

#### IV. ENVIRONMENTAL DATA

##### Sampling and Analytical Methods

Safety is an issue in considering appropriate sampling and analytical methods for monitoring airborne NG and EGDN because these substances and materials made from them are highly explosive [6]. Early battery-operated sampling pumps were considered potential detonation hazards because of their electrical wiring and exposed metal surfaces, and such pumps have generally been avoided in the explosives industry [11,13,100]. An "ejector" (aspirator) sampling unit using an aerosol can containing a liquid fluorocarbon propellant was a feasible alternative to pumps [101]. This ejector apparatus was especially effective for portable sampling units and was used in the past in the NG and EGDN industry [13]. The propellant released under pressure from the aerosol can resulted in aspiration through the venturi. A calibrated rotometer and flow-adjusting valve were integral parts of the commercially available units. Even though a constant-flow device was available to maintain and control the flowrate at a previously set value for the sampling period, there was no easy way to determine how much propellant remained in the can [102]. These units could not be easily attached to the workers to be sampled, and a technician was often required to continuously operate the sampling unit; this posed a problem when long-term samples were required. These "ejector" sampling units are no longer commercially available.

Battery-operated personal sampling pumps that can be used safely to monitor concentrations of airborne NG and EGDN are now available and have been used in the industrial environment [13,102,103]. The US Department of

the Interior and the US Department of Health, Education, and Welfare issued joint regulations for the approval of personal sampler units for evaluating exposure to coal mine dust. These regulations appeared in the Federal Register (35 FR 4356) on March 1, 1970, and were incorporated into the Code of Federal Regulations as Title 30 CFR Part 74 under authority of the Federal Coal Mine Health and Safety Act of 1969 [104]. These regulations state that NIOSH and MESA, through rigid testing programs, certify personal sampling pumps that meet the stated criteria to be intrinsically safe for use in coal mines. These pumps do not pose detonation hazards because they can be run for extended periods of time in atmospheres of methane gas at concentrations optimal for explosion. NIOSH considers pumps meeting this certification to be safe for sampling concentrations of airborne NG and EGDN if all possible safety precautions are taken during sampling. The most recent NIOSH-validated sampling method for NG and EGDN recommends a personal sampling pump [105].

Two methods have been the most effective ones examined by NIOSH for collecting samples of airborne NG and EGDN. One involves the use of midget impingers or bubblers [11,13,35,100,103,106], and the other is based on the use of a Tenax-GC resin adsorption tube [103,107,108]. Various collection liquids have been used in the midget impingers and bubblers, such as alcohol [11,100,103], propylene glycol [35], an aqueous solution of 0.3% potassium chloride [13], and distilled water [13,106]. Einert [11] reported "very nearly 100%" collection efficiency using 95% alcohol at a sampling rate of 0.5-1.0 liter/minute. In potentially explosive environments, the glass impinger units have been enclosed in cardboard containers with cellophane windows; connections are made with short Tygon

tubing that protrudes from the cardboard container [11]. These measures are necessary because the static electricity that may be generated on exposed glass surfaces may pose a possible detonation hazard. The more recently developed sampling method [103,105,107,108] involves the use of Tenax-GC resin. A tube similar to the commonly used charcoal tube is filled with the resin, which serves as the adsorbing medium for both NG and EGDN. This sampling technique involves no liquids and the equipment is small, facilitating its use in the field for the collection of personal samples. Tenax-GC resin has been shown to be effective as a collection medium for NG and EGDN [103,107], and NIOSH therefore recommends its use. The recommended sampling method, using a Tenax GC tube and a personal sampling pump, is described in detail in Appendix I.

EGDN and NG have been estimated using infrared [109,110] and visible [11,13,35] spectrophotometry, thin-layer chromatography [111], polarography [112], and titrimetry [113,114]. A colorimetric technique using spectrophotometry has been the one most frequently used for the analysis of air samples collected in the liquid in midget impingers [11,13,35]. The sample is first hydrolyzed with alcoholic potassium hydroxide [11]. The nitrites formed are determined by diazotizing sulfanilic acid and coupling the product with 1-naphthylamine, which gives a reddish-purple colored product. The concentration of nitrites is then read at 525  $\mu\text{m}$ . Using this method, Einert et al [11] reported that as little as 0.3 mg/cu m of NG or EGDN could be determined using a 10-liter air sample. The colorimetric technique is convenient, inexpensive, and relatively simple, but it is not specific for NG and EGDN [100]. Other nitrites and nitrates present in the sample will interfere in the analysis. In an explosives plant where

dynamite is manufactured, other nitro and nitrate compounds, such as nitric acid, ammonium nitrate, sodium nitrate, and nitrocellulose, are generally present [13].

Direct-reading colorimetric tubes are available [115] that make "on-the-spot" monitoring of NG and EGDN feasible. These tubes, when properly calibrated and used in ways that take their performance characteristics and limitations into account, can provide approximate measurements of NG at concentrations as low as 1.5 ppm (13.9 mg/cu m) or of EGDN at concentrations as low as 0.25 ppm (1.55 mg/cu m). The disadvantages of this method are that it is not specific for any particular nitro-containing compound and that its sensitivity varies widely for different compounds, allowing it to provide only rough estimates of concentrations of total nitrates in mixed exposure situations.

The US Navy has developed a field instrument with colorimetric detector tubes that may be useful for monitoring airborne NG and EGDN [116]. The instrument, called an "Otto Fuel Detector, MK-15," was designed for monitoring propylene glycol dinitrate (PGDN), the major component of several torpedo propellants. It operates on the principle of controlled combustion of nitrated glycol compounds followed by colorimetric determination of the liberated NO<sub>2</sub>. It is compact and lightweight (14 pounds), has a 5-minute minimum response time, and has a tested sensitivity of 0.2 ppm (1.37 mg/cu m) for PGDN. However, the method is not specific in mixed atmospheres, and the detector tubes have also proved quite variable in response. Furthermore, the Otto Fuel Detector has not been tested specifically with NG and EGDN, and its safety for use in potentially explosive atmospheres is questionable at this time.

Both volumetric and potentiometric titrimetry are common techniques for measuring NG concentrations in pharmaceutical preparations [113,114]. The sensitivities of these methods were not reported and, since any alkaline chemicals present in the sample can interfere, these methods may not be suitable for analysis of air samples. Infrared techniques are used to measure NG in drugs [110], and they are also useful in estimating NG or EGDN in explosives [109]. The infrared spectrum from 2 to 15  $\mu\text{m}$  shows nitrate absorption bands. Other nitrates commonly found in the workplace also absorb in this range, interfering with the accuracy of the method.

Determination of fluorescence has been recommended for qualitative spot tests on explosives [117]. Drops of solutions suspected of containing NG or EGDN are placed on filter papers and dried. These stains are observed in ultraviolet light both before and after the addition of a drop of diphenylamine. For NG and EGDN, the dried spot appears greasy and fluoresces yellow to blue-green after addition of diphenylamine. This method is rapid and may be useful to check for the presence of NG or EGDN. Thin layer chromatography [111] has also been recommended for separation and qualitative identification of various explosive powder components, including NG and EGDN.

Polarography is another technique used to analyze propellants [112]. In this method, a current-voltage curve is recorded by a dropping mercury cathode and a calomel anode in an electrolytic cell. The current produced is proportional to the concentration of the reducible substance, in this case NG. Samples can be analyzed quantitatively by comparing the current-voltage curves obtained with their solutions with calibration curves prepared with standard concentrations.

Gas chromatography has been used to analyze NG and EGDN in propellants [118], in blood [119], and in air samples [103,105,107]. Using an electron-capture detector, the minimum amount of EGDN detectable in a single injection was "substantially smaller than 0.25 ng" [105]. The minimum amount of NG detectable in a single injection was "smaller than 2.5 ng" [105]. In a 10-liter air sample, these sensitivities would permit the detection of 0.01 mg/cu m EGDN and 0.10 mg/cu m NG.

The US Navy has also developed a method of using gas chromatography for monitoring PGDN that should be applicable to other nitrated glycols [120]. A 1-ml gas syringe is used to collect a short grab sample that is then injected directly into a portable field gas chromatograph with an electron-capture detector. The method is sensitive to PGDN at concentrations as low as 0.05 mg/cu m, but it has not been tested with NG and EGDN. The safety of this instrument must also be determined before it is used in a potentially explosive atmosphere, but it could be sited in a safe area and have collected air samples carried to it.

Gas chromatography with an electron-capture detector has been validated by NIOSH [105,107] for estimation of both NG and EGDN. This is a convenient method for analyzing air samples collected on Tenax-GC resin, and it offers the advantage of easy separation and quantitative determination of both NG and EGDN. The recommended analytical method, using gas chromatography, is described in Appendix I. This method is adapted from NIOSH Method No. P&CAM 203 [105] which is a Class E method, defined by NIOSH as "Proposed: A new, unproved, or suggested method not previously used by industrial hygiene analysts but which gives promise of being suitable for the determination of a given substance."

### Environmental Concentrations

Most of the environmental level data available for NG and EGDN are from dynamite plants where both nitroesters are manufactured and used to produce explosives [11,13,100,103,106,121]. In 1976, Barrett et al [103] reported data on area sampling for NG and EGDN in a dynamite manufacturing plant. Samples were collected using personal sampling pumps with Tenax-GC or with single bubblers containing 10 ml of ethanol. The flowrate for the bubblers was 1.0 liter/minute, but the sampling flowrate for the sorbent tube method was not given. The sampling period was approximately 30 minutes, and all samples were analyzed by gas chromatography with an electron-capture detector. The results are shown in Table IV-1. The purpose of this survey was to field test the method and to check for possible interferences.

Hercules Incorporated submitted data from area monitoring at its plant manufacturing NG:EGDN and dynamite at Carthage, Missouri, from 1975 to 1977 and provided a description of the sampling and analytical methods used [13]. Area monitoring was conducted with a calibrated, battery-operated pump and a midget impinger containing an aqueous solution of 0.3% potassium chloride. The absorbed nitrate was then determined colorimetrically with diphenylbenzidine reagent. The sampling time was 2 minutes, and 2-4 samples were taken at different sites within 17 buildings. Actual exposure concentrations were expressed as NG:EGDN and ranged from 0.016 to 0.20 ppm. Assuming, on the basis of their relative vapor pressures, that these figures were for essentially 100% EGDN, the concentrations ranged from 0.1 to 1.24 mg/cu m.

TABLE IV-1

CONCENTRATIONS OF EGDN AND NG IN AREA  
AIR SAMPLES AT A DYNAMITE MANUFACTURING PLANT

Sampling Location	Sampling System	Volume Sampled (liters)	Concentration (mg/cu m)	
			EGDN	NG
<u>Mixing shed</u>				
Dope screen	Tenax GC	8.90	0.51	0.02
Oil drop	"	8.10	0.57	0.01
Distributor	Bubbler	48.00	0.43	-
"	Tenax GC	7.81	0.77	0.05
Oil drop	Bubbler	25.00	0.37	-
Distributor	Tenax GC	11.00	1.10	0.04
<u>Outdoors</u>				
Air intake	Tenax GC	7.61	0.01	0.007
"	Bubbler	30.00	0.01	-
<u>Slurry shed</u>				
Ground level	Bubbler	35.00	0.06	-
"	Tenax GC	9.01	0.12	0.007
Floor 2 level	"	8.62	0.04	0.005

Adapted from Barrett et al [103]

In 1959, Yee et al [100] reported atmospheric concentrations of NG and EGDN in an explosives plant manufacturing dynamite. Air samples were collected for 30 minutes in alcohol in a midget impinger and were analyzed colorimetrically. Since oxides of nitrogen, ammonium nitrate, sodium nitrate, and nitrocellulose, which interfere in the analysis, were present in the factory, the results were calculated as total nitrate as well as NG and EGDN. The average concentration of nitrate ranged from 0.03 ppm in the



maintenance building to 0.63 ppm in the dynamite mix house. The corresponding concentrations of NG were 0.02 ppm (0.19 mg/cu m) and 0.38 ppm (3.52 mg/cu m) and of EGDN were 0.02 ppm (0.12 mg/cu m) and 0.31 ppm (1.92 mg/cu m). Analysis of exposure by occupations indicated that the dynamite mixer had the highest exposure, 0.63 ppm as nitrate. Atmospheric concentrations measured in January and March were lower than those measured in August. The authors attributed these findings to the fact that vapor pressures increase with temperature.

In April 1964, the Pennsylvania Department of Health conducted a survey of an explosives manufacturing plant [106]. Breathing-zone air samples were collected in distilled water with midget impingers. The analytical technique employed was not specified, but the concentrations of EGDN and NG combined were reported in terms of EGDN. These ranged from "none detected" (<0.006 mg/cu m) in the nitration building and certain areas of several other buildings to 0.06 mg/cu m in the cartridge-packing and mix houses. Details of the sampling procedure, such as sampling time and flowrate, were not reported.

In 1967, Cavagna et al [121] reported a comparison of concentrations of airborne NG and EGDN in an Italian dynamite factory during 1955 and 1965. The results were reported as EGDN. The average concentration in the packing house in 1955 was 0.30 mg/cu m, with a peak concentration of 0.40 mg/cu m. In the same location, the 1965 average value was 0.37 mg/cu m and the peak concentration was 0.55 mg/cu m. The highest average concentrations recorded were in the mix house: 1.70 mg/cu m in 1955 and 1.45 mg/cu m in 1965. However, the highest recorded peak concentrations occurred in the cartridge-filling house: 3.30 mg/cu m in 1955 and 1.65

mg/cu m in 1965. Although there was not much reduction in the concentrations in the air between 1955 and 1965, the authors noted that improvement in the plant process, automation, and technical control of air contamination had enabled the plant to increase the percentage of EGDN in the dynamite without increasing the EGDN concentration in the air.

As discussed on Effects on Humans in Chapter III, Trainor and Jones [49] attempted to correlate the incidence of headaches in explosives magazine workers with the concentrations of airborne NG and EGDN. Air was sampled with an impinger charged with ethyl alcohol, the solution being analyzed colorimetrically for nitrate with phenol disulfonic acid. The concentrations, expressed as NG, ranged from 0.10 to 0.53 mg/cu m, with a mean of 0.36 mg/cu m.

In 1963, Einert et al [11] reported concentrations of airborne NG and EGDN (calculated as EGDN) in an explosives manufacturing plant. The samples were collected in 95% alcohol in a fritted glass bubbler and analyzed colorimetrically. At the hand-pack house, the concentrations ranged from 0.03 mg/cu m at a crimper operation to 4.35 mg/cu m at the bag closing and taping operation.

The Army Environmental Hygiene Agency [35] reported concentrations of airborne NG in 10 rocket propellant manufacturing installations where EGDN was not used. Most of the NG concentrations were between undetected and 0.3 ppm (2.8 mg/cu m). These figures were based on 10-minute area and breathing zone samples segregated by the general process in which they were engaged, although the exact survey locations and dates were not reported. Air was sampled at a flowrate of 0.1 cfm (2.8 liters/minute) with glass midget impingers containing 10 ml of propylene glycol and were analyzed by

colorimetric determination of the nitrate group [64]. Table IV-2 contains the airborne NG concentrations (range and average) for each installation, the number of processes sampled, the number of samples taken, and the maximum number of workers involved in the sampled processes at each installation.

TABLE IV-2

CONCENTRATIONS OF NG IN AIR IN 10 NG  
AND ROCKET PROPELLANT MANUFACTURING INSTALLATIONS

Installation	Concentration Range* (mg/cu m)	Average Concentration (mg/cu m)	No. of Processes	No. of Samples	Maximum No. of Exposed Workers
A	0-1.30	0.28	23	62	85
B	0-1.94	0.46	11	27	34
C	0-1.48	0.28	12	35	71
D	0-1.30	0.19	4	11	37
E	0-2.50	0.46	10	28	58
F	0-0.09	<0.09	2	4	5
G	-	-	6	-	44
H	1.30-2.87	1.85	6	8	120
I	0.19-1.94	0.93	4	7	28
J	0-5.56	0.46	5	18	-
K	0-12.5	1.85	27	118	-

\*A concentration of 0 means that the analytical method used was unable to detect the chemical

Adapted from reference 35

Installation K had by far the highest concentrations (12.5 mg/cu m); the reasons for this finding are not apparent [35]. Many of the workers in these installations were exposed at these concentrations only sporadically and for brief periods, but many other workers were exposed continuously for 7-8 hours/day. For the great majority of these processes, no special ventilation systems were used. Workers in about half the processes also had skin contact with NG, and only about half of these workers used skin protection in the form of cotton, neoprene, or leather gloves.

#### Control of Exposure

Because of the severe health and explosive hazards of NG and EGDN, engineering controls must be instituted to control vapor and dust exposure in areas where the two substances are manufactured and where they are used to manufacture other materials. Control of exposure can best be accomplished by closed systems, but enclosure of materials, processes, and operations is effective as a control measure only when the integrity of the system can be maintained. Therefore, such systems must be inspected frequently for breakdown and promptly repaired. Special attention should be given to the condition of seals and joints, access ports, and similar places. Similarly, points of probable wear or damage should be inspected regularly. Local exhaust ventilation may be used in conjunction with the closed system to safeguard personnel involved in any part of the operation that requires them to handle directly NG, EGDN, or materials containing these compounds. Because of the toxic and explosive nature of these substances, effective nonsparking local exhaust ventilation systems must be installed wherever total enclosure is not practical. The principles set

forth in Industrial Ventilation - A Manual of Recommended Practice [122], published by the American Conference of Governmental Industrial Hygienists, Fundamentals Governing the Design and Operation of Local Exhaust Systems, Z9.2-1971 [123], published by the American National Standards Institute, and NIOSH's Recommended Industrial Ventilation Guidelines [124] should be applied to control workplace atmospheric concentrations of NG and EGDN. These ventilation systems require regular inspection and maintenance to ensure their effective operation. The effects of any changes or additions to the ventilating system or to the operations being ventilated should be assessed promptly after changes occur, and such assessment should include measurements of airflow and environmental levels of contaminants under the new conditions. Work practices should introduce no obstructions or interferences that would reduce the effectiveness of the ventilating system.

NG and EGDN are commonly manufactured in the United States by the Biazzi process [6], which is automated; nitration, separation, spent acid removal, washing, transfer, storage, and weighing are accomplished without the direct participation of personnel. An operator is necessary only at the startup and shutdown points and for routine checks in the control room. NIOSH's recommended standards for handling nitric acid [125] and sulfuric acid [126] should be followed when applicable.

Dynamite containing NG and EGDN is produced in a variety of consistencies from a dry, granular type to a gel. The manufacturing process for dynamite [11] still follows the basic pattern originally developed by Nobel in 1867. The liquid mixture of NG and EGDN is mixed with a batch of other material called "dope." Dope can consist of

combinations of ammonium nitrate, sodium nitrate, and organic fillers such as, wood pulp, bagasse, corn starch, and rice hulls. Nitrocellulose is added to form the gel type of dynamite. From the mix house, the explosive mixtures are transported to several different packing houses which are equipped to handle the specific types of dynamite. Here the cartridges are filled by automatic or semiautomatic equipment, packed into plastic-lined boxes, and moved to the magazines.

In the manufacturing and packaging processes described above, the danger of detonation can be minimized through the use of engineering controls and work practices. Engineering controls should be designed to prevent detonation and, in the event of accidental explosion, to minimize the propagation of detonation. The latter can be accomplished by the use of a properly designed facility made up of detached units equipped with explosion-venting systems, such as blow-away walls or ceilings and pressure-resistant walls. Whenever practical, each unit should be subdivided with fire- and pressure-resistant walls to restrict hazardous areas and to prevent direct communication with other areas. Additional specifications are provided in NFPA No. 63-1971 [2].

Unintentional detonation can be reduced to a minimum or its force minimized by controlling the concentrations of NG, EGDN, explosive dusts, or particles of solid materials containing these substances in the working environment and by removing sources of ignition. Concentrations in the air can be limited by the use of closed-system operations, local-exhaust ventilation, or combinations of the two. These systems should be constructed of nonsparking and noncombustible materials. For ventilation systems, ample clearance should be provided between fans and casings with

dust-sealed, antifriction bearings mounted outside the fan casing. Dust collectors should be provided to prevent discharge of the explosives into the outside environment, and these collectors should be located outdoors or in detached rooms with adequate explosion vents for collectors and rooms. Collectors should be cleaned at least daily to prevent accumulation of the explosives. Fans should be located so as to draw air from the collector. Additional requirements are provided in NFPA No. 91-1973 [127].

The accumulation of explosive dust can be avoided by following the guidelines of NFPA No. 63-1971 [2]; for slurry or water gel explosives, the Industrial Safety Standard No. V [128] of the Institute of Makers of Explosives (IME) should be referred to. Equipment should be dust-tight and, where the substances are produced, processed, or handled, should be operated under a slight vacuum. All electrical wiring and equipment should conform to the requirements of NFPA No. 70-1971 [129] for hazardous locations and must include explosion-proof fixtures and wiring. The buildup of static electricity can be minimized by humidification, bonding, grounding, and the use of conductive materials. These and other requirements are listed in NFPA No. 77-1972 [130].

NG, EGDN, and materials containing these compounds must be stored in specially designed magazines. Exact specifications for the construction of these facilities and storage provisions are provided in NFPA No. 495-1973 [2] and the IME's Industrial Safety Standard No. 17 [131]. In brief, magazines should be bullet-resistant, be constructed of steel, wood, concrete, or brick, and be used solely for the storage of explosives and blasting accessories.

The siting of magazines must conform to the requirements of the American Table of Distances for Storage of Explosives set by the Institute of Makers of Explosives [1]. Adherence to these distances should minimize the effect of detonation on vehicles, inhabited dwellings, and passenger railways and prevent propagation of an explosion.

#### Biologic Monitoring

As mentioned in Effects On Humans in Chapter III, a limited amount of work has been done on determining the concentrations of NG and EGDN in the blood and urine of workers exposed to these substances [71,72]. Williams et al [71] measured EGDN concentrations in the blood of exposed workers, but the concentrations in air and the amounts deposited on skin to which these workers were exposed were not measured. Sundell et al [72] reported that blood EGDN concentrations in workers were related to airborne EGDN exposure in the absence of skin contact, but there was no correlation between the concentrations in blood and urine. There is at present insufficient information to suggest an adequate method for biologic monitoring of industrial workers exposed to NG or EGDN. Additional research may make feasible the routine measurement of these compounds or their residues in blood or other body fluids.