TEST GAS MIXTURES -
THE BRIDGE FROM SENSING TO QUANTIFICATION

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ABSTRACT

Test gas mixtures are the key tools required to take a sensing technique from the laboratory curiosity stage to the reliable measurement technique stage. Yet relatively little attention is given to the definition, production and delivery of effective test mixtures. Factors addressed in this presentation are test mixture requirements, techniques for creating known trace concentration mixtures of reactive vapors, atmosphere simulation, interferent identification, and test mixture delivery. For compounds that are reactive or have limited stability, test mixtures must be dynamically blended and used immediately. Techniques for creating trace concentration mixtures (ppm, ppb, ppt) are reviewed and compared together with strategies for effectively delivering the mixtures to a test chamber.

INTRODUCTION

Throughout the last thirty plus years, detection and measurement of trace concentrations of explosive compound vapors has been an ongoing and increasingly important field of study throughout the world. The challenges of this field are unique. There is a wide range of compounds. Some have very low vapor pressure, so that the maximum concentration possible at ambient conditions is in the low ppb or ppt range. Some products are multi-component formulations, and many of the compounds are notoriously adsorptive.

This work has resulted in the development of methodologies ranging from detection by canines to ion mobility spectroscopy to luminescence and antibodies. In the course of this work, test gas generators for explosive compound vapor have been designed and evaluated by several workers for testing the stability, limits of detection, etc. But to compare the various technologies and evaluate potential for 'real world' applications, one must have reliable (preferably traceable) gas standards of explosive and 'marker' compounds that simulate 'real world' samples where there is a variable range of temperatures and relative humidity. Additionally, there may be diesel fumes, vegetation emissions, insect repellants, cleansers, paint fumes, etc., in any combination. Creating effective test atmospheres for explosives detector evaluation is itself a major undertaking.

REQUIREMENTS & CHALLENGES

The low vapor pressure characteristics of explosive compounds dictate that effective detection requires sensitivity of at least low parts-per-billion (ppb) and ranges down through the parts-per-trillion (ppt) and into the parts-per quadrillion (ppq) regions. Table 1 lists a few explosive compounds together with published vapor pressure data and the maximum concentrations of vapor expected at the source at 25°C.

TABLE 1
PROPERTIES OF EXPLOSIVES AND RELATED COMPOUNDS

Compound	MW (gm/mol)	BP (°C)	VP @ 25°C (torr)	Max. Conc. @ 25°C (ppb v/v)	K_0 (l/gm@STP)	Comments
Nitrobenzene	123.1	210	2.4×10^{-1}	316,000	0.181	Perm Tube ~1 – 5,000ppb (single dil.)
2 Nitrotoluene	137.1	214	1.4×10^{-1}	180,000	0.163	Perm Tube ~1 – 1,000ppb (single dil.)
2 Nitrophenol	139.1	225	1×10^{-1}	132,000	0.161	Perm Tube (est) 1 – 1,000ppb (single dil.)
2,4 DNT	182	300	2.63×10^{-4}	346	0.123	Perm Tube ~1.5 – 200ppb (single dil.)
Nitric Acid	63	84	48	N.A.	0.356	Perm Tube 1 – 5,000ppb (single dil.)
Ammonia	17	(gas)	N.A.	N.A.	1.31	Perm Tube <10 – >15,000ppb (single dil.)
EGDN	152.1	d	7.6×10^{-2}	100,000	0.147	Diff. Tube (operate @ lower temps)
TATP	222	>100 d	4.6×10^{-2}	60,000	0.101	Diff. Tube (operate @ lower temps)
(Acetone)	58.1	56.5	230	N.A.	0.385	Perm Tube <5 - ~10,000ppb (single dil.)
Nitroglycerin	227	160	4.8×10^{-4}	630	0.099	Diff. Tube, Headspace, or Droplets
2,4,6 TNT	227	295	5.5×10^{-6}	7	0.099	Diff. Tube, Headspace, or Droplets
RDX	222	>300 d	3.3×10^{-9}	0.0043	0.101	Diff. Tube, Headspace, or Droplets
PETN	316	>300 d	1.1×10^{-8}	0.015	0.071	Headspace or Droplets
Ammonium Nitrate	80		9.8×10^{-6}	13	0.28	Diff. Tube, Headspace, or Droplets

The combination of low vapor pressure and 'stickiness' of the compounds preclude the possibility of using static mixtures (i.e., cylinder gas). Mixtures must be generated and used in-situ. An additional complication is that explosives are often formulations made up of several compounds. Simulating the vapor from such mixtures can lead into substantial instrumentation complication.

Table 2 lists four techniques known to be effective for creating a 'base concentration' of low vapor pressure compounds. The base mixture can then be modified with relative humidity, interfering compounds, etc.

TABLE 2
TECHNIQUES FOR CREATING VAPOR MIXTURES

Diffusion Tubes
Permeation Tubes
'Ink Jet' Droplet Injection
Dynamic Headspace Saturation

DYNAMIC BLENDING TECHNIQUES

DYNAMIC HEADSPACE SATURATION

Earlier devices described in the literature for generating explosives vapors have generally used a form of Dynamic Headspace Saturation. Figure 1 shows a schematic diagram of a headspace saturation system. A sample of the analyte compound, generally as a finely divided powder or a liquid suspended on an inert substrate, is confined in a controlled temperature chamber. A carefully controlled flow of clean carrier gas passes over/through the sample and is saturated with analyte at the vapor pressure of the analyte at the sample temperature. The resulting concentration is

$$C_{max(ppb)} = \frac{Vp}{P_{total}}(10^9)$$

This establishes the maximum concentration of analyte possible at the designated operating conditions. Lower concentrations are created by additional dilution with a 'zero' matrix gas.

This is an extremely useful technique for low vapor pressure analytes. It creates a useable base mixture of vapor whereas the other techniques start with such high dilution as to be useless. It also creates a representative vapor mixture for substances that are mixtures of multiple compounds.

The method, however, comes with challenges. First is the need to know the actual vapor pressure (Vp) of the analyte. In the case of explosive compounds, Vp citations vary greatly, so the actual concentration created is in question, and may show bias compared to mixtures produced by other techniques. Obtaining traceability to NIST would require some way of referencing concentration to other physical standards. Still, reproducible mixtures and dilutions can be prepared and used for testing and comparison.
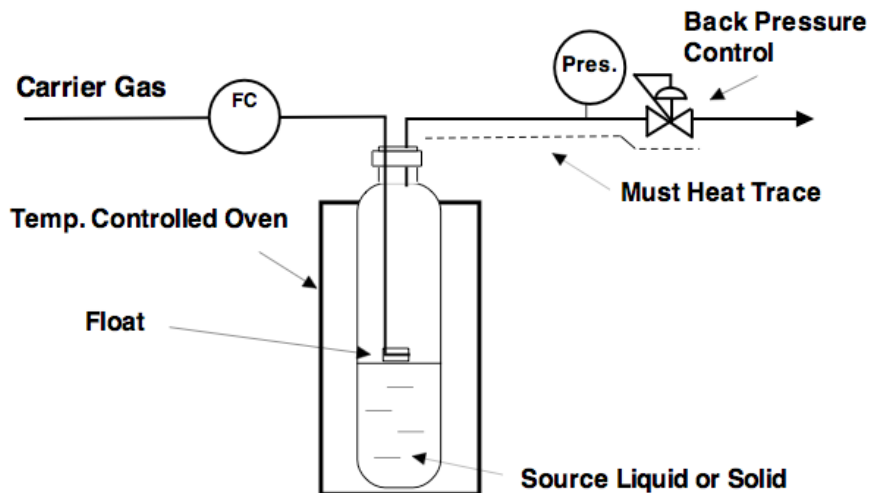
FIGURE 1

DYNAMIC HEADSPACE SATURATOR SCHEMATIC

 The second challenge is assuring a saturated mixture. Vaporization (sublimation) requires the addition of heat. If heat transfer is inadequate the analyte will be cooled, thus altering its vapor pressure. The problem is minimal for very small carrier flow rates, but at larger flow rates it can become very significant.

The third challenge is maintaining stability of the saturated mixture until it is diluted. Generally, this can be addressed by the following methods: a) maintaining the mixture above the saturation temperature until dilution, and/or b) saturating the carrier at elevated total pressure, then immediately reducing the pressure so that mixture is slightly below saturation.

PERMEATION TUBES

Permeation Tubes are the technique best suited for generating concentrations traceable to NIST. Figure 2 shows a sketch of a typical permeation tube. Analyte is in contact with one side of a permeable membrane – usually Teflon®. A flow of clean carrier gas passes over the other side. Analyte vapor permeates through the membrane and is picked up by the carrier to form the base mixture.
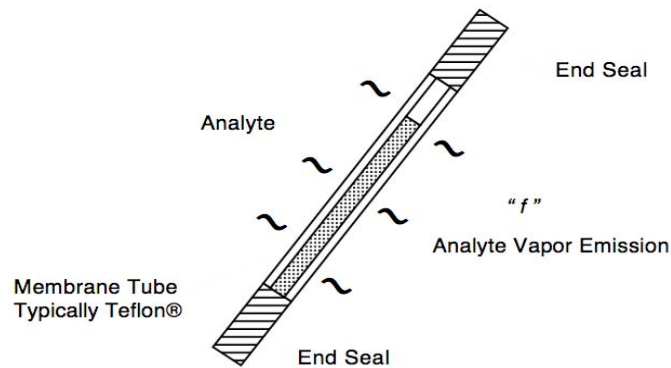
FIGURE 2

TYPICAL PERMEATION TUBE

A key advantage of the permeation tube method is that the membrane separates the analyte compound from the gas stream. The membrane limits vapor flow and acts as a 'molecular' flow control device. The permeation rate is determined by the physical characteristics of the specific membrane and vapor pressure of the analyte compound. Since the vapor pressure is set by temperature, the flow of permeate is set by the operating temperature. The concentration created is simply the ratio of the permeate flow to the total dilution flow and is unaffected by carrier gas pressure.

$$C_{(ppb)} = \frac{E_{(ng/\min)}K_0}{F_{(l/\min)}}$$

The emission rate of the tube is determined by holding it at constant temperature for an extended time and measuring weight loss rate. The mixture concentration is thus set by temperature, rate of weight loss, and dilution gas flow rate. Each of those variables can be made traceable to NIST standards, thus establishing a measure of traceability to the concentration. Integrity of the analyte compound and vapor must be established separately.

Figure 3 shows the flow path for a typical permeation system. With the permeation tube method the first dilution step is huge. For high vapor pressure compounds that is a great advantage, but for compounds with low vapor pressure the method becomes essentially useless. Even if concentrations in the low ppq are desired, one must be able to reasonably measure the weight loss rate of the tube to use the method effectively. Using current designs and weighing technology, weight loss rates below about 20 ng/min are impractical to measure.
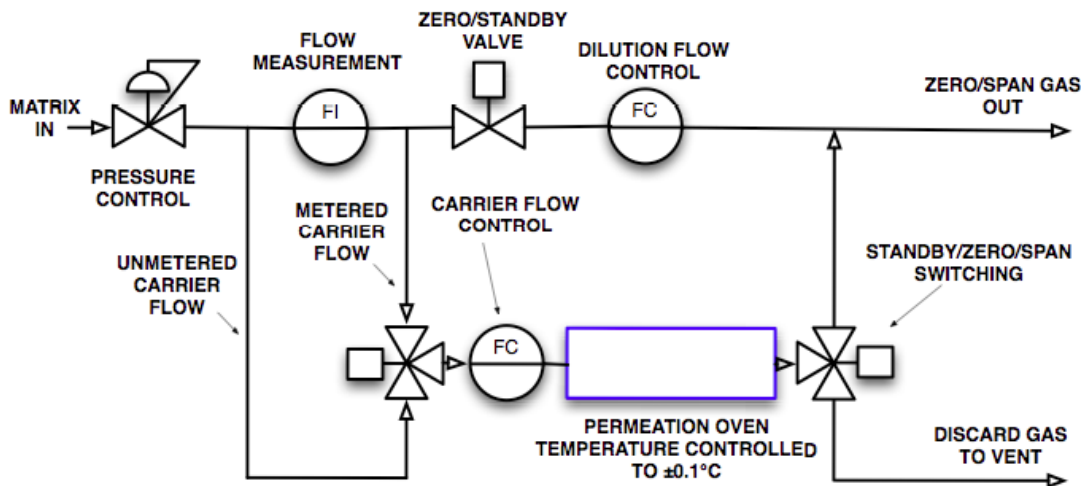
FIGURE 3
TYPICAL DILUTION SYSTEM FOR
PERMEATION OR DIFFUSION TUBES

DIFFUSION TUBES

The diffusion tube method is a close cousin to the permeation tube method. Instead of using a membrane as the flow control device, a diffusion tube uses diffusive flow across a length of capillary tubing. A wide range of flow rates can be obtained by varying the diameter and length of the capillary.

Diffusion across a capillary is well characterized, and can be mathematically predicted if the appropriate data is available. In practice, the emission from a diffusion tube can be measured gravimetrically just as with permeation tubes. Unlike permeation tubes, capillary flow is affected by total pressure, so weight loss measurements must be made under actual operating conditions. An additional complication is that typical diffusion tubes used for liquids are capillary tubes with a glass reservoir sealed on one end. This design cannot be used effectively with solids. An alternate design with a refillable reservoir is required.

INK JET DROPLET INJECTION

An emerging technology that shows promise for creating mixtures of a wide range of compounds including the very low vapor pressure explosives is injecting droplets and vaporizing them into a flowing carrier gas stream using the same technology used in ink jet printing. Figure 4 shows a schematic of the method.
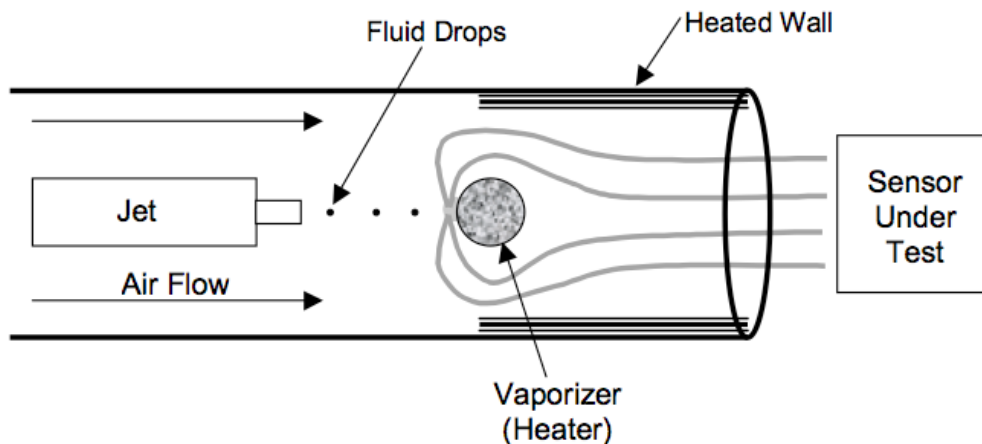
FIGURE 4
PRINCIPLE OF INK-JET DROPLET INJECTION
(Drawing Courtesy of MicroFab Technologies)

Advantages of ink-jet injection technology include the ability to vary concentration (within mixture stability limits) by varying the droplet injection rate (or maintaining a concentration level over a range of dilution flow rates) and ease of creating multi-component mixtures.

Disadvantages include the fact that the injected analyte must be a liquid, so common explosives must be dissolved in a solvent. The solvent vapor is part of the mixture delivered and must be accounted for in the measurement. The pre-dilution step also means that traceability must come through external analytical means in addition to physical variables.

ATMOSPHERE SIMULATION

Each of the techniques described creates a base mixture that is further diluted for use. The matrix gas will typically be 'zero air.' When measurement levels are in the parts-per-trillion range and below, achieving 'zero' may be a non-trivial exercise. While explosives are notoriously 'sticky' compounds, at ppt levels a significant number of molecules may pass through the purification apparatus.

Recommended practice for calibration instruments is to arrange the flow path so that the base mixture can be diverted into or away from the main dilution flow. This allows the zero air to flow through system and establish the working zero. Contamination of the zero air supply or residual system contamination will be revealed. When contamination exists, the method of standard additions can be used to evaluate system sensitivity.

The additional dilution also provides opportunity to introduce other compounds into the mixture. In particular, moisture should be added to simulate ambient humidity. Even

when the detector itself is not sensitive to moisture, the presence of water vapor can influence the delivery of trace concentrations of explosives. The influence of water vapor on adsorption of polar compounds (particularly on metals) is well known, and even the ability of dogs to detect buried mines improves in moist conditions.

Also interfering compounds can be added to the diluent to test the effect on the detection system. Common vapors from diesel exhaust, insect repellent, paint, and cleaning solutions may also affect the performance of detection systems.

DELIVERING MIXTURES

A final challenge in creating test gas mixtures for explosives detection is delivering the mixture to the test device. Generally, contact with adsorptive surfaces must be minimized. Unavoidable contact should only be with highly inert surfaces. Transfer lines should be appropriately heated. The question is "Which, if any, materials can be considered inert for the various explosive compounds?" Current technology suggests Teflon®, silanized glass and possibly SilcoTek® coated stainless steel.

Experience working with other 'sticky' compounds indicates that heat tracing of transfer tubes to about 60°C is usually a good choice. It is important to stabilize both temperature and pressure in transfer lines. Instability of either results in variations in system output that cannot be distinguished from variations in base mixture concentration.

An additional aspect of the delivery challenge is choosing a suitable output configuration. Typically, test gas mixtures are delivered by transferring the gas through a tube to a test chamber or to the final test device. Given the variety of detection systems, it may be more effective to modify that paradigm and make the generator system integral to the delivery system.

CONCLUSIONS

The diversity of chemical and physical properties of explosives and associated compounds makes creation of vapor standards a complex problem. Generally, four techniques have been used successfully: a) permeation tubes, b) diffusion tubes, c) dynamic headspace saturation, and d) ink-jet droplet injection. Each has value for some applications, but none of these techniques is universally applicable. For achieving traceability of mixture concentration, permeation tubes offer the best current route.

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