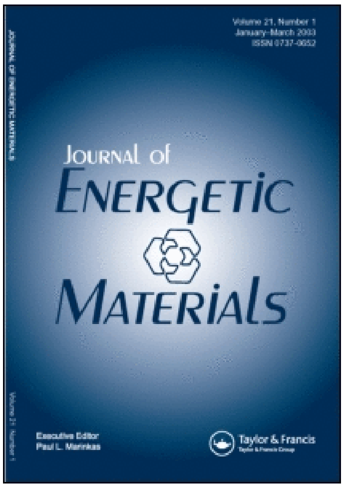


Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Transport and preconcentration of explosives vapors by liquid sampling modules

D. P. Lucero[a]; E. M. Boncyk[b]
[a] IIT Research Institute, Lanham, Maryland, USA [b] U.S. Army Belvoir RD&E Center, Fort Belvoir, Virginia, USA

To cite this Article Lucero, D. P. and Boncyk, E. M.(1986) 'Transport and preconcentration of explosives vapors by liquid sampling modules', Journal of Energetic Materials, 4: 1, 473 — 510
To link to this Article: DOI: 10.1080/07370658608011354
URL: http://dx.doi.org/10.1080/07370658608011354

TRANSPORT AND PRECONCENTRATION
OF
EXPLOSIVES VAPORS BY LIQUID SAMPLING MODULES

D.P. Lucero
IIT Research Institute
Lanham, Maryland 20706
USA

AND

E.M. Boncyk*
U.S. Army Belvoir RD&E Center
Fort Belvoir, Virginia 22060-5606
USA

ABSTRACT

For most explosives vapor detection scenarios, the lower detection limit (LDL) requirements are at part-per-trillion (ppt) concentration levels. Further sensitivity constraints are imposed on the detector modules by attendant sampling dilution and inefficient transport of explosives vapor molecules through the detection system sample train. Efficient transport and large preconcentration factors ($\simeq$ 100,000) can be achieved simultaneously by using a liquid sampling module, comprising a wetted-wall column in the sample train. Liquid sampling modules are interfaced most effectively to wet-chemical detectors. The

---

*Contact for reprints.

Journal of Energetic Materials vol. 4, 473-510 (1986)

Published in 1986 by Dowden, Brodman & Devine, Inc.

transport and preconcentration processor introduces a 60-s or longer lag to the overall system time rate-of-response depending on the preconcentration requirements. Despite the long delay time of liquid preconcentrators and the relatively slow rate-of-response time and limited sensitivity of wet-chemical vapor detectors, it appears that their use is feasible for some applications. For example, those detectors with a liquid transport and preconcentration sample train can monitor the atmosphere within enclosures such as rooms, buildings, etc. The inlet to the sample can be located at some convenient and effective point, e.g., in the main air conditioning or ventilation duct upstream of the blower.

An explosives vapor detection system comprising a liquid sampling module and a wet-chemical detector and their ancillary equipment can be an effective device for some applications. Integration of a liquid sampling module into a system can extend the LDL of an enzymatic bioluminescent TNT detection technique to an equivalent 0.001 ppt gas phase concentration. It is accomplished by the extraordinary sample preparation achieved by a liquid sampling module in the form of efficient sample transport and sample concentration.

Currently two liquid sampling modules for vapor detection systems are in development by the U.S. Army. Fort Belvoir is developing Spincon: a batch-type sampling module for an explosives detection system employing an enzymatic bioluminescent technique. The Aberdeen Proving Ground is developing BezeTrog: a continuous liquid sampling module for the detection of hazardous waste gas molecules in the flue streams employing a coloriometric technique.

A liquid sampling module is used as an end-line device interfacing directly with the detector. It contributes significantly to the detection system's performance in meeting the very stringent requirements imposed on explosives vapor detection systems. Although a liquid sampling module fits easily into the general scheme of a typical vapor detection network its design and implementation is a major engineering undertaking.

EXPLOSIVES VAPOR DETECTION SYSTEM REQUIREMENTS

The continuous and automatic analysis for vapors in air or any other similar atmosphere is performed by detection systems comprising three functional modules: a sample train, a calibrator, and a detector. Figure 1 illustrates the general pneumatic interfaces for each module and shows the system primary gas flow network. For a typical case of atmospheric analysis, air enters the sample train where it is processed to some degree and transported to the detector. In some applications, only a small fraction of the total sample train flow rate is transported as a sample bleed stream to the detector for analysis. To stabilize and adjust the detector response to the analyte molecule con-

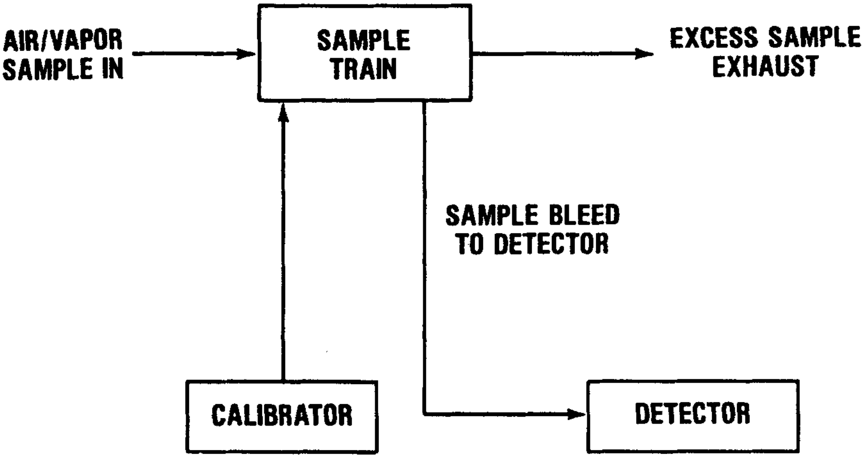


FIGURE 1 — VAPOR DETECTION

centration, calibration of the system is performed periodically with an air stream containing stable and known concentration levels of the analyte molecules. The calibration gas is supplied by the calibrator (Figure 1).

The use of a liquid sampling module in an explosives detection system is confined primarily as an appendage to the sample train. For explosives detection, it is used (1) promote efficient sample transport, (2) preconcentrate the sample, and (3) interface with a wet-chemical detector. Generally wet-chemical detectors do not possess the sensitivity limits that gas phase detectors possess. However, in a system using a sample train with a liquid sampling module promoting 100% efficient sample transport and preconcentration factors near 100,000, the system compares favorably with gas phase vapor detection systems for specific applications.

The efficient transport and large preconcentration factors obtained with a liquid sampling module affects a wet-chemical system very favorably. However, this performance does not provide relief nor significant design trade-off margin from the user requirements and corresponding performance specifications.

All design aspects of any system are constrained by the detection application and the corresponding user requirements. The relative importance of each module to the system and its functional characteristics are established by the user requirements, the performance specifications of each module, and specific characteristics of the analyte molecules. Table 1 lists the basic

TABLE 1 — EXPLOSIVES VAPOR DETECTION SYSTEM USER REQUIREMENTS(1)

APPLICATION(2)/ REQUIREMENT(3)	PROCESSING — ITEM/PERSONNEL EXAMINATION @PROCESSING STATION	SEARCHING — AREA SEARCH AND EXAMINATION	MONITORING — ENCLOSURE MONITORING
MAXIMUM MISSED-ALARM PROBABILITY	$<5 \times 10^{-4}$	$<5 \times 10^{-4}$	$<5 \times 10^{-4}$
MAXIMUM FALSE-ALARM PROBABILITY	$<5 \times 10^{-4}$	<0.05	$<5 \times 10^{-4}$
PROCESSING/ EXAMINATION RATE	15 (ITEM-PEOPLE/MIN)	28m^3 (1000 FT^3/MIN)	CONTINUOUS
MAINTENANCE INTERVAL (MONTHS)	6	1	6
UNSERVICED OPERATION (DAYS)	30	1	30

(1) FROM D.P. LUCERO, "USER REQUIRMENTS AND PERFORMANCE SPECIFICATIONS FOR EXPLOSIVE VAPOR DETECTION SYSTEMS," JOURNAL OF TESTING AND EVALUATION, 13, p 222-233, MAY 1985.

(2) PROCEDURAL ASPECTS OF APPLICATIONS, e.g., ITEM/PEOPLE RECYCLING, SEARCH TECHNIQUES AND ALARM DELAYS ARE NOT CONSIDERED.

(3) SEE REFERENCE (1) FOR SUBSTANTIATING DATA AND ASSUMPTIONS.

user requirements of an explosives vapor detection system for three applications:[1]

- Processing - item and personnel examination at a processing station, e.g., controlled and limited access areas.
- Searching - area search and examination for detection and location of hidden explosives.
- Monitoring - enclosure atmospheric monitoring of explosive vapors, e.g., auditoriums and transportation terminals.

The user requirements of Table 1 establish the corresponding explosives vapor detection system performance specifications[1] that define and dictate the system design and define and limit the performance trade offs available between the system modules. Table 2 lists the more important explosives vapor detection system performance specifications.[1]

Examination of Tables 1 and 2 illustrates the extraordinary performance demands on the detection system. The relatively low false- and missed-alarm probabilities allowed together with the rapid processing and examination rate establish a correspondingly low alarm set point concentration for the detection system. However, the absolute level of the alarm set point concentration can be ascribed more directly to particular characteristics of

TABLE 2 – EXPLOSIVES VAPOR DETECTION SYSTEM PERFORMANCE SPECIFICATIONS(1)

APPLICATION(2)/ SPECIFICATION(3)	PROCESSING-ITEM/ PERSONNEL EXAMINATION @ PROCESSING STATION	SEARCHING-AREA SEARCH AND EXAMINATION	MONITORING-ENCLOSURE MONITORING
MINIMUM DETECTABLE CONCENTRATION @ SAMPLE TRAIN INLET, ppt	1	1	0.001
MAXIMUM ALLOWABLE ALARM SET POINT CONCENTRATION, ppt	5	5	0.005
MAXIMUM ALLOWABLE FALSE ALARM PROBABILITY @ 5 ppt	$< 10^{-4}$	< 0.04	10^{-4}
MAXIMUM ALLOWABLE MISSED ALARM PROBABILITY @ 10 ppt	$< 10^{-4}$	< 0.04	$< 10^{-4}$
MAXIMUM FALSE ALARM PROBABILITY WITH INTERFERENT @ 1 ppt(4)	2.3×10^{-3}	< 0.06	2.3×10^{-3}
MAXIMUM MISSED ALARM PROBABILITY WITH INTERFERENT @ 1 ppt(4)	2.3×10^{-3}	< 0.06	2.3×10^{-3}

(1) FROM D.P. LUCERO, "USER REQUIREMENT AND PERFORMANCE SPECIFICATIONS FOR EXPLOSIVE VAPOR DETECTION SYSTEMS," JOURNAL OF TESTING AND EVALUATION, 13, p 222-233, MAY 1985

(2) PROCEDURAL ASPECTS OF APPLICATIONS, e.g., ITEM/PEOPLE RECYCLING, SEARCH TECHNIQUES AND ALARM DELAYS ARE NOT CONSIDERED.

(3) SEE REFERENCE (1) FOR SUBSTANTIATING DATA AND ASSUMPTIONS

(4) FOR MAXIMUM DETECTOR NOISE & DRIFT @ ± 1.2 ppt; MAXIMUM INTERFERENCE EQUIVALENT RESPONSE @ ± 1 ppt.

explosives vapor molecules. More specifically, explosives exert very low vapor pressures[2] at or near room temperatures, and the vapor molecules are highly polar and thus adsorb strongly to all surfaces.[3-5] These characteristics result in proportionally low vapor concentration levels at equilibrium and in low transport efficiencies in moving the gas sample through the sample train to the detector. The combination of these characteristics together with the packaging, location, and rapid detection requirements of a clandestine explosives cache establish the critical performance specifications of the detection system: low minimum detectable concentration and maximum allowable set point concentration. The maximum allowable false- and missed-alarm probabilities together with the alarm set point concentration establish the detection system instability limits, i.e., noise and drift and, of equal of importance, the maximum allowable interferent equivalent response.[6]

Currently, it appears that the performance specifications of Table 2 are at or beyond the state-of-the-art for explosives detection systems and detectors, including electron capture, ion mobility spectrometer, and mass spectrometer modules available commercially.[7-10]

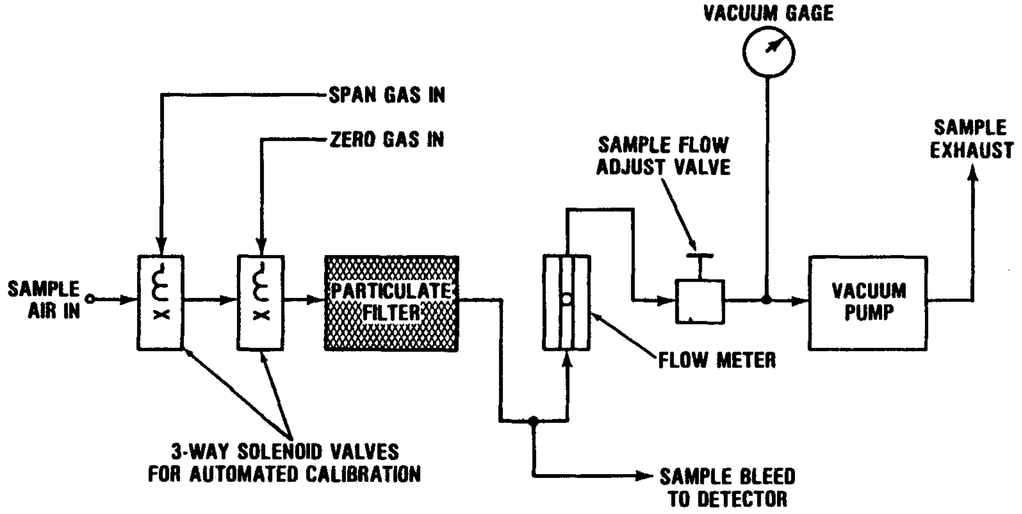
Because the time rate-of-response of wet-chemical vapor detector systems is relatively slow, its applications in explosives vapor detection are limited to the monitoring applications described. Although the system may respond slowly, its minimum detectable concentration specification is relatively low: ≈ 0.001

parts per trillion(ppt). The large preconcentration factor provided by a sample train using a liquid sampling module permits the system to detect 0.001 ppt concentration levels as discussed later.

THE SAMPLE TRAIN

In its simplest and most widespread configuration for manual or higher concentration level systems(>1 part per billion), the sample train is merely a segment of tubing: it transports the sample to the detector. More sophisticated configurations include in-line elements and components that provide the means for automatic field operation, e.g., sampling and calibration for both zero and span. In addition, other in-line devices are present to monitor or supply information regarding the status of the sample train operation and to extend its service or maintenance period. (See Figure 2.) The network downstream of the junction tee for the sample bleed line provides sample air flow rate control and adjustment and operating status regarding the pneumatic condition of the vacuum pump and the system pressure drop. This is essential information that eases troubleshooting, maintainability, and serviceability. As configured upstream of the junction tee, the network described is probably impractical as a sample train for an explosives vapor detection system. Three in-line components are present: two solenoid valves and a particulate filter. These components usually contain relatively large dead volumes and

FIGURE 2 — SAMPLE TRAIN



correspondingly large amounts of surface area onto which explosives vapor molecules will adsorb. For practical use of a sample train of this configuration, special purpose components that minimize the total dead volume and surface area and that can operate at elevated temperatures[3,4] must be used upstream of the sample bleed line. Automated calibration is in most cases impractical due to the adsorption on the solenoid valve surfaces. Other means of automating calibration must be invoked. In addition, the particulate filter should be relocated in-line between the junction tee and the flowmeter. This change is recommended despite the fact that more airborne debris will be ingested by the detector. Adherence to this design approach is prescribed to minimize explosives vapor molecule surface adsorption and to eliminate the attendant spurious signal characteristics associated with the inefficient and variably inefficient transport of vapor molecules in the sample train and sample bleed line.

The design of an automated, relatively maintenance-free sample train for the efficient transport of explosives vapor molecules is a major engineering undertaking for a detection system operating to the performance specifications of Table 2. Designing to these constraints severely compromises the simplicity of the sample train, even though the main function of the sample train is to provide only efficient sample transport. Introduction of other functional requirements to the sample train will further constrain the design options and consequently bestow more complications.

SAMPLE PRECONCENTRATION

Over the past several years, designers of explosives vapor detection systems have introduced significant changes to the function and form of the sample train. It is being transformed from solely a sample transport module into a transport and sample processing module. This change is driven by user requirement demands to augment the detection system's lower detection limit (LDL) and to ensure the system approaches more closely the performance specifications of Table 2.

The sample processing is denoted more specifically as sample pre-concentration. In general terms, it is the action of processing or transforming a large air volume containing explosives vapor molecules at low concentrations into a small air or gas volume containing explosives vapor molecules at proportionally higher concentration levels. Thus sample preconcentration will provide a sample concentrated or amplified in the analyte species within range of the detector module response limits or LDL concentration. For example, a sample train with a preconcentrator permits a detector with a 1-ppt LDL to respond to an explosives vapor air sample at lower concentration levels proportional inversely to the sample train preconcentration factor.

In general terms, the degree of sample concentration or amplification obtained from a preconcentrator is described by its preconcentration factor:

$$P_f = C_o/C_i \tag{1}$$

P_f = preconcentration factor, dimensionless;

C_o = explosives vapor concentration out of the preconcentrator, ppt; and

C_i = explosives vapor concentration into the preconcentrator, ppt.

Equation (1) does not describe the form or the sample train sample processing action of the preconcentrator. A more descriptive analytical model of the preconcentration operation is obtained from an engineering analysis of its operating principles and parameters and specific preconcentrator configuration.

Gas Phase Preconcentration

Adsorption-desorption action is the operational basis of most gas phase preconcentrators. Usually it is implemented in a discontinuous or batch sampling mode,[10] although some engineering efforts have been devoted to developing continuous adsorption-desorption preconcentrators.[11] In many cases, the gas concentrator module serves a dual function: preconcentration and elimination or reduction of interfering atmospheric substances such as oxygen, water vapor, common air pollutants, etc., which may generate spurious detector signals or interfere with the signal mechanism.

Briefly, discontinuous preconcentration is characterized by the operation of adsorption cartridges or surface elements.

Sample air is passed through the cartridge at relatively high flow rates. The explosives vapor molecules are adsorbed with an efficiency dependent upon the cartridge geometry, dimensions, and sample air flow rate and dwell time in the cartridge. Subsequently, the cartridge is sealed and heated to an elevated temperature to desorb the explosives vapor molecules and yet not decompose them. This action is followed by removal of the molecules from the cartridge by a purge gas that flows through the preconcentrator at a lower rate for a relatively short time.

The preconcentration factor of discontinuous sampling preconcentrators is described as a function of its operating parameters:

$$P_f = [\, Q_i \, (\Delta t)_i / Q_o (\Delta t)_o \,] \, \eta_i \eta_o \tag{2}$$

Q_i = sample gas flow rate into the preconcentrator, l/min;

Q_o = purge gas flow rate out of the preconcentrator, l/min;

$(\Delta t)_i$ = sampling time increment, min;

$(\Delta t)_o$ = purge time increment, min;

η_i = preconcentrator adsorption efficiency, dimensionless; and

η_o = preconcentrator desorption and sample removal efficiency, dimensionless.

Continuous preconcentrators are typified currently by a rotating adsorbing surface matrix attached to belts, wheels, etc.[11] Relatively large volumes of slow moving air pass through slots adjacent to the adsorbing elements, which can be loosely woven belts or screens coated with an adsorbing film.[12] After the adsorption matrix passes the sample air slot, it is heated quickly by electrical, radiative, or convective means to desorb the explosives vapor molecules. Almost simultaneously, as the adsorbing surface passes a slot through which purge gas flows, the purge gas flows through the surface matrix and transports the vapor molecules downstream to the detector. The preconcentration factor for a continuous sampling preconcentrator is described as a function of its operating parameters:

$$P_f = [\,Q_i/Q_o](\eta_i \eta_o) \qquad (3)$$

A cursory examination of equations (2) and (3) reveals that for a 100% efficient process, P_f is a function directly of the preconcentrator flow rate ratio (Q_i/Q_o). At high sample and low purge gas flow rates, e.g., Q_i = 100 l/min and Q_o = 0.1 l/min, preconcentration factors near 1000 can be achieved. However, it is not simple to perceive such high levels for both η_i and η_o. The geometry, configuration, and dimensions of a cartridge to achieve high η_i and η_o are at cross-purposes for such a disparity in Q_i and Q_o. Thus, it appears that the best compromise in the cartridge design and operation is that which yields $\eta_i = \eta_o = 0.5$, and for this case, a maximum P_f = 250 would be obtained. On the basis of limited experience, it appears that large preconcentration factors (P_f>250) are not attainable in a single adsorption/desorption stage. However, gains in P_f can be achieved by increasing ($\Delta t)_i$ in batch preconcentrators with proportional increases in the detection system response time.

Despite the amount and intensity of work devoted to preconcentration, quantitative measurements of P_f have not been reported as defined by equations (1), (2), or (3). Designers and users of preconcentrators have descried the efficacy of preconcentrators only in the before-and-after response of detectors with and without a preconcentrator in the sample train.

Gas/Liquid Phase Preconcentration

The extraction of explosives vapor molecules from an air sample stream followed by their solution in a liquid medium is the basis of gas/liquid preconcentration. Bubblers, spargers, etc., used as samplers for subsequent laboratory analysis are the precursors of gas/liquid preconcentrators. The primary constraint on these preconcentrators is that of miscibility of explosives vapor molecules in the liquid medium. In addition, to obtain and utilize the relatively large preconcentration factors available from gas/liquid preconcentrators, it is essential that they interface with wet-chemical detectors. Otherwise another extraction step is necessary to interface with a gas phase detector.

As mentioned earlier, two gas/liquid preconcentrators are currently in development for the U.S. Army: the Spincon[13] for Fort Belvoir and BezeTrog[14] for the Edgewood Arsenal. Both operate on the principles of wetted-wall column gas extraction. Spincon is an intermittent or batch sampler; BezeTrog operates on a continuous basis.

A wetted-wall column gas extractor or preconcentrator is a mass exchange device that removes specific molecules from a gas stream and deposits them in solution, in a liquid film stream. Gas flows through the core of the column while the liquid flows as an annular film attached to the column's inside surface. Film flow is promoted mainly by the aerodynamic drag forces arising from the gas stream shearing action on the liquid film at the liquid-gas interface. In the process, a thin laminar boundary layer of gas is formed at the liquid-gas interface. The diffusional transport of gas molecules through the gas boundary to the liquid film is the rate-limiting step of the mass exchange process. As the sample molecules traverse the boundary layer, they are absorbed into solution by the liquid film. High solubility ensures that the sample holding capacity of the liquid film is large, which leads to relatively high exchange efficiencies, and, equally important, does not limit the preconcentration action. Mass exchange efficiency is determined by the column dimensions, gas transport and thermodynamic properties, gas velocity, and more specifically, molecular diffusion and mass transfer coefficients of the sample gas molecules, TNT.

The preconcentration factor of the Spincon sample processor is described by the expression

$$P_f = \eta_s Q_g (\Delta t)/V_l \tag{4}$$

Q_g = gas flow rate, ml/min;

(Δt) = gas sampling time increment, min;

V_l = liquid sample volume obtained from the column, ml; and

η_s = Spincon TNT mass exchange or collection efficiency, dimensionless.

The preconcentration factor of the BezeTrog sample processor is

$$P_f = \eta_B Q_g/Q_l \tag{5}$$

η_B = BezeTrog TNT mass exchange or collection efficiency, dimensionless, and

Q_l = liquid flow rate, ml/min.

It is apparent that the Spincon and BezeTrog sample processors are identical in concept but depart in geometry, configuration, and operating modes. The mass exchange efficiency of each is dependent functionally on identical parameters. For the Spincon sample processor, the mass exchange efficiency is[15]

$$\eta_s = 1 - \exp\left[\frac{-4\ k_m\ S\ D_t}{V_g\ (D_t^2 - D_i^2)}\right] \tag{6}$$

S = column length, cm;

k_m = TNT mass transfer coefficient of the gas boundary layer, cm/s;

V_g = average gas velocity in the column, cm/s;

D_t = column diameter, cm; and

D_i = semi-stagnant air core diameter, cm.

The airflow within the Spincon sample processor moves in a circular helical fashion along the column circumference, as described below. Because of this airflow pattern, a core of semi-stagnant air or air moving upward at a relatively low velocity exists within the sample processor. Thus the larger fraction of TNT transport is from the higher velocity air adjacent to the liquid film. D_i in equation (6) reflects this condition.

For the BezeTrog sample processor, the mass exchange efficiency is[16]

$$\eta_B = 1 - \exp\left[\frac{-4\ S\ k_m}{V_g\ D_t}\right] \qquad (7)$$

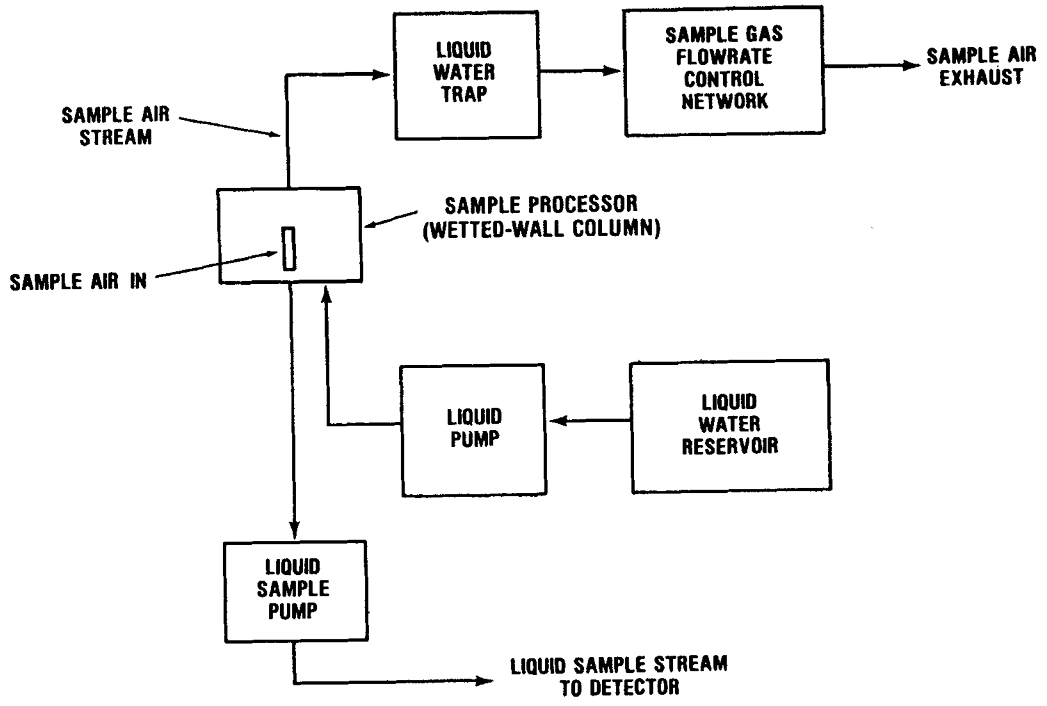
Note that equations (6) and (7) contain the gas stream residence time in the column as a ratio of tube length to gas velocity (S/V_g). Further examination shows that the liquid film hydrodynamic properties--flow rate, velocity, and thickness--are absent. The effect of changes in the liquid film parameters on gas exchange efficiency is usually negligible for most conditions sustaining film flow.

SPINCON

The Spincon preconcentrator system comprises a wetted-wall column liquid water sampling module or sample processor and its attendant hydraulic and pneumatic networks. Figure 3 illustrates the Spincon system schematically. The functional center of the system is the sample processor. All other subsystems and modules act to support its operation. Sample air enters the sample processor where it immediately encounters the liquid water film, and the TNT vapor molecule collection process begins. Upon emerging from the sample processor, the air sample stream flows through the liquid water trap to the sample gas flow rate control network and is vented from the system. Because of mist carryover in the sample air stream, a liquid water trap is required to prevent liquid water from interfering with the downstream gas flow rate control and monitoring components. The flow rate control network comprises a flow rate, a flow adjustment valve, and a vacuum blower. Liquid water is supplied to the sample processor from a reservoir through a liquid pump as shown by Figure 3. At the end of the air sampling process, the liquid water remaining in the sample processor is transported by the liquid sample pump to the detector.

Note that the sample processor is an end-line device in the sample train, i.e., the air sample enters the sample train through the sample processor directly. There are no intermediate components, tubing segments or fitting, or any other interfaces present. Only the liquid film is present as an adsorbing surface. For these conditions, there are no TNT vapor losses to surfaces in entering or traversing the sample processor. Subsequently all

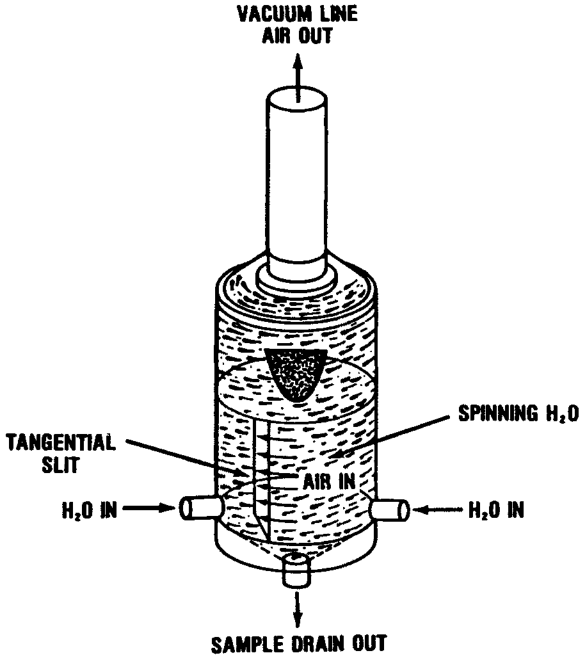
FIGURE 3 — SPINCON PNEUMATIC/ HYDRAULIC NETWORK



sample handling is performed in the liquid phase. Thus the explosives detection system with a Spincon sample preconcentrator performs the sample transport function at near 100% efficiency.

The sample processor is configured in the form of an upright circular cylinder with a small length-to-diameter (L/D) ratio ($L/D \simeq 1.5$) as depicted by Figure 4: L = 7.6 cm, D = 5.1 cm. Its wall and ends are penetrated by access ports to introduce and remove liquid water and the sample air stream. A sampling cycle consists of three steps: liquid water injection, air sampling, and liquid water sample removal. Initially, the sample processor is charged with 3 ml of liquid water by the liquid pump. The vacuum blower is turned on, and air is sampled at 150 l/min for a set time period. Sample enters the tangential slit shown in Figure 4. The slit is 38 mm long and 0.9 mm wide. At a 150-l/min sampling rate, the air velocity in the slit is 7180 cm/s and the Reynolds number is 8700. These aerodynamic conditions are conducive to maintaining film or annular liquid water flow immediately downstream of the entrance,[16] i.e., the flow is turbulent (Reynolds number = 8700) and the gas velocity is above 500 cm/s. However, some liquid water is entrained by the air stream in the form of mist particles at the entrance because of the relatively high gas velocity. The water entrainment accounts for the sample processor water loss over that required to saturate the air stream. Also there is a reasonable certainty that some fraction of TNT extracted from the air stream is carried out of the sample proc-

FIGURE 4 — SPINCON LIQUID SAMPLING MODULE



essor dissolved in the mist particles. Within the sample processor, the aerodynamic conditions continue to promote liquid flow on the column wall in an upward circumferential direction, i.e., helical. Assuming that the bulk of the air sample also flows in an upward circumferential fashion and in a 1.3-cm annular gap, the air velocity is 520 cm/s and the Reynolds number is 6720. The TNT mass transfer coefficient (k_m) of equation (6) at these conditions and for a TNT molecular diffusion coefficient of 0.043 cm^2/s is 0.98cm/s.[16] It is estimated by equation (6) that the TNT sample processor collection efficiency is 37% at the operating condition described above.

Experiments were performed with the Spincon sample processor to measure its TNT collection efficiency.[13] The results show η_s was close to that estimated at the lower sample processor air flow rates ($\approx$ 100 l/min) and near 52% at larger flow rates ($\approx$150 l/min). It is suggested that the higher η_s measured indicates that a second mass transport process is acting within the sample processor. As mentioned previously, liquid water entrainment at the sample processor entrance slit can form mist particles, which themselves collect and dissolve TNT vapor molecules. Because it is probable that some fraction of the mist population formed is deposited subsequently on the liquid water film, the overall effect is to increase the apparent Spincon TNT collection efficiency. It is probable that the effect can be reversed if a larger fraction of TNT is collected by the mist than by the liquid film or if a smaller fraction of the mist population is deposited on the liquid film. Because TNT vapor molecules may be collected by the liquid film and mist particles, it is prudent to not extrapolate TNT collection efficiency data beyond the sample air flow rates of the experiments.

This observation suggests that a spray or mist form of liquid water is more efficient in collecting vapor molecules than a liquid water film of equal mass. This observation seems reasonable solely due to the larger surface area developed by the mist. An engineering analysis shows that other effects work at cross purposes. For example, a larger charge of liquid water is required to make up for increased mist carryover into the exhaust. This dilution effect is significant and can negate the increased vapor collection efficiency of the mist.

At the end of the air sampling period, the vacuum in the sample gas flow rate control network is shut down, the airflow ceases, and the liquid water film collapses to the bottom of the cylinder. Subsequently, the liquid water containing the extracted TNT is transported by the action of the liquid sample pump to the detector for analysis. When 2 ml of liquid water sample is obtained at the end of a 5-min sampling period, the experimental Spincon preconcentration factor is 2×10^5.[13] It is a very significant preconcentration factor.

BEZETROG

The BezeTrog preconcentration system also comprises a wetted-wall column liquid sampling module or sample processor and its attendant hydraulic and pneumatic networks. Figure 5 illustrates the BezeTrog system schematically. It is very similar to the Spincon system: the sample air enters the sample processor where it encounters immediately the liquid water film, and the TNT molecule collection process begins. At the sample processor exit, a stream splitter separates the air and liquid into two streams as shown by Figure 5. The sample air flows to the flow rate control network comprising components and devices similar to the Spincon preconcentrator and is vented from the system. Simultaneously the liquid water sample stream is transported to the detector by the sample liquid pump.

As with the Spincon system, the BezeTrog sample processor is an end-line device in the sample train and promotes a sample transport function at near 100% efficiency.

The BezeTrog sample processor is the functional center of the system. It is configured in the form of a coiled tube with a large L/D ratio (L/D = 360) as depicted by Figure 6: L = 458 cm, D = 1.27 cm. Sample air and liquid water enter the sample processor through a liquid injector assembly and flow through the length of the tube. At the tube exit, the liquid and gas stream are kept separate by the stream splitter assembly[16] through which the fluid streams flow to the sample gas flow rate control network and the sample liquid pump shown in Figure 6.

Aerodynamic conditions conducive to forming and maintaining liquid film flow are attained at a 150-l/min sample air flow rate.

FIGURE 5 — BEZETROG HYDRAULIC/ PNEUMATIC NETWORK

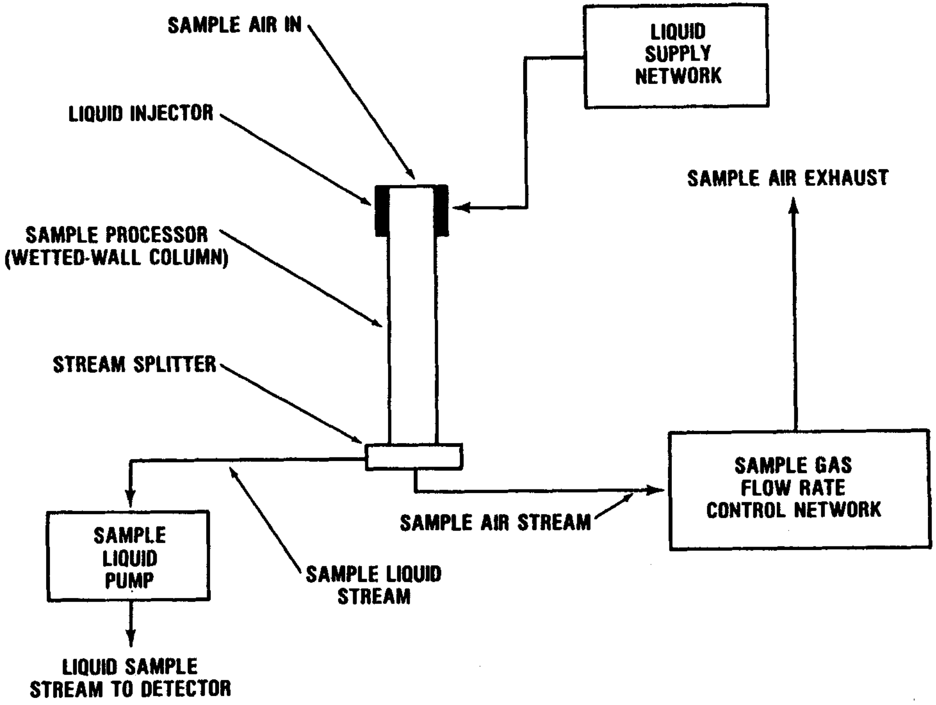
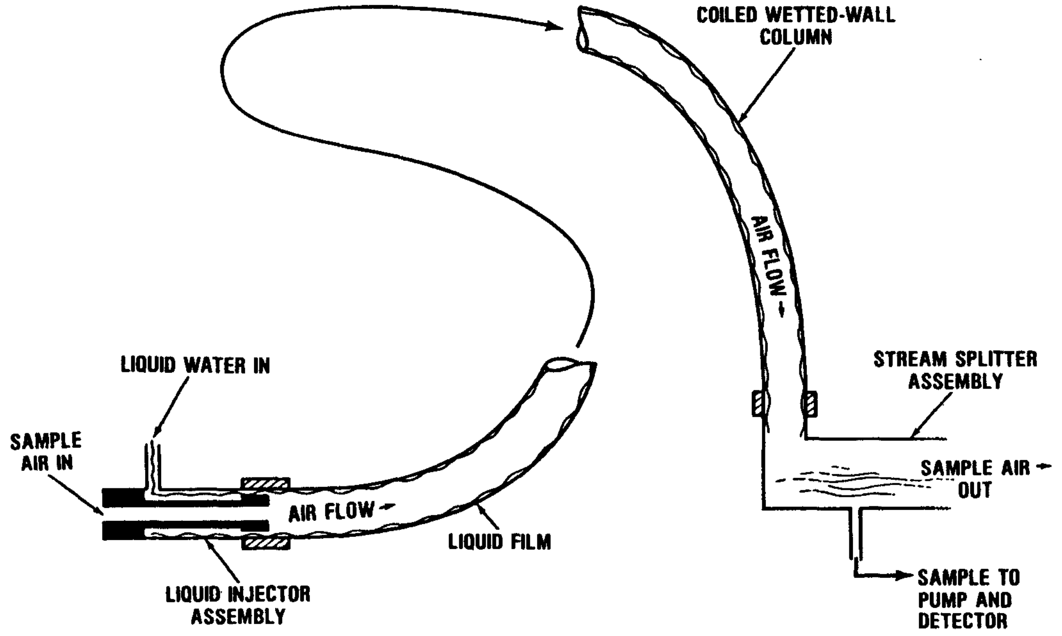


FIGURE 6 — BEZETROG LIQUID SAMPLING MODULE



These conditions are 1980 cm/s air velocity and 17,100 Reynolds number. The TNT mass transfer coefficient (k_m) of equation (7) at these conditions for a TNT molecular diffusion coefficient of 0.043 cm^2/s is 3.09 cm/s. It is estimated by equation (7) that the TNT collection efficiency of the BezeTrog liquid sampling module is 90% at the operating conditions listed above.

Some experimental data are available relative to the BezeTrog sample processor collection efficiency.[17] The experiments were performed with tributylamine vapor at approximately 23-ppb concentration levels in air. The tributylamine was collected with an apparent 70% collection efficiency. Because of the experimental conditions and equipment used, the measured efficiency included the production and transport efficiency of a vapor generator and the gas mixing efficiency of a simulated incinerator flue used in series with the BezeTrog sample processor. It is very probable that the BezeTrog sample processor collection efficiency approaches the 90% level discussed earlier. For example, a measured 70% collection efficiency is obtained when the vapor generator and simulated flue efficiencies are 90% each, i.e., the BezeTrog, vapor generator, and simulated flue modules operating at 90% efficiency will yield an overall or measured efficiency close to 70%.

When 2 ml/min of liquid water sample is produced, the experimental BezeTrog preconcentrator factor is 6.7×10^4. This is a very significant preconcentration factor and is extremely significant for a continuous preconcentrator.

APPLICATION

Air explosives vapor detection systems using a gas/liquid phase preconcentrator or a liquid sampling module in the sample train attain maximum utility for the system using a wet-chemical detector. For systems with gas phase detectors, a special-purpose interface is required to transpose the vapor molecules collected in liquid solution into gas solution with a minimum loss in the preconcentration level achieved. To examine the most fitting application in explosives vapor detection, the Spincon and BezeTrog preconcentrators' operating parameters discussed earlier are listed in Table 3. It is revealing to compare them to the requirements and specifications of Tables 1 and 2 for the applications listed. The performance specifications of the detector module need not be considered to make prudent judgements regarding the utility of Spincon and BezeTrog: the processing and examination rate requirement for the processing and searching applications is significantly beyond the performance of Spincon and BezeTrog. On the basis of 15 examinations/min for the processing application, the time rate-of-response of the vapor detector must be less than 4 s. For the searching application, Spincon and BezeTrog would require 187 min to process 28 m^3 of gas. Thus, even with a detector possessing instant response, both preconcentrators introduce untenable delays.

The monitoring application, however, is amenable. For example, consider a scenario in which a building or a large room

TABLE 3—SPINCON AND BEZETROG OPERATING CHARACTERISTICS

PARAMETER	PRECONCENTROR		REMARKS
	SPINCON	BEZETROG	
PRECONCENTRATION FACTOR (P_f)	200,000	67,000	SPINCON P_f ACHIEVED AFTER 5 MINUTES OF SAMPLING. BEZETROG P_f ACHIEVED AFTER 1 MINUTE DELAY IN LIQUID TRAVERSING WETTED-WALL COLUMN
CALCULATED TNT VAPOR MOLECULE COLLECTION EFFICIENCY (η)	37	90	1) MOLECULAR DIFFUSION COEFFICENTS ESTIMATED BY GILLILAND METHOD, IND. ENG. CHEM., 26, 681 (1934); 2) MASS TRANSFER COEFFICIENTS ESTIMATED BY SHERWOOD EQ., ibid.
MEASURED VAPOR MOLECULE COLLECTION EFFICIENCY (η)	0.53	0.70	1) SPINCON η MEASURED DIRECTLY FOR TNT "IN" VERSUS "OUT" IN LIQUID SAMPLE. 2) BEZETROG η MEASURED FOR TRIBUTYLAMINE (TBA). MAXIMUM ESTIMATED BEZETROG η FOR TBA IS 0.85.
SAMPLE AIR FLOW RATE (ℓ/min)	150	150	
SAMPLE LIQUID WATER STREAM (mℓ/min)	0.4	2	SPINCON PRODUCES A 2mℓ LIQUID WATER SAMPLE AFTER 5 MINUTES OF SAMPLING.
TIME DELAY (MIN)	5+	1	DELAY IN TRANSPORTING LIQUID SAMPLE TO DETECTOR IS NOT INCLUDED.
OPERATING MODE	BATCH	CONTINUOUS	
LIQUID TNT CONCENTRATION FOR 0.001 ppt SAMPLE AIR CONCENTRATION, gm/mℓ	2×10^{-12}	7×10^{-13}	1) SPINCON TNT LIQUID CONCENTRATION BASED ON MEASURED η_S 2) BEZETROG TNT LIQUID CONCENTRATION BASED ON CALCULATED η_B

is under continuous 24-h explosives vapor surveillance. One likely sampling location is the return manifold of the air conditioning duct work, i.e., the manifold leading to the blower and upstream of the filters and heat exchanger coils or fins. At this location, the explosives vapor concentration will approach 0.001 ppt for a TNT source emitting 1×10^{-9} l/min of TNT vapor.[1,5,18]

A Spincon preconcentrator operating on a 5-min cycle at 150 l/min will produce a 2-ml liquid sample with a TNT concentration of 8.9×10^{-15} moles/ml or 1.9×10^{-12} g/ml. The BezeTrog preconcentrator operating continuously at 150 l/min will produce a 2-ml/min liquid sample with a TNT concentration of 3×10^{-15} moles/ml or 7×10^{-13} g/ml.

The explosives vapor detection system or, more accurately, the TNT vapor detection system requires a detector module with an LDL near 0.2×10^{-12} to 2.0×10^{-12} g/ml. A recent survey of wet-chemical detectors available commercially with an LDL near this requirement has not been performed, Several years ago, the LDL for high performance liquid chromatography (HPLC) systems was reported to be near the low 10^{-9} g/ml or 4.39×10^{-12} mole/ml range.[19,20] On this basis, HPLC systems are out of range by a factor of 100 for the Spincon and BezeTrog liquid sampling modules.

However, a liquid chromatographic system with a TEA (thermal energy analyzer) detector is reported to display LDL levels near 5×10^{-12} g/ml.[21] This detection system interfaced with either a Spincon or BezeTrog preconcentrator appears to be within range of the 0.001-ppt explosives vapor level for the monitoring application of Tables 1 and 2.

Recent work on enzymatic bioluminescent detection techniques for TNT reported an LDL near 5 x 10^{-14} mole/ml or 1.1 x 10^{-11} g/ml.[22] An explosives vapor detector system comprising this enzymatic detector and a sample train with a Spincon or BezeTrog preconcentrator subsystem also approachs the user requirements and performance specifications for the monitoring application discussed in Tables 1 and 2. The integration of these modules into an explosives vapor detector exhibits significant promise of success for this application, and it is in the early stages of development. To date, only experiments with the breadboard models of individual modules have been performed. The modules have not been integrated into a breadboard system.

Although the enzymatic detection technique is limited to TNT, it may be that other bacteria can be grown on other medium exploiting the methodology developed for TNT.[23] The TNT methodology included a search for TNT- and DNT-specific enzyme systems; the search was conducted on soil microorganisms. Microorganisms that transform TNT were isolated from soil samples taken from a TNT dump site. The enzymes responsible for the TNT transformation were extracted, partially purified, and characterized with respect to suitability for the proposed detector system. The enzyme chosen, TNT reductase, was deemed suitable for the detector system because it was specific for TNT and DNT and could provide chemical linkage with luciferase reactions. The final method of detection involves coupling the TNT-specific enzyme reaction with a highly sensitive bioluminescent reaction. Bacteria living on EGDN, DNT, RDX, and PETN molecules would produce the corresponding enzymes sensitive to these vapors. A mixture of the enzymes may be the basis of a single explosives module responsive to these explosives vapors.

REFERENCES

(1) D.P. Lucero, J. Test. Eval., 13., 222-233 (1985).

(2) P.A. Pella, Anal. Chem. 48 (1976).

(3) P.K. Peterson and F.J. Conrad, in "Proceedings, New Concepts Symposium and Workshop on Detection and Identification of Explosives", NTIS No. PB296055, 1978, p.85.

(4) D.P. Lucero, in "Proceedings, New Concepts Symposium and Workshop on Detection and Identification of Explosives", NTIS No. PB296055, 1978, p.65.

(5) C.T. Pate, "Characterization of Vapors Emanating from Explosives", LEAA Contract J-LEAA-025-73, Analytical Research Laboratories, Inc., June 1975.

(6) Federal Register 40, 33, (1975).

(7) W.D. Williams and J.K. Syverson, "Explosives Detector Field Tests", Research and Development Division, Bureau of Alcohol,

Tobacco and Firearms, U.S. Department of the Treasury, Washington DC, April 1981.

(8) J.A. Buckley, J.B. French and N.M. Reid, in "Proceedings, New Concepts Symposium and Workshop on Detection and Identification of Explosives", NTIS No. PB290055, 1978, p. 109.

(9) R.F. Wernlund, M.J. Cohen and R.C. Kindel, in "Proceedings, New Concepts Symposium and Workshop on Detection and Identification of Explosives", NTIS No. PB290055, 1978, p.185.

(10) W.D. Williams and J.K Syverson, "Explosives Detector Field Tests", Research and Development Division, Bureau of Alcohol, Tobacco and Firearms, U.S. Deparment of the Treasury, Washington DC, April 1981, pp 24-34.

(11) P.J. Thomas, J.H. May, D.E. Elisco and F.J. Conrad, in "Proceeding, New Concepts Symposium and Workshop on Detection and Identification of Explosives", NTIS No. PB296055, 1978, p 81.

(12) F.J. Conrad, T.A. Burrows and W. David Williams, "Selection of a Gas Chromatographic Material For Use In Explosives Vapor Preconcentration", Sandia Laboratories, Albuquerque, New Mexico, August 1978.

(13) B.R. Cage, "Design and Develop a Vapor/Liquid Interface, Project Status Report No. 2", Belvoir Research, Development, and Engineering Center Contract DAAK70-83-C-0068, August 1985.

(14) D.P. Lucero "BezeTrog: An Engineering and Configuration Analysis", TR-86(6174)-1, IIT Research Institute, Lanham, Maryland June 1986.

(15) A.H.P. Skelland, "Diffusional Mass Transfer", John Wiley & Sons, New York, 1974, pp. 266-268.

(16) D.P. Lucero, J. Chromatog. Sci. 23, 293, July 1983.

(17) T.G. Albro, "BZ Stack Alarm Acceptance Package", US Army Toxic and Hazardous Materials Agency, Department of the Army, Aberdeen Proving Ground, Maryland, July 1986.

(18) G.I. Senum, R.P. Gergley, E.A. Cote, and R.N. Diety, "Detection of Vapor Taggants Used for Explosive Predetonation Detection in a Boeing 727 Aircraft", Report BNL-27099, Brookhaven National Laboratory, September 1979.

(19) J.O. Doali and A.A. Juhasz, Anal. Chem. 48, 1859 (1976).

(20) J.O. Doali and A.A. Juhasz, J. Chromatag. Sci. 12, 51 (1974).

(21) Personal Communication, J. Hobbs, Transport Systems Center, U.S. Department of Transportation Kendall Square, Cambridge, MA USA.

(22) D. Vellom, J. Hinkley, A. Loucks, H. Egghart and M. Deluca, "Analytical Applications of Bioluminence and Chemiluminescence", The Academic Press, Inc., 1984, p. 133.

(23) Interview with Dr. Marlene DeLuca, Professor of Chemistry, University of California, San Diego, San Diego, CA, May 7,1986.

ACKNOWLEDGEMENTS

The authors also thank Susan Hendrickson of the IITRI - East Engineering staff for organizational and editorial services in the preparation of this manuscript.