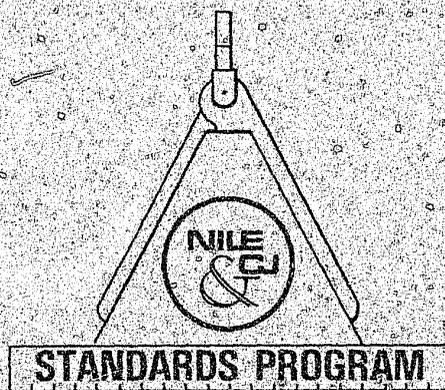


LESP-RPT-0604.00

MARCH 1977

LAW ENFORCEMENT STANDARDS PROGRAM

A TRACE VAPOR GENERATOR FOR TESTING EXPLOSIVES VAPOR DETECTORS



LOAN DOCUMENT

RETURN TO:

NCJRS

P. O. BOX 24036 S. W. POST OFFICE
WASHINGTON, D.C. 20024

U.S. DEPARTMENT OF JUSTICE
Law Enforcement Assistance Administration
National Institute of Law Enforcement and Criminal Justice

LAW ENFORCEMENT STANDARDS PROGRAM

**A TRACE VAPOR GENERATOR FOR TESTING
EXPLOSIVES VAPOR DETECTORS**

prepared for the
National Institute of Law Enforcement and Criminal Justice
Law Enforcement Assistance Administration
U. S. Department of Justice

by

Peter A. Pella
Analytical Chemistry Division

Robert M. Mills
Law Enforcement Standards Laboratory

National Bureau of Standards

NCJRS

MAR 30 1977

MARCH 1977 ACQUISITIONS

U.S. DEPARTMENT OF JUSTICE
Law Enforcement Assistance Administration
National Institute of Law Enforcement and Criminal Justice

**NATIONAL INSTITUTE OF LAW ENFORCEMENT
AND CRIMINAL JUSTICE**

Gerald M. Caplan, *Director*

**LAW ENFORCEMENT ASSISTANCE
ADMINISTRATION**

Richard W. Velde, *Administrator*

Paul K. Wormeli, *Deputy Administrator*

ACKNOWLEDGMENTS

This report was prepared by the Law Enforcement Standards Laboratory of the National Bureau of Standards under the direction of Robert Mills, Manager, Investigative Aids Program, and Jacob J. Diamond, Chief of LESL. The authors wish to thank Edwin C. Kuehner for constructing the temperature controller in the generator, and Lorne Elias for his helpful suggestions.

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402-Price 65 cents
Stock Number 027-000-00453-9

There is a minimum charge of \$1.00 for each mail order.

A TRACE VAPOR GENERATOR FOR TESTING EXPLOSIVES VAPOR DETECTORS

CONTENTS

	<i>Page</i>
Foreword	v
1. Introduction	1
2. Description of Generator	1
2.1 Electronic Metering Valve	2
2.2 Temperature Control	3
2.3 Expected Vapor Concentrations	3
3. Analytical Methodology	3
3.1 Vapor Collection Tubes	4
3.2 Collection of the Dilute Vapors	5
3.3 Analysis of the Collected Vapors	6
4. Measurements of Vapor Concentrations	7
4.1 Flow Rates and Column Temperatures	7
4.2 Variation of Equilibrium Vapor Concentration With Column Temperature	7
4.3 Output Concentration	10
5. Applicability to Explosives Vapor Detectors	11
Appendix A—Column Design	15
Appendix B—Heats of Sublimation and Heats of Vaporization	17
Appendix C—References	18

FOREWORD

Following a Congressional mandate¹ to develop new and improved techniques, systems, and equipment to strengthen law enforcement and criminal justice, the National Institute of Law Enforcement and Criminal Justice (NILECJ) has established the Law Enforcement Standards Laboratory (LESL) at the National Bureau of Standards. LESL's function is to conduct research that will assist law enforcement and criminal justice agencies in the selection and procurement of quality equipment.

In response to priorities established by NILECJ, LESL is (1) subjecting existing equipment to laboratory testing and evaluation and (2) conducting research leading to the development of several series of documents, including national voluntary equipment standards, user guidelines, state-of-the-art surveys and other reports.

This document, LESP-RPT-0604.00, A Trace Vapor Generator for Testing Explosives Vapor Detectors, is a law enforcement equipment report prepared by LESL and issued by NILECJ. Additional reports as well as other documents are being issued under the LESL program in the areas of protective equipment, communications equipment, security systems, weapons, emergency equipment, investigative aids, vehicles and clothing.

Technical comments and suggestions concerning the subject matter of this report are invited from all interested parties. Comments should be addressed to the Program Manager for Standards, National Institute of Law Enforcement and Criminal Justice, Law Enforcement Assistance Administration, U.S. Department of Justice, Washington, D.C. 20531.

George Shollenberger
Program Manager for Standards
National Institute of Law
Enforcement and Criminal Justice

¹Section 402(b) of the Omnibus Crime Control and Safe Streets Act of 1968, as amended.

A TRACE VAPOR GENERATOR FOR TESTING EXPLOSIVES VAPOR DETECTORS

1. INTRODUCTION

Vapors from such explosives as trinitrotoluene (TNT) and ethylene glycol dinitrate (EGDN), at known low concentrations below one part per billion ¹ (ppb), are required for the determination of the limits of detection of commercial explosives vapor detectors. These detectors are used in a variety of law enforcement applications, and are primarily designed for the detection of TNT and dynamite. The vapors of other constituents present in explosives, such as dinitrotoluene (DNT) in TNT, may also be detected.

A dynamic gas blending system has been developed for producing known low concentrations of vapors of 2,4,6 TNT, 2,4 DNT, 2,6 DNT, and EGDN. The dynamic dilution of TNT and EGDN vapors had previously been employed for this purpose by several workers. Wall et al. (1) developed a system based on weight loss, using a thermogravimetric analyzer and measured flow rates. Liebel and Roberts (2) described a device for TNT vapor generation, and Dravnieks (3) used a double-stage system for the dilution of EGDN vapors at room temperature by a factor of 10^6 .

The vapor generator constructed by us uses a single dilution stage for simplicity in design and construction. Instruments of this kind have been evaluated at the National Bureau of Standards for a number of applications (4). In this system, an equilibrium vapor concentration of TNT, DNT, or EGDN is generated by passing nitrogen through a column containing the explosive deposited on an inert support. The nitrogen becomes saturated with the explosive vapor while passing through the column. The column is maintained at a controlled temperature which can be varied to obtain a range of equilibrium vapor concentrations. The output of the column is connected to a mixing manifold where the equilibrium vapor is diluted with air to provide the desired final vapor concentration.

This report describes the design of the generator, and the measurements made to verify that the output vapor concentrations are close to the expected values. Three explosives vapor detectors of different designs were used to demonstrate the applicability of this system for testing the performance of detectors. Vapor pressures and heats of sublimation were calculated from the equilibrium vapor concentrations measured in this work and were compared to the data reported by other workers.

2. DESCRIPTION OF GENERATOR

A diagram of the system is presented in figure 1. Dry nitrogen passes through a charcoal filter and molecular sieve (13 x - 40/60 mesh) trap before entering the column containing the explosive material. The preparation of these columns and the purification of the explosive materials are discussed in Appendix A. The equilibrated explosive vapor from the column enters an electronic metering valve which precisely dispenses a predetermined flow of vapor to the mixing manifold. The explosive vapor is diluted with air in the mixing manifold, and then passes to the sampling manifold where it exits the system through two ports.

The flow rates of the equilibrated explosives vapor and diluent air must be well regulated. This is accomplished by means of differential flow controllers (UFC and DFC) which maintain constant pressure drops across external needle valves (V-2 and V-4) so that the downstream flows are

¹ 10^{-9} moles of explosive vapor per mole of air.

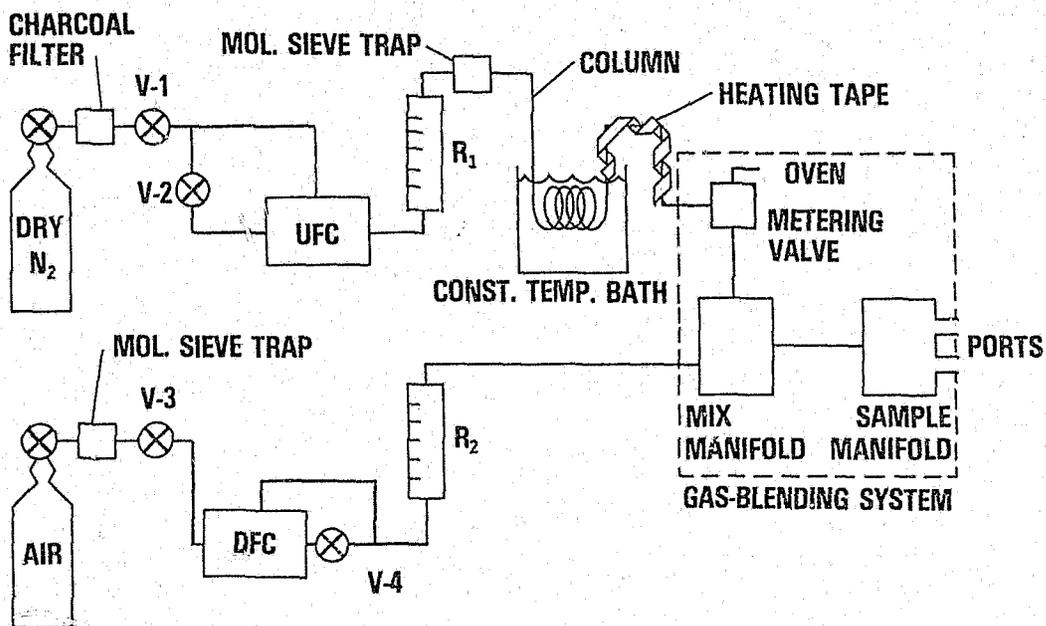


Figure 1. Schematic Diagram of the Trace Vapor Generator.

functions of the needle valve openings. The flow rates are measured using flowmeters R_1 and R_2 . Flow rate calibrations were performed using a bubble-type flow meter for measuring the equilibrium vapor and a wet-test meter for measuring the diluent air. To minimize the adsorption and condensation of explosives vapors on the glass surfaces, the glass tubing at the column exit is heated to 80–90°C. The metering valve, mixing manifold and sampling manifold are maintained at 40–50°C.

2.1 Electronic Metering Valve

The flow rates through the column range from 30 to 50 ml/min. The diluent air flow rates range from 1,000 to 7,000 ml/min, permitting a dilution of up to about 200 times. However, dilutions greater than 1000 times are necessary to produce output EGDN concentrations of less than 0.5 ppb. This was accomplished by reducing the flow of the equilibrium vapor to the mixing manifold by means of an electronic metering valve. The valve is operated so that a pre-selected fraction of the equilibrium vapor from the column enters the mixing manifold while the rest of the gas flow is vented through a bleed outlet. The fraction of gas flow delivered to the mixing manifold is determined by a thumbwheel setting and is equal to:

$$F = \frac{NF_1}{1000}, \quad (1)$$

where N is the thumbwheel setting (which can be varied from 50 to 999), and F_1 is the flow rate of the equilibrium vapor from the column. The accuracy of the metering valve was checked with a bubble-type flow meter at various thumbwheel settings. The valve has a small internal volume in order to minimize adsorption problems.

A thumbwheel setting of 999 permits essentially the total flow from the column to pass to the mixing manifold. When the valve is switched off, the total flow is vented through the bleed outlet.

Although the valve is actually required only for producing low concentrations of EGDN vapor, it was kept in the system when generating TNT and DNT vapors.

2.2 Temperature Control

Column temperatures were maintained constant within $\pm 0.05^\circ\text{C}$. The accuracy of the temperature controller was checked at 0°C and -33°C with an NBS platinum resistance thermometer, and found to be better than $\pm 0.2^\circ\text{C}$.

2.3 Expected Vapor Concentrations

The expected output concentration is given by

$$C_o = C_e \frac{NF_1}{NF_1 + 1000F_2} \quad (2)$$

where C_o is the output concentration in ppb; C_e is the equilibrium vapor concentration, in ppb, from the column at a constant temperature; F_2 is the flow rate of the diluent air entering the mixing manifold; N and F_1 are as defined above.

The temperature dependence of the equilibrium vapor concentration is predicted from the Clausius-Clapeyron equation, which can be written:

$$\log p = - \frac{\Delta H}{2.3 RT} + A, \quad (3)$$

where p is vapor pressure in mm of Hg, R is the gas constant in calories per mole, T is the absolute temperature in degrees Kelvin, ΔH is the heat of sublimation or vaporization in cal/mole, and A is a constant. Equation (3) can be rewritten in terms of vapor concentration, C , expressed in ppb, using:

$$C = \frac{p \times 10^9}{760} \quad (4)$$

Thus:

$$\log C_e = a_1 \frac{1}{T} + a_0, \quad (5)$$

where T is the absolute temperature of the column,

$$a_1 = - \frac{\Delta H}{2.3 R}, \text{ and} \quad (6)$$

$$a_0 = A + 6.11919. \quad (7)$$

A plot of $\log C_e$ versus $1/T$ yields a straight line with slope a_1 and intercept a_0 .

3. ANALYTICAL METHODOLOGY

A gas chromatographic procedure was developed to confirm the accuracy of the trace vapor generator. This same technique was used to measure the output concentrations and the concentrations of the equilibrium vapors from the column.

A known volume of explosive vapor is passed through a collection tube, shown in figure 2, containing glass wool and charcoal. These adsorbents completely adsorb the explosive material. The explosive material is then removed from the adsorbent by elution with either benzene for TNT and

DNT, or acetone-cyclohexane solutions for EGDN. The quantity of the explosive in solution is measured by comparing the chromatogram peak area from this solution and from a standard solution. The explosive vapor concentration, C , in ppb, is calculated from the equation:

$$C = \frac{C_S A_E V_E G \times 10^9}{A_S V M}, \quad (8)$$

where C_S = the concentration of the standard solution in nanograms (ng) per ml of solution
 A_E = chromatogram area of eluted sample
 A_S = chromatogram area of standard sample
 V_E = volume of eluted sample in milliliters
 V = volume of vapor collected in liters (i.e., flow rate in liters/min \times time in minutes)
 G = molar gas volume in liters/mole
 M = molecular weight of the explosive

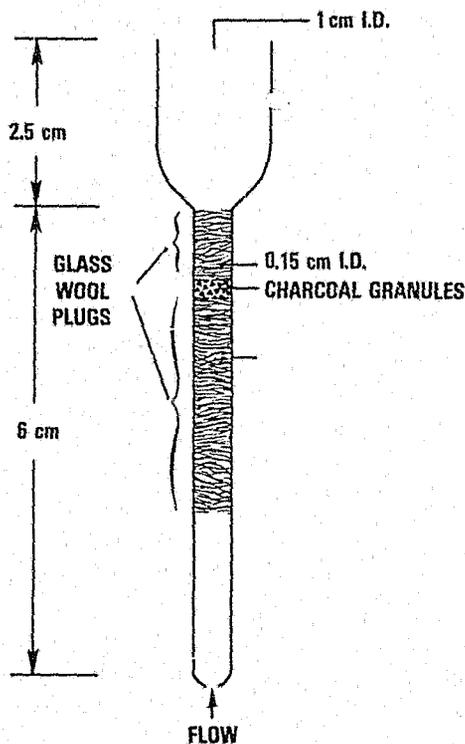


Figure 2. Vapor Collection Tube.

3.1 Vapor Collection Tubes

The collection tubes were made from disposable transfer pipettes, as shown in figure 2. The adsorbent consisted of a glass wool plug about 3 cm long followed by a 1 mg of finely divided charcoal and a 1 cm glass wool plug.

The collection efficiency of the collection tubes was determined by collecting known volumes of equilibrated DNT vapors flowing at 30 ml/min in a tube 13 cm long containing double sections of the glass wool/charcoal adsorbent. The vapors were collected at the exit of the column, as shown in figure 3. Each adsorbent section was removed and analyzed separately. Less than two percent of the total amount of the DNT collected was found on the second section. Additional measurements showed that the collection efficiency was essentially 100 percent for flow rates (F_1) between 10 and 100 ml/min. The collection efficiency was also checked when the tubes were used to collect output vapors from the sampling manifold and was found to be essentially 100 percent for flow rates up to 410 ml/min.

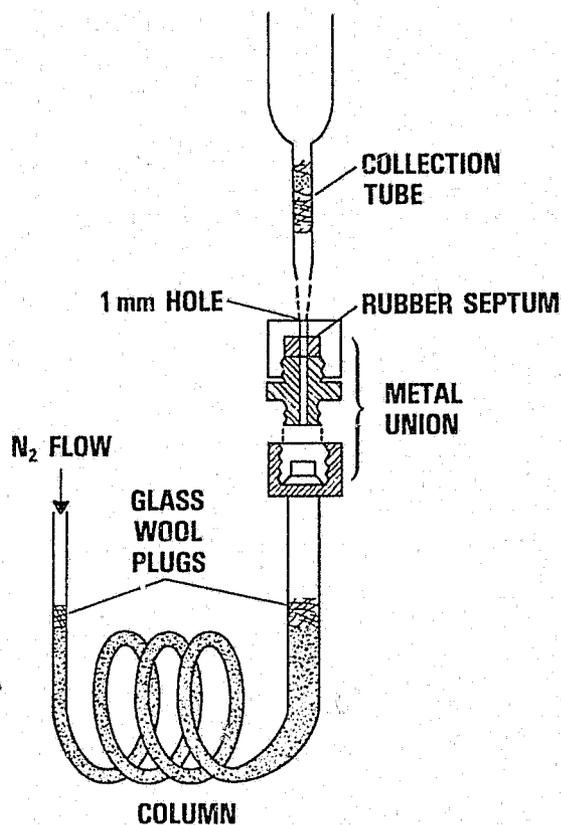


Figure 3. Collecting Vapors From Exit of Column.

3.2 Collection of the Dilute Vapors

In order to measure diluted output concentrations below 1 ppb, the collection and concentration of relatively large volumes of vapor (e.g., 10–50 liters) was necessary. A device for collecting large volumes of vapor, similar to one described by Cadoff (5), was constructed for this purpose and is shown in figure 4. The collection flow rate is adjusted with a fine needle control valve (V-5); rates from 50 to 1000 ml/min can be selected. When the stopcock is in the bypass position, the flow rate is measured with a flowmeter. This flowmeter is calibrated at atmospheric pressure, and thus cannot be incorporated into the sampling line because of the pressure drop encountered when the collection tube is in place. A pressure gauge indicates the differential pressure drop when the collection tube is inserted. Once a flow rate is selected, pressure drops as high as 500 mm Hg can be tolerated without any measurable change in the flow rate through the tube. To ensure reliable operation, a tight packing of the glass wool in the tube is avoided. A flow rate of 300 ml/min can be maintained constant at a pressure drop of 500 mm Hg or less. Variation in the flow rate was checked with a collection tube in place by monitoring the flow rate at periodic intervals for 48 hours. The maximum observed deviation from 300 ml/min did not exceed ± 6 ml/min, or two percent. Collection flow rates were calibrated using a wet-test meter (not shown in the figure) upstream from the collection tube. When this variable flow device was used to sample diluted vapors exiting the system, the flow rate of the diluted vapor was at least four times the collection rate. The collection tube was inserted through a latex rubber sleeve and fitted onto the bottom port of the sampling manifold as shown in the figure. Collection of the vapor was begun when the stopcock was rotated to the sample position. Collection times varied from about 30 minutes to 10 hours.

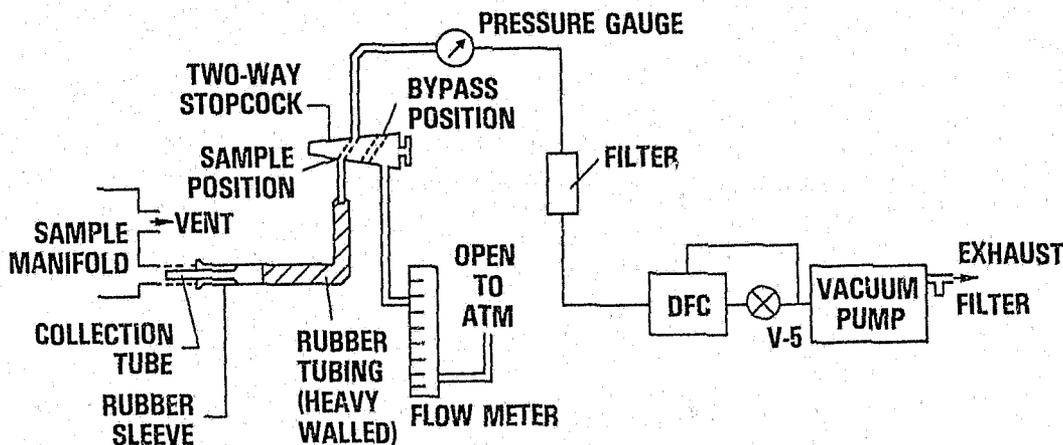


Figure 4. Variable Flow Collection System

3.3 Analysis of the Collected Vapors

3.3.1 Preparation of Calibration Solutions

Standard solutions for calibration of the gas chromatograph were prepared by dissolving known amounts of purified TNT and DNT in benzene in volumetric flasks. Working standards were made by serial dilution. An EGDN standard solution was prepared by dilution of a 60 percent EGDN, 40 percent acetone solution with acetone. Working EGDN standards were prepared by serial dilution with cyclohexane so that the acetone concentration in these solutions did not exceed two percent. Higher acetone concentration were avoided because of severe tailing of the acetone chromatograms.

3.3.2 Gas Chromatographic Conditions

A gas chromatograph operated isothermally was used in these experiments. The electron capture detector contained either a titanium tritide foil operated at 200°C or a scandium tritide foil at 230–270°C. A 1.8 meter glass column packed with 4 percent UCW-98 on Chromosorb WHP (100/120 mesh)-AW-DMCS was used for measurements of TNT and DNT. The column temperature was adjusted between 140 and 160°C to give retention times of 83 seconds for TNT, 70 seconds for 2,4 DNT, and 110 seconds for 2,6 DNT. The injection port temperature was 165°C. The standing current during operation was at least 1.3×10^{-8} A. High purity nitrogen containing less than 0.5 ppm O_2 was used as the carrier gas, at a flow rate of 60 ml/min.

For EGDN measurements, a 0.2 cm I.D. x 70 cm glass column was packed with 12 percent DEGS on Chromosorb WHP (100/120 mesh) and operated at 125°C to give retention times of about 70 seconds.

3.3.3 Analytical Procedure

TNT and DNT were eluted from the collection tubes with benzene. It was found that 0.5 to 0.7 ml of benzene completely elutes the explosive; small volumes of solvent improve the analytical accuracy. EGDN was eluted with 12-25 μ l of acetone followed by cyclohexane. These samples were collected in volumetric flasks. From 1 to 5 μ l of sample was injected into the chromatograph, and the areas of the chromatograms were measured using electronic integration. In the same manner, aliquots of standard solutions were injected and the corresponding chromatogram areas were measured. The working standard concentrations were prepared in order to give chromatogram areas within ± 20 percent of the areas of the sample chromatograms.

4. MEASUREMENTS OF VAPOR CONCENTRATIONS

4.1 Flow Rates and Column Temperatures

By using vapor flow rates and column temperatures such that the nitrogen carrier gas is saturated with explosive vapor, the equilibrium concentration from the column is predictable from equation (5). If the nitrogen is saturated with explosive vapor, the explosive vapor concentration is insensitive to variation in flow rate and to the quantity of explosive material used to fill the column.

No significant differences in 2,4 DNT concentrations were observed when the nitrogen flow rate, F_1 , was varied from 10 to 100 ml/min with the column temperature at 25°C. A nitrogen flow rate of 30–40 ml/min was considered appropriate for generating equilibrium vapor concentrations over the temperature ranges from 14.0 to 56.5°C for TNT, 4.0 to 71.0°C for 2,4 DNT, and 4.0 to 50.0°C for 2,6 DNT. The size of the columns used, including the amount of dispersed explosive, was essentially identical for TNT, 2,4 DNT, and 2,6 DNT.

Measurements made with EGDN showed no differences in vapor concentrations when the nitrogen flow rate was varied from 30 to 40 ml/min, but a 15 percent decrease in the vapor concentration was noted at a nitrogen flow rate of 70 ml/min. For this reason, the nitrogen flow rates used for generating EGDN equilibrium vapor concentrations did not exceed 37 ml/min over the temperature range from -33 to +25°C.

4.2 Variation of Equilibrium Vapor Concentration With Column Temperature

Tables 1 through 4 show measured equilibrium concentrations, C_e , for TNT, 2,4 DNT, 2,6 DNT, and EGDN at various column temperatures. Equilibrium concentrations for TNT and EGDN (Tables 1 and 4) were measured directly at the column exit. However, for 2,4 DNT and 2,6 DNT (Tables 2 and 3), the diluted output vapor concentrations, C_o , were measured at the sampling manifold, while varying both the column temperature and the dilution ratio, $F_1/(F_1 + F_2)$. Equilibrium concentrations were then calculated using equation (2), with $N = 999$.

TABLE 1. TNT Equilibrium Concentration As a Function of Temperature

Run No.	Temperature °C	Measured C_e (ppb)	Run No.	Temperature °C	Measured C_e (ppb)
1	14.0	2.8	19	45.0	152
2	14.0	2.9	20	45.0	132
3	14.0	3.0	21	45.0	142
4	21.0	3.8	22	45.0	173
5	21.0	4.3	23	45.0	182
6	25.0	8.9	24	45.0	151
7	25.0	11.8	25	45.0	155
8	25.0	10.8	26	50.0	251
9	25.0	11.0	27	50.0	269
10	25.3	12.4	28	55.0	457
11	25.3	12.9	29	55.0	460
12	26.5	16.9	30	55.0	506
13	35.0	74	31	55.0	521
14	35.0	76	32	56.5	584
15	35.0	59	33	56.5	614
16	40.0	91	34	56.5	577
17	40.0	93	35	56.5	610
18	45.0	130	36	56.5	577

TABLE 2. 2,4 DNT Equilibrium Concentration as a Function of Temperature

Run No.	Temperature °C	$\frac{F_1}{F_1+F_2}$	Measured C_o (ppb)	C_c (ppb) = $C_o \frac{(F_1+F_2)}{F_1}$
1	4.0	0.02509	0.397	15.8
2	4.0	0.02453	0.405	16.5
3	10.0	0.02368	0.877	37.0
4	10.0	0.02398	0.897	37.4
5	20.0	0.02287	3.92	171.4
6	20.0	0.02287	4.03	176.2
7	30.0	0.02301	9.8	425
8	30.0	0.02301	10.8	471
9	40.0	0.02401	43.5	1.81×10^3
10	40.0	0.02401	38.4	1.60×10^3
11	40.0	0.02233	35.3	1.58×10^3
12	40.0	0.02233	44.0	1.97×10^3
13	40.0	0.02233	34.8	1.56×10^3
14	40.0	0.02096	33.9	1.62×10^3
15	50.0	0.02274	154.2	6.78×10^3
16	50.0	0.02274	157.6	6.93×10^3
17	60.0	0.009049	146.6	1.62×10^4
18	60.0	0.009049	149.9	1.66×10^4
19	71.0	0.009326	457	4.89×10^4
20	71.0	0.009326	519	5.57×10^4

TABLE 3. 2,6 DNT Equilibrium Concentration as a Function of Temperature

Run No.	Temperature °C	$\frac{F_1}{F_1+F_2}$	Measured C_o (ppb)	C_c (ppb) = $C_o \frac{(F_1+F_2)}{F_1}$
1	4.0	0.02424	0.825	34.0
2	4.0	0.02424	0.812	33.5
3	10.0	0.02319	2.45	105.6
4	10.0	0.02319	2.44	105.3
5	20.0	0.02387	9.43	395
6	20.0	0.02387	9.89	414
7	20.0	0.02300	8.59	373
8	20.0	0.02300	7.77	338
9	20.0	0.02300	8.53	371
10	30.0	0.009233	13.2	1.43×10^3
11	30.0	0.009233	13.5	1.46×10^3
12	30.0	0.009350	13.8	1.48×10^3
13	30.0	0.009350	14.4	1.54×10^3
14	30.0	0.02332	31.1	1.33×10^3
15	40.0	0.02348	114	4.84×10^3
16	40.0	0.02348	113	4.83×10^3
17	40.0	0.02348	108	4.61×10^3
18	50.0	0.009167	153	1.67×10^4
19	50.0	0.009167	157	1.71×10^4

TABLE 4, EGDN Equilibrium Concentration as a Function of Temperature

Run No.	Temperature °C	Measured C _e (ppb)
1	-33.0	148
2	-33.0	143
3	-33.0	156
4	-33.0	148
5	-30.0	234
6	-30.0	225
7	-30.0	228
8	-30.0	252
9	-18.5	1.18x10 ³
10	-18.5	1.04x10 ³
11	-18.5	1.11x10 ³
12	- 5.0	5.13x10 ³
13	- 5.0	5.42x10 ³
14	- 5.0	4.93x10 ³
15	- 5.0	5.76x10 ³
16	25.0	9.66x10 ⁴
17	25.0	10.70x10 ⁴
18	25.0	8.98x10 ⁴
19	25.0	10.27x10 ⁴
20	25.0	9.95x10 ⁴

A least-squares analysis was performed for the data in Tables 1-4, solving for values of a₁ and a₀ in equation (5), with the following results (C_e in parts per billion, T in °K):

For TNT

$$\log C_e = -5175.4 \frac{1}{T} + 18.431 \quad (9)$$

For 2,4 DNT

$$\log C_e = -4991.9 \frac{1}{T} + 19.201 \quad (10)$$

For 2,6 DNT

$$\log C_e = -5139.1 \frac{1}{T} + 20.111 \quad (11)$$

For EGDN

$$\log C_e = 3475.6 \frac{1}{T} + 16.666 \quad (12)$$

The agreement between the measured concentrations and those calculated from equations 9 through 12 is generally better than 15 percent.

Since the regression coefficients for 2,4 DNT and 2,6 DNT were determined using several values of the dilution factor, a few additional 2,4 DNT equilibrium vapor concentrations were measured directly at the column exit at 25°C. The average of nine determinations was 314 ppb, with a relative standard deviation of 15 percent. The equilibrium concentration predicted from equation 10 for 25°C is 287 ppb, a nine percent difference.

More definitive information about the "goodness of fit" of these equations is given in Table 5. Refer to any text on regression analysis (14) for definitions of the terms listed in Table 5.

TABLE 5. "Goodness of Fit" of Equations 9-12

	TNT	2,4 DNT	2,6 DNT	EGDN
Residual Standard Deviation	0.091	0.056	0.035	0.030
Standard Error of a_1	105	59.4	52.3	21.5
Standard Error of a_0	.336	0.193	0.175	0.083

An independent check was made of the data in Tables 1 through 4 - and thus of equations 9 through 12 - by considering the data to be a measure of the vapor pressures of the explosive materials. After converting back to equation 3 in order to calculate vapor pressures instead of vapor concentrations, the regression coefficients corresponding to data from this work were compared with similar coefficients obtained from the literature. The results are shown in Table 6. (Heats of sublimation are listed in Appendix B).

TABLE 6. Comparisons of Vapor Pressures with Literature Values

	°C	Intercept, A	Std. Dev. of A	Slope, $\Delta H/(2.3R)$	Std. Dev. of Slope	No. of Data Points	Residual Std. Dev.
<i>For TNT:</i>							
This Work	14-56.5	12.31	0.34	5172	105	36	0.091
Lenchitz & Velicky (6)	54-76	13.08	0.38	5401	130	11	0.024
Edwards (7)	50-143	12.10	0.25	5066	90	27	0.090
<i>For 2,4 DNT:</i>							
This Work	4-71	13.08	0.19	4992	59.4	20	0.056
Lenchitz & Velicky (6)	59-69	12.59	0.38	5130	128	12	0.013
Molard (8)	81-165.6	9.36		3664			
<i>For 2,6 DNT:</i>							
This Work	4-50	13.99	0.175	5139	52.3	19	0.035
Molard (8)	71.5-153.5	9.40		3586			
<i>For EGDN:</i>							
This Work	-33-(+25)	10.55	0.083	3476	21.5	20	0.030
Brandner (11)	20-50	10.90	0.096	3578	29	7	0.008
Belyaev (12)	74.5-117	9.85	0.063	3253	23	6	0.006

4.3 Output Concentration

Equations 9-12 relate to the concentrations of the equilibrium vapors coming from the column. The utility of this trace vapor generator comes, however, from knowing the concentration of the

output from the sampling manifold. The output concentration can be selected by adjustment of the column temperature and by selection of the dilution factor, $NF_1/(NF_1 + 1000F_2)$. The accuracy with which the dilution factor in equation 2 can be used to predict output concentrations is therefore of interest.

Experimental control was demonstrated directly for DNT (Tables 2 and 3), since several dilution factors were used with good accuracy. To demonstrate this control for the dilution of TNT and EGDN, predicted (from equations 2, 9, and 12) and measured values of the output concentration were compared for various dilution factors, using one column temperature (30°C) for TNT and three column temperatures (-33°C, -30°C, and -20°C) for EGDN. The results are tabulated in Table 7 for TNT and Table 8 for EGDN. The measured output concentrations were generally within 15 to 20 percent of the predicted concentrations for TNT. But for EGDN, a negative bias of up to 40 percent was found. These low values are probably caused by adsorption losses. Measurements made with and without the electronic metering valve in the system gave essentially the same results, indicating that the bias was not attributable to adsorption in the valve assembly.

5. APPLICABILITY TO EXPLOSIVES VAPOR DETECTORS

In order to demonstrate the utility of the system, and particularly that the range of vapor concentrations produced is suitable, data were obtained using three explosives vapor detectors of different manufacture. Each instrument was used to measure one explosive material; instrument A was tested with TNT, instrument B with 2,4 DNT, and instrument C with EGDN. The data obtained are presented in figures 5 to 7. The measurement procedure consisted of placing the sampling probe of the detector at the bottom port of the sampling manifold while the top port was vented into a fume hood. The vapor sampling rates of these instruments differed considerably from one another. This difference can be important if the detection sensitivity depends on the volume of vapor sampled by the instrument.

TABLE 7. Comparisons of Measured and Predicted TNT Output Concentrations

Equilibrium Vapor Concentration = 22.85 ppb*
Column Temperature = 30°C

Run No.	Dilution Factor, $NF_1/(NF_1 + 1000F_2)$	Predicted C_o , from Eq. 2, ppb	Measured C_o , ppb	Per Cent Difference
1	0.04325	0.988	0.973	-1.5
2	0.04249	0.971	0.824	-15.1
3	0.02369	0.541	0.497	-8.1
4	0.02365	0.540	0.429	-20.6
5	0.02307	0.527	0.498	-5.5
6	0.02307	0.527	0.521	-1.1
7	0.009758	0.223	0.223	0
8	0.009493	0.217	0.161	-25.8
9	0.009341	0.213	0.179	-16.0
10	0.009195	0.210	0.186	-11.4
11	0.009136	0.209	0.208	-0.5
12	0.004974	0.114	0.122	7.0
13	0.004854	0.111	0.120	8.1
14	0.004845	0.111	0.0837	-24.6

*Calculated from equation 9.

TABLE 8. Comparisons of Measured and Predicted EGDN Output Concentrations

Equilibrium vapor concentrations were 864* ppb, 235* ppb, and 156* ppb at -20°C, -30°C and -33°C respectively.

Run No.	Dilution Factor, $N_{F_1}/(N_{F_1}+1000 F_1)$	°C	Predicted C_o from Eq. 2; ppb	Measured C_o , ppb	% Difference
1	0.02469	-20	21.332	21.486	0.72
2	0.02337	-20	20.192	20.204	0.06
3	0.009313	-20	8.046	7.825	-2.7
4	0.02848	-30	6.693	6.077	-9.2
5	0.02363	-30	5.553	4.634	-16.5
6	0.005068	-20	4.379	4.201	-4.1
7	0.02938	-33	4.583	3.592	-21.6
8	0.02938	-33	4.583	3.576	-22.0
9	0.01138	-30	2.674	2.533	-5.3
10	0.01059	-33	1.652	1.315	-20.4
11	0.009424	-33	1.470	1.129	-23.2
12	0.009010	-33	1.406	1.246	-11.4
13	0.004990	-30	1.173	0.898	-23.4
14	0.007080	-33	1.104	0.853	-22.7
15	0.004625	-33	0.722	0.572	-20.8
16	0.002373	-33	0.370	0.244	-34.1
17	0.00115	-30	0.270	0.233	-13.7
18	0.00115	-30	0.270	0.228	-15.6
19	0.00115	-30	0.270	0.231	-14.4
20	0.00116	-33	0.181	0.123	-32.0
21	0.000580	-33	0.0905	0.0553	-38.9

*Calculated from equation 12.

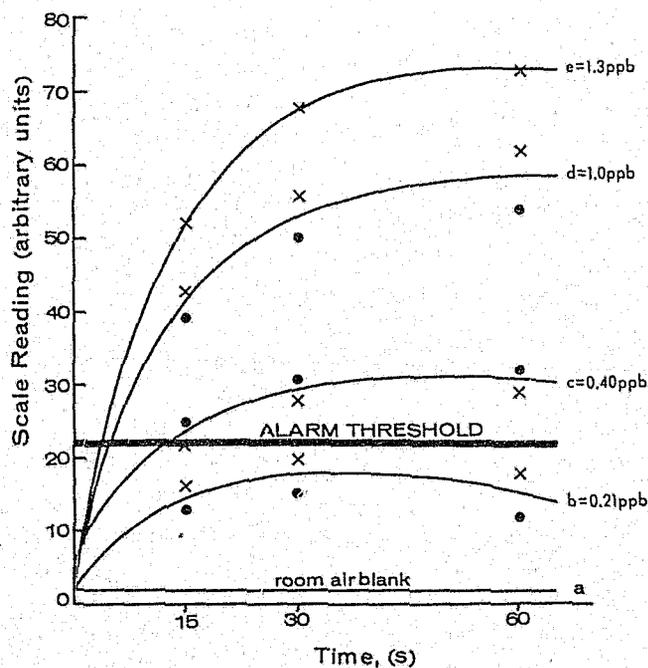


Figure 5. Instrument A Response to TNT.

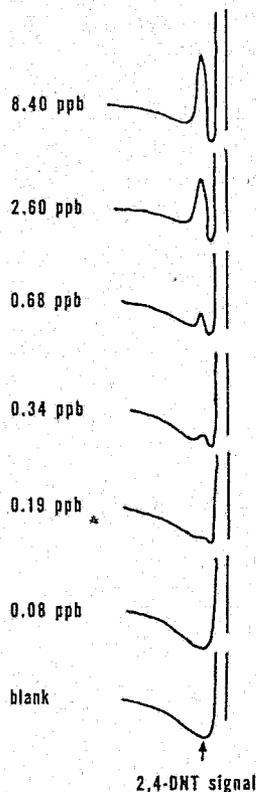


Figure 6. Instrument B Response to 2,4 DNT

The time-dependent response of instrument A to various TNT concentrations from 0.2 to 1.3 ppb is plotted in figure 5. Maximum readings were obtained after 40 to 60 seconds. If the TNT vapor sampling was continued for two minutes, the scale reading actually decreased. The alarm threshold for this instrument was preset by the manufacturer so that the alarm was triggered when a reading slightly above 20 was reached. After the 1.3 ppb response curve was obtained, the TNT column was disconnected. A blank measurement was then made after about 1 minute. It appears that traces of TNT vapor were still present in the generator but decreased rapidly after about 1 minute.

For instrument B, the flow rate is high (7-8 l/min) at the start of the vapor sampling cycle, but then decreases rapidly to a few ml/min at the end of the cycle. Unlike instruments A and C, the sampling cycle time was fixed in this instrument. Measurements of 2,4 DNT from 0.08 to 8.4 ppb were made using instrument B, and are shown in figure 6. Blank air sample traces were also recorded and are shown in the figure. An alarm can be triggered by this instrument by setting the appropriate controls, but this feature was not used in these experiments.

Data obtained with instrument C are shown in figure 7 for EGDN concentrations from 0.04 to 0.64 ppb. This instrument operates at a constant sampling flow rate and allows the operator to select the sampling time. The data shown in figure 7 were taken at a sampling rate of about 1 liter/min for 20 seconds.

For proper sampling, the flow rate from the sampling manifold must be greater than the sampling rate of the explosives detector. In these experiments, the output flow rate of the explosives vapors from the generator was 6 liters/min, which is many times greater than the vapor sampling rate of instruments A and C. For instrument B, the vapor sampling rate was approximately equal to the

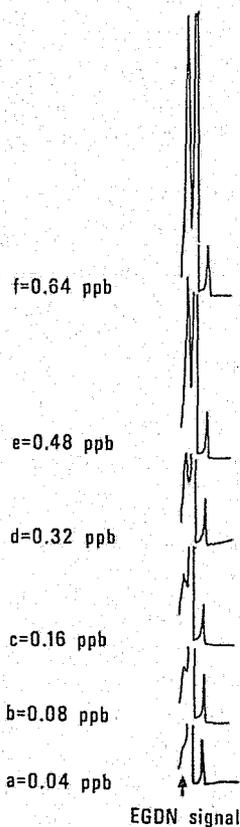


Figure 7. Instrument C Response to EGDN.

flow rate from the generator for a few seconds at the start of the sampling cycle. This, however, was not considered to be a problem because of the relatively long vapor sampling time of this instrument.

It was concluded from these data that this trace vapor generator can be used effectively to determine the explosive vapor concentration for which a detector alarm is triggered, or to determine the explosive vapor concentration at which detector response is just recognizable.

APPENDIX A—COLUMN DESIGN

A.1 Materials and Purification

Table 9 lists the melting points of the TNT and DNT samples used in this work, after the samples were purified by recrystallization from benzene. The suppliers are also shown.

TABLE 9. Melting Points of Explosive Materials

Material	Eastman Kodak	K&K Lab.	Military Grade	Literature
2,4 DNT	69.6–70.1 °C	69.8–70.9 °C	—	70–70 °C(13)
2,6 DNT	—	57.3–57.7 °C	—	56.6 °C(10)
2,4,6 TNT	—	80.2–81.2 °C	80.4–31.0°C	82 (13)

At one point, there was some question regarding the purity of the 2,4 DNT sample. A check, equilibrium vapor concentration measurements were made on a sample of recrystallized 2,4 DNT which had been heated at 60°C in a vacuum oven for two weeks. The measured vapor concentrations were the same as those from the original sample, within the experimental error of the measurements. The mass spectrum of dinitrotoluene was confirmed by comparison with a reference spectrum (9) but positive identification of the 2,4 isomer could not be made using this gas chromatographic-mass spectrometric technique. Gas chromatography was used to search for the presence of isomers in the sample, but no detectable amounts were found.

EGDN(lot#E-B-28) was synthesized at the Trojan U.S. Powder Corporation, Allentown, Pa., from reagent grade thylene glycol and nitric acid. The assay that was reported was 0.0302 percent moisture, 0.0002 percent nitric acid, and 99.67 percent total nitrogen. The material as received contained 60 percent EGDN and 40 percent reagent acetone by weight.

Solvents consisted of benzene (Mallinckrodt Nanograde; or Matheson, Coleman, and Bell pesticide quality), triple-distilled pentane (used in the recrystallization of TNT and DNT from benzene), ACS reagent acetone, and spectrograde quality cyclohexane.

A.2 Preparation of Columns

Three spiral-shaped glass columns (0.64 cm O.D. by 190 cm long), the glass tubing connections, and the glass mixing and sampling manifolds were first silanized by treatment for 20 minutes with a 10 percent solution of dimethyl dichlorosilane, followed by thorough rinsing with toluene, and then drying at 110°C. Two grams of either TNT, 2,4 DNT, or 2,6 DNT were mixed with 18 grams of Chromosorb G (60/80 mesh) and 25 ml of benzene. The slurry was stirred thoroughly until the explosive material dissolved, then placed in a vacuum oven and heated below 50°C until nearly all the benzene was removed. The slurry was again vigorously stirred to ensure good mixing of the material with the Chromosorb particles, and then returned to the vacuum oven and heated at 60–70°C until dry. Each of the three glass columns was then filled with approximately 20 grams of one of these mixtures and plugged with silanized glass wool at both ends.

Because of the hazardous nature of pure EGDN, a different procedure was used to prepare the EGDN column. A spiral-shaped glass column (0.64 cm O.D. by 110 cm long) was filled with about 3 grams of Chromosorb P (hexamethyl disilazane treated, 100/120 mesh) and plugged with silanized glass wool at both ends. A 4.0 ml aliquot of an EGDN-acetone solution having an EGDN

concentration of 77.2 mg/ml was added to the column. Sufficient air pressure was applied to the end of the column containing the solution until the entire length of the column was wetted with the solution. Dry nitrogen was passed through the column at room temperature at a rate of 50 ml/min for about 5 hours to completely remove the acetone. It was estimated from the vapor pressure and the flow rate that the amount of EGDN removed in the process did not exceed 15 mg. The columns containing the explosive materials were preconditioned at each temperature used by flowing dry nitrogen through them for several hours.

APPENDIX B—HEATS OF SUBLIMATION AND HEATS OF VAPORIZATION

The heat of sublimation or vaporization can be obtained from the slope of the Clausius-Clapeyron equation (see section 2.3). In table 10 are summarized the values obtained in this work and those obtained by other workers.

TABLE 10. Heats of Sublimations

FOR TNT

Reference	Temperature Range	ΔH_s kcal/mol	Std. Error* kcal/mol
This work	14.0–56.5°C	23.7	0.5
L&V	54–76°C	24.7	0.6
Edwards	50–80°C	28.9	0.6

FOR 2,4 DNT and 2,6 DNT

Reference	Temperature Range	Compound	ΔH_s kcal/mol	Std. Error* kcal/mol
This work	4.0–71.0°C	2,4 DNT	22.9	0.3
L&V	59–69°C	2,4 DNT	23.5	0.6
This work	4.0–50°C	2,6 DNT	23.5	0.2

FOR EGDN

Reference	Temperature Range	ΔH_s kcal/mol	Std. Error* kcal/mol
This work	–33—+25°C	15.9	0.09
Brandner	20–50°C	16.4	0.13
Belyaev	74.5–117°C	14.9	0.11

*Standard errors are calculated from the std. dev. of the slopes of the fitted equations.

APPENDIX C—References

1. William A. Wall, Herbert M. Gage and Hugh T. Reilly, "Calibration of Effluvia Detectors, Techniques and Results", Tech. Report 74-85, USALWL, Aberdeen Proving Ground, MD. 21005.
2. B. W. Liebel and R. M. Roberts, "Final Report of Trace Gas Acquisition System (TGAS)," Analytical Research Laboratories, Inc., Monrovia, Calif. 91016.
3. A. Dravnieks, "Bomb Detection System Study", IITRI Technical Report No. ADS-81 (October 1966).
4. E. E. Hughs, W. D. Dorko, E. P. Scheider, L. C. Hall, A. L. Bielby and J. K. Taylor, "Gas Generation Systems for the Evaluation of Gas Detecting Devices", National Bureau of Standards Report NBSIR 73-292 (1973).
5. B. Griefer, B. C. Cadoff, J. Wing and J. K. Taylor, "Development of Solid State Samplers for Work Atmospheres", National Bureau of Standards Report NBSIR 74-527 (June 1974).
6. C. Lenchitz and R. W. Velicky, *J. Chemical and Engineering Data*, 15, No. 3, 401 (1970).
7. G. T. Edwards, *Trans. Faraday Soc.*, 46, 423 (1950).
8. L. Molard, *Mem. Poudres*, 40, 13 (1958).
9. "Eight Peak Index of Mass Spectra", compiled by Imperial Chemical Industries Ltd., Dye-stuffs Division, in collaboration with the Mass Spectrometry Data Centre, Vol. 1, 1970, Mass Spectrometry Data Centre, AWRE, Aldermaston, Reading, RG 74PR, UK.
10. W. C. McCrone and J. H. Andreen, *Anal. Chem.*, 26, 1997 (1954).
11. J. D. Brandner, *J. of Industrial and Engineering Chemistry*, 30, No. 6, 681 (1938).
12. A. F. Belyaev, *Acta Physicochem. USSR*, 14, 523 (1941).
13. R. C. Weast and S. M. Selby, "Handbook of Chemistry and Physics", 48th ed., Chemical Rubber Co., Cleveland, Ohio (1967-68).
14. For example, W. J. Dixon and F. J. Massey, Jr., "Introduction to Statistical Analysis," McGraw Hill (1969).

PUBLICATIONS OF THE LAW ENFORCEMENT STANDARDS PROGRAM

The following publications of the Law Enforcement Standards Program issued by the National Institute of Law Enforcement and Criminal Justice are for sale by the U.S. Government Printing Office. For information concerning the availability and price of any of the publications write to: Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

NATIONAL INSTITUTE OF LAW ENFORCEMENT AND CRIMINAL JUSTICE STANDARDS (NILECJ-STD)

NILECJ-STD	TITLE	GPO STOCK NO.
0102.00	Hearing Protectors for Use on Firing Ranges, March 1973	027-000-00182-3
0301.00	Magnetic Switches for Burglar Alarm Systems, March 1974	027-000-00238-2
0302.00	Mechanically Actuated Switches for Burglar Alarm Systems, May 1974	027-000-00258-7
0303.00	Mercury Switches for Burglar Alarm Systems, May 1974	027-000-00254-4
0103.00	Portable Ballistic Shields, May 1974	027-000-00253-6
0205.00	Mobile Antennas, May 1974	027-000-00250-1
0601.00	Walk-Through Metal Detectors for Use in Weapons Detection, June 1974	027-000-00256-1
0202.00	Mobile FM Transmitters, October 1974	027-000-00287-1
0104.00	Riot Helmets, October 1974	027-000-00286-2
0201.00	Fixed and Base Station FM Transmitters, September 1974	027-000-00358-3
0602.00	Hand-Held Metal Detector for Use in Weapons Detection, October, 1974	027-000-00285-4
0203.00	Personal/Portable FM Transmitters, October 1974	027-000-00293-5
0307.00	Metallic Handcuffs, October 1974	027-000-00292-7
0304.00	Passive, First Generation Night Vision Devices, June 1975	027-000-00325-7
0211.00	Batteries for Personal/Portable Transceivers, June 1975	027-000-00342-7
0207.00	Mobile FM Receivers, June 1975	027-000-00344-3
0603.00	X-Ray Systems for Bomb Disarmament, June 1975	027-000-00343-5
0305.00	Active Night Vision Devices, June 1975	027-000-00346-0
0105.00	Crash Helmets, June 1975	027-000-00347-8
0212.00	RF Coaxial Cable Assemblies for Mobile Transceivers, September 1975	027-000-00357-5
0206.00	Fixed and Base Station FM Receivers, September 1975	027-000-00358-3
0208.00	Personal/Portable FM Receivers, October 1975	027-000-00366-4
0106.00	Ballistic Helmets, September 1975	027-000-00370-2

LAW ENFORCEMENT STANDARDS PROGRAM REPORTS (LESP-RPT)

LESP-RPT	TITLE	GPO STOCK NO.
0201.00	Batteries Used with Law Enforcement Communications Equipment—Comparison and Performance Characteristics, May 1972	027-000-00156-4
0202.00	Batteries Used With Law Enforcement Communications Equipment—Chargers and Charging Techniques, June, 1973	027-000-00216-1
0203.00	Technical Terms and Definitions Used With Law Enforcement Communications Equipment, June, 1973	027-000-00214-5
0401.00	Terms and Definitions for Police Patrol Cars, May 1974	027-000-00252-2
0304.00	Simplified Procedures for Evaluating the Image Quality of Objective Lenses for Night Vision Devices, May 1974	027-000-00255-2
0303.00	Image Quality Criterion for the Identification of Faces, May 1974	027-000-00261-7
0204.00	Voice Privacy Equipment for Law Enforcement Communications Systems, May 1974	027-000-00260-9
0302.00	Test Procedures for Night Vision Devices, May 1974	027-000-00257-9
0301.00	Survey of Image Quality Criteria for Passive Night Vision Devices, June 1974	027-000-00259-5
0801.00	Life Cycle Costing Techniques Applicable to Law Enforcement Facilities, May 1974	027-000-00284-6
0205.00	Automatic Vehicle Location Techniques for Law Enforcement Use, September 1974	027-000-00282-0
0502.00	Summary Report on Emergency Vehicle Sirens, September 1974	027-000-00289-7
0206.00	Repeaters for Law Enforcement Communications Systems, October 1974	027-000-00288-9
0305.00	Terms and Definitions for Intrusion Alarm Systems, October 1974	027-000-00290-1
0403.00	The Police Patrol Car: State of the Art, July 1976	027-000-00345-1
0307.00	Photographic Terms and Definitions, October 1975	027-000-00373-7
0101.01	An Evaluation of Police Handgun Ammunition (Summary Report, October 1975)	027-000-00374-5
0309.00	Directory of Security Consultants, October 1975	027-000-00372-9
0207.00	Electronic Eavesdropping Techniques and Equipment, September 1975	027-000-00362-1

NATIONAL INSTITUTE OF LAW ENFORCEMENT AND CRIMINAL JUSTICE GUIDES (NILECJ-GUIDE)

NILECJ-GUIDE	TITLE	GPO STOCK NO.
0301.00	Selection and Application Guide to Fixed Surveillance Cameras	027-000-00281-1

END