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## SELECTION OF A GAS CHROMATOGRAPHIC MATERIAL FOR USE IN EXPLOSIVES VAPOR PRECONCENTRATION

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### SUMMARY

The effectiveness of explosives vapor detectors can be enhanced by the addition of a preconcentrator which collects explosives molecules and releases this concentrated sample to the detector for analysis. Candidate preconcentrator materials for detector applications were evaluated using a gas chromatograph and a commercial explosives vapor detector. The saturation time and release temperature for nine materials were obtained using ethylene glycol dinitrate and 2,4-dinitrotoluene explosives. Based on these data, the best candidate for use in a thin-screen preconcentrator for the above explosives is OV-275.

### INTRODUCTION

Commercial explosives detectors are used in a number of security systems to detect explosives carried by individuals. The effectiveness of these detectors is limited, however, by the low concentrations of available explosives vapors. The extent of this problem is illustrated in Table I, which lists the vapor pressures of some common explosives.

TABLE I

#### EQUILIBRIUM VAPOR PRESSURES OF HIGH EXPLOSIVES AT ROOM TEMPERATURE AND ATMOSPHERIC PRESSURE

Abbreviations: EGDN = ethylene glycol dinitrate; TNT = 2,4,6-trinitrotoluene; DNT = 2,4-dinitrotoluene; PETN = pentaerythritol tetranitrate; RDX = cyclonite; C-4 = principally, cyclonite.

<i>High explosives</i>	<i>Relative partial concentration<sup>1-6</sup> (ppb)</i>
Dynamite:	
Nitroglycerin	300
EGDN	63,900
TNT	6
DNT	145
PETN (chemically pure)	0.0005
RDX	0.0015
C-4 (91% RDX)	0.0013

Although progress continues to be made in increasing the sensitivity of explosives vapor detectors, the performance of these detectors could be enhanced by preconcentration of the explosives vapors<sup>7</sup>. Vapor preconcentration can be accomplished by a device which collects a high percentage of small amounts of vapor dispersed throughout a large volume of air. The enriched vapor sample is then delivered to a detector system for analysis. Of particular interest are thin layers of preconcentrator materials which are applied to a screen mesh for use in conjunction with existing explosives vapor detectors.

Several materials were investigated for possible use in explosives vapor preconcentration. Each material was tested to determine vapor collection efficiency and the optimum temperature for vapor release.

## EXPERIMENTAL

Columns constructed of 304 stainless-steel tubing were filled with candidate preconcentrator materials on Chromosorb P AW support and used as a first approximation to a thin-layer sample. Each tube measured 5 cm  $\times$  3.2 mm O.D. After being loaded with a candidate material, the ends of each column were closed with a 10- $\mu$ m stainless-steel screen. The columns were then preconditioned in a flow stream of 95% argon-5% methane. Preconditioning consisted of heating the columns to a temperature of 20° below the maximum operating temperature of the preconcentrator materials or 300°, whichever was lower.

Both saturation time and release temperature were investigated. Saturation time is a measure of the molecular collection efficiency and retention capacity of a material<sup>8</sup>. Materials which exhibit long saturation times are preferred for preconcentration applications. Release temperature is the temperature at which a material releases the captured vapor molecules to the surrounding media. The best release temperature is the lowest temperature above ambient which results in the release of substantial quantities of the captured vapor molecules.

Table II lists the nine candidate preconcentrator materials which were studied. These materials were chosen because they included a wide range of the McReynold's constants<sup>9</sup> and several porous polymer materials which have been used previously as collection media.

### *Saturation time*

The test columns were attached to an explosives-filled glass coil of a P.A. Pellatype generator<sup>10</sup>. Air (Zero Gas, Matheson) was passed through a temperature-controlled coil containing solid explosives material. The explosives vapor effluents from the coil then passed into the test column. Petrogel<sup>TM</sup>, Atlas HV 60% dynamite, was used as the explosive. Since this dynamite contains a high concentration of ethylene glycol dinitrate (EGDN), it will have a high vapor pressure (see Table I). The effluent from the column was monitored continuously with an Ion Track Instruments (ITI) Model 70 explosives vapor detector. Saturation time of the column was recorded as the elapsed time from the start of the effluent flow through the column until the detector produced a continuous alarm.

TABLE II

## PROPERTIES OF CANDIDATE PRECONCENTRATION MATERIALS

The activated coconut charcoal (100–200 mesh) was obtained from Coast Engineering Lab. (Gardena, Calif., U.S.A.), the Tenax GC (60–80 mesh) from Applied Science Labs., (State College, Pa., U.S.A.) the Ultrabond 20M (100–200 mesh) from Alltech (Arlington Heights, Ill., U.S.A.); all other materials were obtained from Supelco (Bellefonte, Pa., U.S.A.). Physical form refers to the basic material not the substrate.

Material	Temp. range (°C)		McReynolds constants <sup>8</sup>					Physical form
	Min.	Max.	x'	y'	z'	u'	s'	
3% OV-101	0	250	017	057	045	067	043	viscous liquid
5% OV-275	25	250	629	872	763	1106	849	viscous liquid
5% DEGS-PS	20	200	496	746	590	837	835	viscous liquid
5% Carbowax 20M-TPA	60	2255	321	537	367	573	520	low-melting solid
Tenax GC	—	375	—	—	—	—	—	porous polymer
Porapak Q	—	250	—	—	—	—	—	porous polymer
Activated charcoal	—	—	—	—	—	—	—	solid
5% SP-1200–5% Bentone 34	25	180	—	—	—	—	—	liquid–solid
Ultrabond 20M	—	250	—	—	—	—	—	solid

*Release temperature*

A Hewlett-Packard HP-5840A gas chromatograph with an electron capture detector (ECD) was used to determine the release temperature of each of the candidate preconcentrator materials. The test columns were placed into the HP-5840A and subjected to a 95% argon–5% methane gas flow. Separate samples of EGDN and 2,4-dinitrotoluene (2,4-DNT) were dissolved in acetone to a concentration of 98 mg/l and used to test the columns.

The oven of the gas chromatograph was temperature stabilized at 50°. This temperature was selected as the initial oven temperature for collection of the explosives molecules from the explosives–acetone solution since this temperature exceeds the “worst case” temperature that might be encountered in field operation of an explosives vapor detector. Following temperature stabilization, 1  $\mu$ l of the explosives–acetone solution was injected onto the column, using the solvent plug technique, and the oven temperature–profile program was begun. The oven temperature–profile program contained a 3-min hold at 50° followed by a temperature increase at a rate of 20°/min to 225° and was terminated with a 10-min hold at the maximum temperature. All of the candidate materials were tested using this profile except the 5% SP-1200–5% Bentone 34 sample, which had a maximum operating temperature of 170°.

A 3-min hold period was included in the chromatographic oven temperature–profile program since a 5-cm column is not a good approximation to a thin screen. This hold period more closely normalizes the 5-cm column to the thickness of the screen. Any preconcentrator material that releases the collected explosives vapors during the 3-min hold period would probably not be useful as a screen coating for practical detection applications.

The release temperature of EGDN and 2,4-DNT with each of the preconcentrator materials was measured. This release temperature was read directly from the chromatogram.

## RESULTS

The results of the saturation-time and temperature-release tests are summarized in Table III. For the saturation test, only the data on EGDN vapors are reported since the low partial pressure of the 2,4-DNT vapors leads to exceedingly long saturation times. The saturation time of the columns provides a measure of the holding power of each candidate preconcentrator material. A longer saturation time for a particular material therefore indicates that the material has the capacity to retain a large amount of explosives vapor.

TABLE III  
SUMMARY OF TEST RESULTS

Material	Total weight (mg)	EGDN saturation time (min)	Mass-normalized saturation time (min/mg coating)	Release temp. (°C)	
				EGDN	DNT
3% OV-101	47.2	5	3.5	50	99
5% OV-275	51.2	58	22.7	86	151
5% DEGS-PS	54.2	55	20.3	50	134
5% Carbowax 20M-TPA	54.1	103	38.1	50	115
Tenax GC	24.9	120	4.8	136	194
Porapak Q	73.0	450	6.2	155	225
Activated charcoal	71.0	~5750	~80	>225	>225
5% SP-1200-5% Bentone 34	49.8	91	18.3	113	165
Ultradond 20M	52.1	3	—	50	—

The mass-normalized saturation times are included in Table III to illustrate the difference in application of certain materials. In canister or environmental sampling applications, porous polymers such as Tenax GC have proven to be excellent preconcentrating materials. However, this material would probably not be suitable for screen applications in which consideration must be given to collection efficiency *versus* weight of material since it has a relatively low mass-normalized saturation time (4.8 min/mg coating). In contrast, several tested materials exhibited efficiencies that are four to five times that of Tenax GC and could be used for coating a screen.

Release temperatures for both the EGDN vapors and the 2,4-DNT vapors are also shown in Table III. The release characteristics of each of the candidate materials are as important in the design of a practical vapor preconcentrator as are the collection characteristics. None of the candidate materials exhibited any degradation of the explosives molecules upon release and equal area peaks were observed for all materials except those which "bleed," *i.e.*, give a broad background, at 50°. Bleeding materials which have a release temperature of 50° or lower were judged to be poor candidates for use as preconcentrators. Activated charcoal did not release absorbed explosives vapors even when heated to 300° and consequently is, for all practical purposes, a poor explosives vapor preconcentrator material in heat release applications.

## CONCLUSION

Analysis of the data summarized in Table III leads to the conclusion that the

best candidate material of those tested for use as a thin-screen preconcentrator of EGDN and 2,4-DNT vapors from 100 to 1000 l, high-flow air samples is OV-275. OV-275 exhibited good collection properties at its 22.7 min/mg mass-normalized saturation time and desirable release characteristics in a warm (*ca.* 150°) release temperature. In addition, OV-275 takes the form of a highly viscous liquid, which is a practical form for the desired thin-screen geometry.

A further experiment was performed to verify this conclusion. A "column" was constructed for the HP-5840A gas chromatograph that consisted of a stainless-steel screen (6.35 mm O.D., 60 mesh) coated with 0.5 mg of OV-275. This screen was pressed into a thin-walled, stainless-steel tube (6.35 mm O.D.). The chromatographic parameters in this experiment were the same as those used in the release temperature studies. A 1- $\mu$ l solution of EGDN, dissolved in acetone to a concentration of 98 mg/l, was injected onto the column. The resulting collection and elevated temperature release parameters were consistent with the findings given in Table III.

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