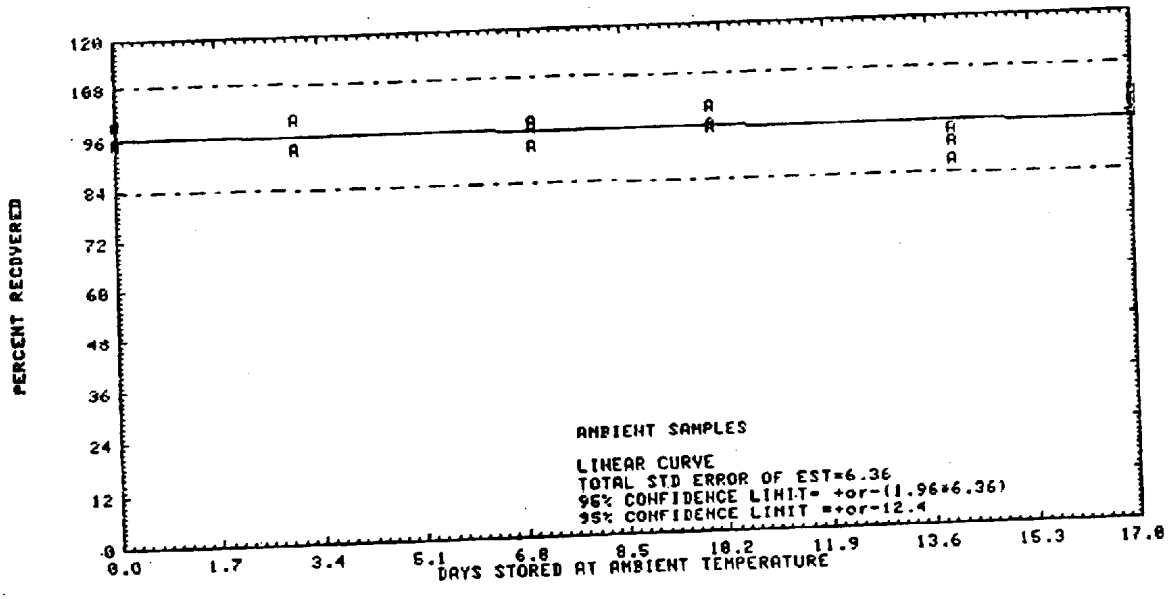


Figure 4.7.4. Ambient temperature storage test for NG.

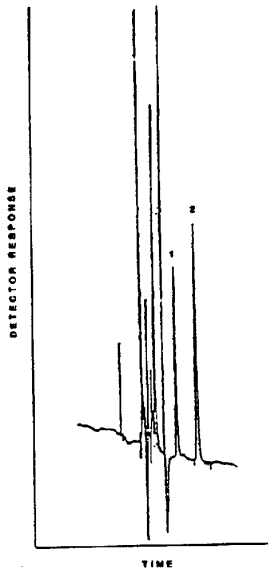


Figure 4.8.1. HPLC/UV chromatogram. Peak identification was as follows: 1, EGDN; 2, NG.

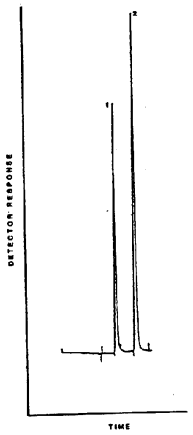


Figure 4.8.2. HPLC/TEA chromatogram. Peak identification was as follows: 1, EGDN; 2, NG.

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