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Standardisation of a Vapour Generator for Calibration of Environmental Monitoring Instruments

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ABSTRACT

Very low vapour pressure of 2,4,6 trinitrotoulene (TNT) yields extremely low vapour concentrations at different flow rates in the air, yet considerable quantity of vapours and TNT dust during handling may be present at the workplace environment which is harmful to the health of the personnel working there. The explosive vapours, such as TNT, 2,6-dinitrotoluene (DNT), etc., though harmful to the health of the personnel, are not covered either in the emission standards or in the ambient air quality standards. Presently, no instrument is available for air monitoring of TNT vapours. These vapours need to be collected on-site to estimate TNT concentration. Realising the need for real-time air monitoring of TNT, efforts have been made to understand and device an instrument for on-site determination of TNT vapours parts per billion (ppb) range. Low-level TNT vapours and TNT buried in the soil in military operations are required to be detected. The instruments for this require careful calibration to yield accurate and reliable results. Hence, an effort has been made to develop a trace-level ppb vapour generator. The vapour generator of a spiral glass column of length 170 cm and inner diameter 4 mm ± 0.5 mm has been used. An activated charcoal glass tube has been used for sampling TNT vapours. The adsorbed TNT vapours were desorbed and analysed using high performance liquid chromatography. The solid support used has been studied. These vapours generated at different flow rates have been evaluated. The calibrated instrument can be used for in *situ* and on-site analysis of samples of TNT and also for samples collected.

Keywords: 2,4,6 Trinitrotoulene, TNT vapours, health hazard, vapour generation unit, environmental monitoring instrument, explosives, human carcinogen, pollutant, mutagenic agent

1. INTRODUCTION

1.1 TNT Vapours as Workplace Pollutant

Although the inherent physical properties of TNT do not encourage these vapours to emanate in large quantities into the air, considerable quantity of TNT vapours are expected to be present at the workplace environment. This poses threat to the safety and health of the personnel[1] working there. Apart from this, a significant amount of TNT finds its way into the water and land during washing, filtration, drying, and packing. All these contribute to overall deterioration of the environment.

1.2 Effects of TNT on the Health of Personnel

The US Environmental Protection Agency (EPA) has listed TNT as a priority pollutant. Prolonged exposure and skin contact with TNT at the workplace may lead to rashes, skin eruption, and to more serious consequences, such as nose bleeding,

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haemorrhage of the skin, as well as mucus and blood disorders. Dust inhalation may result in nausea, vomiting, toxic hepatitis, and anemia[1]. TNT is also toxic to algae and invertebrates, and chronic exposure of TNT on human beings causes harmful health effects like abnormal liver function, cataract development, and skin irritation[2,3].

The EPA has categorised TNT as a possible human carcinogen, based on animal studies[2]. Investigations have revealed that TNT produces the following toxic effects:

- Irritation of the digestive tract
- Methaemoglobinanemia (and the effects induced by oxygen deficiency), disturbes heart function, liver and kidney trouble, and a dysfunction of the whole vascular system.
- A particular harmful effect on the liver tissues, causing severe jaundice, which in 25-30 per cent cases may end in death.

  Aplastic anemia, manifesting itself by a fall in the number of red and white blood corpuscles, caused by dysfunction of the bone marrow. Almost all of these end in death[4].

The mutagenic and carcinogenic potential of TNT and its congeners have been reported and there is need to clean up these from the environment[5]. It has been observed that TNT, present in wastewater in concentration of 25–80 mg/l, lowered the oxygen consumption of the bacteria by 5–30 per cent, possibly because it inhibited their activity. In addition, TNT and DNT, like other compounds, were also toxic to some seaweeds and fishes[6].

1.3 Air Monitoring for TNT Vapours

Work reported in the literature in the field of TNT detection in the atmosphere is scanty. Explosive detectors are available for use in a variety of law-enforcement applications. Though these are designed for the detection of vapours of TNT in the air at trace concentrations, there is a need for further research in this field. Trace vapour generators employing dynamic dilution of vapours of TNT have been developed by several workers for testing their explosive vapour detector performances[7,8]. A TNT vapour generator developed by Pella was evaluated by measuring the diluted vapour concentrations of TNT using gas chromatographic method. Measurements of TNT concentrations were also made as a function of temperature. Performance data were obtained with three explosive vapour detectors of different makes to determine if the range of vapour concentrations generated by this system was suitable for calibration[7].

Until now, no instrument has been designed for the determination of gaseous samples of TNT directly. Hence, on-site and quick determination of TNT vapours concentration in the air is not possible. This is a major problem for the instant determination of TNT vapours concentration in the air. The air samples are not only difficult to collect but also to store, as these are prone to unknown diffussional leakages and dilution, whereas the soil samples are relatively easy to handle and store due to the stability of TNT in a solid form. Extractions can be prepared using suitable organic solvents as adopted in EPA method[9] 8515.

There is a need to develop a portable field detector for rapid interference-free analysis using small samples, which requires little technical training to analyse, and also presents no health hazards to inexperienced technicians[10].

Realising the need for real-time monitoring of gaseous samples, lots of efforts have been made to understand and device an instrument for on-site determination of TNT vapours in the atmosphere. These instruments require proper calibration to yield reliable results. In the absence of a suitable calibrator, these instruments, though sensitive, would give unreliable results[11]. Hence, an effort has been made to develop a suitable vapour generation unit to generate required concentrations of respective analyte. The calibrated instrument can be used to determine TNT in the samples collected.

2. OBJECTIVES

- To design and setup a vapour generation unit based on vapour saturation technique. Coiled glass column containing TNT-coated material is used as vapour generation unit.

- To find the longevity of the column to produce uniform concentration of vapours throughout the experiment.
- To identify and select a suitable solid support for making source of TNT vapours in the vapour generation unit. Solid support is selected on the basis of its particle size, surface area, and adsorption capacity.
- To regulate operating parameters like temperature and flow rate to get uniform TNT concentration, varying steadily with a steady change in the mentioned parameters. Different sets of adsorptions are carried out at different temperatures and flow rate ranges, and later analysed.
- To find the desorption efficiency of TNT adsorbent tube, organic solvents are used to desorb TNT from the adsorption material. The resulting extractions are used for the determination of the concentration of TNT using high preformance liquid chromatogrpahy (HPLC).

3. MATERIALS & TECHNIQUES

A vapour generation unit has been designed as described by Pella[7] to produce vapour concentrations of explosive TNT and this can also be used to calibrate the instruments and standardise the techniques for the detection of low concentration levels of TNT in the workplace or in the atmosphere. The saturated TNT vapours coming out of the vapour generator are diluted to the desired low concentrations, up to ppb level, using on-line dilution arrangement available in the TNT vapour generation unit[12].

Adsorbent tube containing activated charcoal sampling and HPLC method was used to evaluate this system. The organic vapours were adsorbed onto the charcoal. The adsorbed vapours were desorbed using a suitable solvent and analysed using HPLC and an ultraviolet detector.

This method is also valid for the measurement of mixtures of explosive vapour concentrations. In such cases, the unique properties of each compound have to be considered while determining the volume of air to be sampled[13].

4. EXPERIMENTAL PROCEDURE

4.1 Description of TNT Vapour Generation Unit

A schematic diagram of the TNT vapour generation unit along with on-line dilution setup is shown in the Fig. 1.

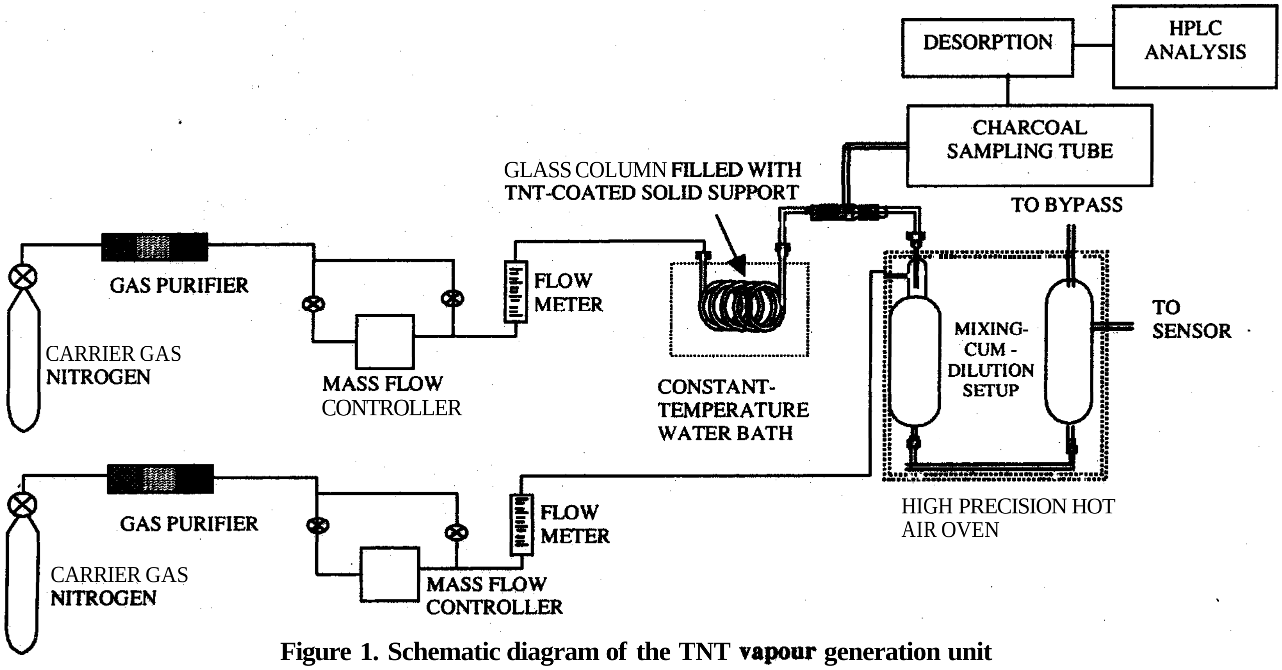

Figure 1. Schematic diagram of the TNT vapour generation unit

The vapour generation system consists of the following parts:

- *Carrier gas source:* Nitrogen cylinder provides carrier gas at a controlled and continuous flow rate.
- *Gas purification setup:* This consists of three separated but interconnected columns consisting of silica gel, molecular sieve, and activated charcoal, consecutively.
- *Mass flow controller:* Bronkhorst model CE hitech has been used to control the flow of carrier gas emanating from the gas source with an accuracy of ± 0.1 ml. Depending upon the requirement, the flow rate of the carrier gas can be adjusted.
- *Vapour generation column:* A spiral glass column with 5-6 coils of diameter 10 cm ± 2 cm has been used. Length of the coil used was 170 cm. Total length of the column used was 350 cm comprising 170 cm of the coil and 180 cm for rest of the column. The outer and the inner diameters of the column were 6.4 mm and 4 mm ± 0.5 mm. Also, glass U-tube with a total volume of approx. 50 mm^3 was used for vapour generation column .

4.2 Preparation of TNT-coated Solid Support

4.2.1 *Dried Activated Alumina Spheres*

Dried activated alumina spheres (5-8 mm) and TNT were taken in the ratio 10:1, ie, 1 g of TNT was used to coat 10 g of activated alumina. 1g of TNT was dissolved in 20 ml of benzene. This solution was added to 10 g alumina spheres and stirred well to dissolve TNT crystals and to ensure uniform coating of TNT on alumina spheres. The TNT-coated spheres were kept in the oven at 60 "c–65 "C for 8 h so that the TNT-coated spheres became completely free of trace benzene.

4.2.2 *Activated Alumina Spheres*

Activated alumina spheres (0.7-2.0 mm) were crushed to the mesh size between 16 ASTM and 25 ASTM sieve were selected. Rest of the processing and the coating method was the same as mentioned above.

4.2.3 *Molecular Sieve*

Molecular sieve (0.7-2.0 mm) was crushed to the mesh size between 16 ASTM and 25 ASTM sieve. It was processed in the same manner as used for activated alumina.

4.3 TNT Vapour Collection Device

The TNT vapour adsorption tube was designed as per the international standard ISO-9487. Activated charcoal (area) of mesh size 0.4 mm to 0.8 mm was used. The main adsorbing section contained 100 mg of charcoal and the backup section contained 50 mg of charcoal. The contents of the tube were held in place with loosely packed inert glasswool. To ensure reliable operation, tight packing of the glasswool was avoided[14].

4.4 Extraction of TNT from the Sample Tube

Mobile phase for HPLC analysis was Emerck, HPLC-grade, Lichrosolv methanol and water in the ratio 4:6. Each adsorbent section was removed and analysed separately. Activated charcoal or adsorbing material recovered after the first extraction was used to make the second extraction. Activated charcoal obtained after filtration could be used for third extraction, depending upon the vapour generating efficiency of the solid support and the adsorption efficiency of the activated charcoal used. HPLC of Waters make equipped with a (Waters 515) pump capable of achieving 4000 psi, (Waters 717) auto-sampler and (Waters 2487) dual λ absorbance1 ultraviolet detector was used for the estimation.

5. RESULTS & DISCUSSION

TNT vapours for each condition of flow rate and temperature were collected in a vapour collecting charcoal tube. The adsorbing material in the sample tube was extracted and analysed to determine the concentration of the TNT vapours adsorbed. Data obtained from HPLC was interpreted and represented through graphs. These are shown in the Figs 2 to 5. This followed the calculations,

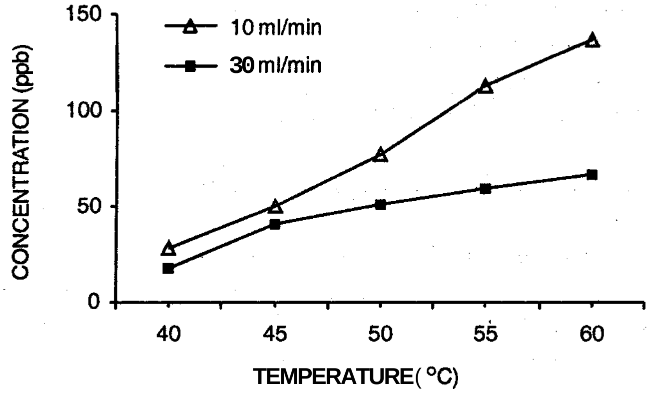

Figure 2. TNT concentration (**ppb**) for glass U-tube filled with TNT-coated activated alumina spheres. Graph shows concentration versus temperature at different flow rates.

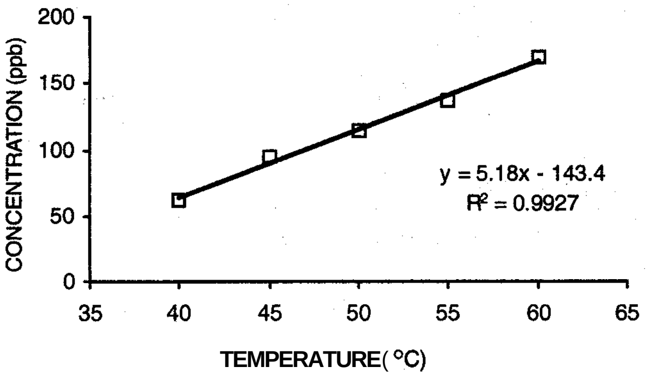

Figure 3. TNT concentration (ppb) for glass U-tube filled with TNT-coated activated alumina chips. Graph shows concentration versus temperature at the 10 **ml/min** flow rate.

to draw results to evaluate the suitability of the experiment in designing an efficient and useful vapour generation unit for calibrating TNT measurement systems.

Results can be used to assess the adsorption efficiencies of the various solid supports used in the vapour generation unit. Glass U-tube was also used as a vapour generator. However, coiled glass column gave better performance. Physical parameters like temperature and flow rate also affected the concentration of vapours produced by this vapour generation unit. The relative differences have been described and values are shown in the Tables 1 to 5 along with desorption and adsorption efficiencies of the adsorbing **material** for different sets of conditions. It has been found that with an

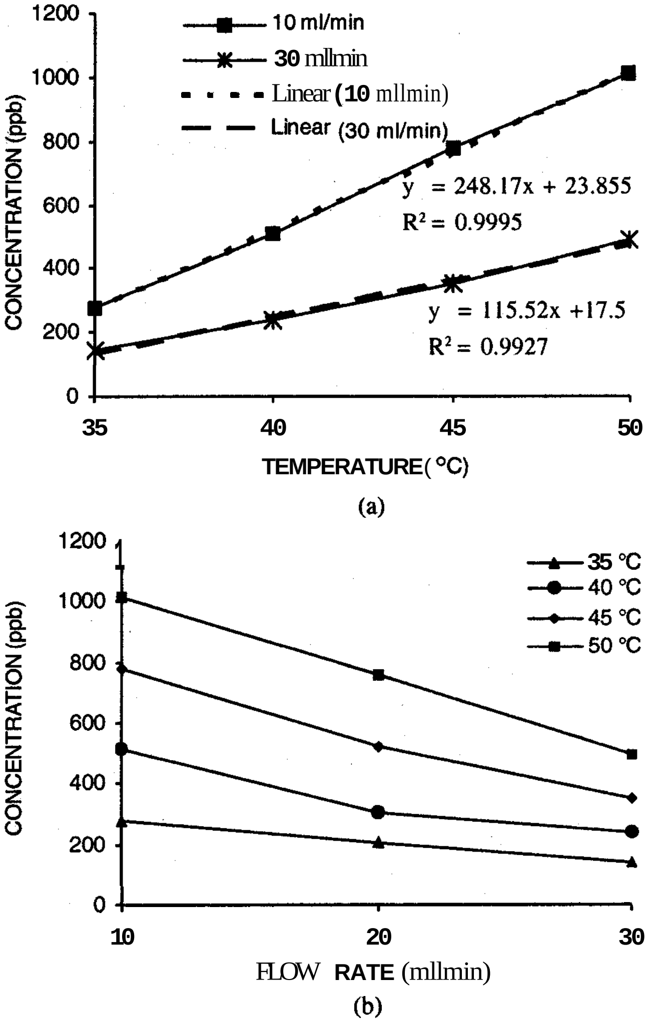

Figure 4. TNT concentration (ppb) for glass column **filled** with TNT-coated activated alumina chips: (a) concentraton versus temperature at different flow rates and **(b)** concentration versus flow rate at different temperatures.

Table 1. Generation of TNT vapours (ppb) from glass U-tube filled with TNT-coated alumina spheres (5-8 **mm)** and alumina chips (0.7-2 **mm)**

Temperature (°C)	TNT vapour (ppb)		
	10 ml/min (alumina chips)	20 ml/min (alumina sphere)	30 ml/min (alumina sphere)
40	62	28.2	17.5
45	94	49.6	40.1
50	115	76.9	51.7
55	137	112.9	59.0
60	170	136.9	67.0

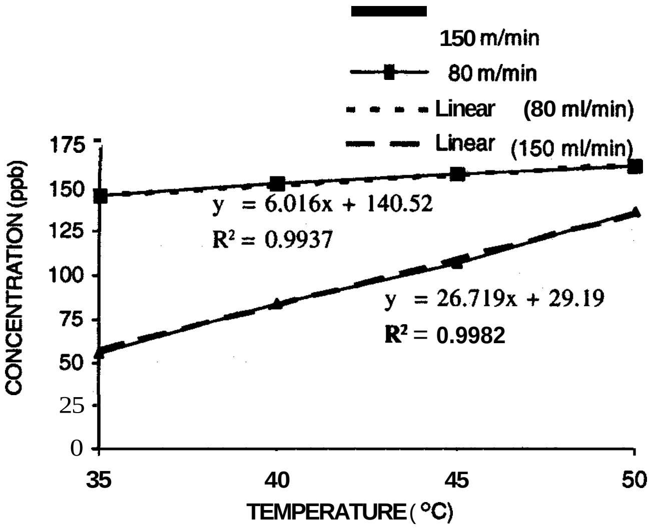

Figure 5. TNT concentration (ppb) for spiral glass column filled with TNT-coated molecular sieve. Graph **shows concentraton versus temperature at** different flow rates.

increase in the temperature, generation of TNT vapours also increased. However, the concentration of TNT vapours was more at lower flow rates when the same solid support was used.

5.1 Suitability of Vapour Generation System

The spiral glass column and the glass U-tube used for the TNT vapour generation were compared and suitability of these systems were evaluated. From the results, it has been found that the spiral glass column is producing uniform vapour concentration as compared to the glass U-tube and the fluctuations are the minimum. Glass column produces steady concentration due to higher retention time as compared to the glass U-tube. On an average, the retention time for the spiral glass column is around four times the glass U-tube time.

Table 2. Generation of TNT vapours (ppb) from glass column **fillled** with TNT-coated alumina chips (0.7-2.0 **mm)** at carrier gas flow rate of 10 **ml/min**

Temperature (°C)	TNT vapours (ppb)					
	Main		Backup	Total	Adsorption efficiency (%)	Desorption efficiency (%)
	Ex-1	Ex-2				
	(A)	(B)	(C)	(D=A+B+C)	[(A +B) / D] X 100	[A / (A+B)] X 100
35	252	18.0	5	275.0	·98.10	93.3
40	475	31.9	5	511.9	99.02	93.7
45	732	38.0	6	776.0	99.20	95.1
50	957	47.2	10	1014.2	99.00	95.2

Table 3. Generation of TNT vapours (ppb) from glass column **fillled** with TNT-coated alumina chips (0.7-2.0 **mm)** at carrier gas flow rate of 30 **ml/min**

Temperature (°C)	TNT vapours (ppb)					
	Main		Backup	Total	Adsorption efficiency	Desorption efficiency
	Ex-1	Ex-2				
	(A)	(B)	(C)	(D=A+B+C)	[(A +B) / D] X 100	[A / (A+B)] X 100
35	133	3.20	7	140.0	95.1	97.7
40	217	6.86	16	239.8	93.3	96.9
45	329	9.83	12	350.8	96.6	96.6
50	461	15.26	15	491.2	96.9	96.7

Table 4. Generation of TNT vapours (ppb) from glass column filled with TNT-coated molecular sieve chips (0.7-2.0 mm) at carrier gas flow rate of 80 ml/min

Temperature (°C)	TNT vapours (ppb)			
	Main		Total	Desorption efficiency (%)
	Ex-1	Ex-2		
	(A)	(B)	(A+B)	[A / (A+B)] × 100
35	145.3	0.8	146.1	99.5
40	151.4	1.2	152.6	99.2
45	156.0	3.3	159.3	97.9
50	158.0	6.0	164.0	96.3

Table 5. Generation of TNT vapours (ppb) from glass column filled with TNT-coated molecular sieve chips (0.7-2.0 mm) at carrier gas flow rate of 150 ml/min

Temperature (°C)	TNT vapours (ppb)			
	Main		Total	Desorption efficiency (%)
	Ex-1	Ex-2		
	(A)	(B)	(A+B)	[A / (A+B)] × 100
35	50	5.7	55.7	89.8
40	78	6.0	84.0	92.9
45	100	7.4	107.4	93.1
50	130	6.9	136.9	94.9

The retention time for glass column is 21 min and for the glass U-tube, it is 5 min approx. for the same operating conditions. Since desorption coefficient of molecular sieve is significantly higher than alumina chips, higher flow rates of carrier gas were kept in the experiment of spiral glass column. Also, the retention time in spiral glass column was four times higher than the glass U-tube and to maintain comparable retention time, higher flow rate was kept in the molecular sieve experiment. Hence, glass column has been found to be a more suitable device for uniform vapour generation. Differences in the concentration values due to changes in parameters are clearly depicted by the graphs.

5.2 Suitability of Different Solid Supports

In these experiments, three types of solid supports have been used: (i) activated alumina spheres: (5-8 mm), (b) activated alumina chips: (0.7-2.0 mm), and (c) molecular sieve chips: (0.7-2.0 mm). Molecular sieve was found to be the most suitable solid support. .

5.2.1 *Surface Area*

On the basis of these results, it can be said that the size of the coated material and its surface area have a major role to play. With a decrease in size of the solid support, available surface area for the coating increases. Hence, solid support with small size was preferred as it allows greater surface for adsorption of TNT.

5.2.2 *Chemical Composition*

Further, changes were observed in the linearity of results due to the composition of the solid support. It was noted that molecular sieve gave better results than activated alumina; differences in the concentration of the samples at different conditions were more linear and steady in the case of molecular sieve solid support than activated alumina.

5.3 Sampling Technique & Dimensions

The sampling technique was found out to be suitable and extremely reliable. Also, this technique is widely used in organic vapour chemical analysis using gas chromatography. The same method can also be used for TNT vapour collection as it is used for various volatile organic vapours. Results given in the tables show that more than 90 per cent of the vapours got collected in the main section of the adsorbent tube and only fraction of the vapours were adsorbed in the backup section.

The desorption and adsorption efficiencies of the adsorbing material have been calculated and compared in the tables. Desorption efficiency of the adsorbing material was interpreted by carrying out the second extraction of the samples. Results of both the extractions were added to know the total concentration of TNT vapours adsorbed on the activated charcoal.

5.4 Analytical Techniques

The analytical technique used was the HPLC. Since the vapour concentration expected in this experiment was very low, up to ppb level; therefore sample concentration technique was adopted. This technique was found to be convenient and reliable to quantify trace levels of TNT vapours.

6. CONCLUSION

The vapour generation system described is capable of producing uniform concentrations in low levels. The designed vapour generation unit setup was found to be appropriate for trace TNT vapour generation that could be used to calibrate equipment for detecting TNT in the vapour phase. The sample collection technique based on activated charcoal adsorption was found to be appropriate in terms of adsorption as well as desorption efficiencies of TNT vapours. These results would help to get the desired concentration of TNT by setting the relevant operating parameters.

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