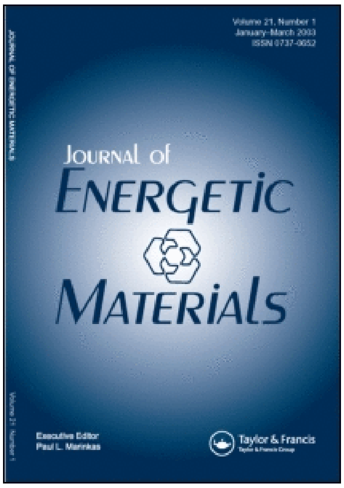

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TNT vapour measurements above buried landmines. Model experiments using [methyl-^{14}C] TNT

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TNT VAPOUR MEASUREMENTS ABOVE BURIED LANDMINES.
MODEL EXPERIMENTS USING [METHYL-^{14}C] TNT.

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ABSTRACT

As many land-mines are no longer made of metallic substances, locating mines by detection of the vapour of explosives has been proposed as an alternative.
In order to set a goal for these detectors a required detection limit was generated. The vapour concentration of TNT above buried land-mines was estimated using model experiments with radioactive labelled TNT, which was synthesized for this purpose.
When burying TNT sealed in PVC under a 6 cm thick layer of soil after 50-60 hours breakthrough of TNT vapours was observed. Extrapolating from these measurements to a real minefield situation yielded concentrations in the sub-ppt range inside as well as in the neighbourhood of the field.

INTRODUCTION

For military purposes explosives are usually packed in metal casings like mines or bombs. For the detection of these objects in the ground or in water the presence of metal has always been explored rather than the explosives themselves i.e. a close relationship between the metal and the explosive was assumed. The most common detection method employs artificial magnetic fields: disturbances in these fields reveal the presence of metals.

As many casings are no longer constructed of metal, but are composed of wood or polymeric materials, locating mines becomes more and more difficult. Therefore in recent years research has been initiated to find alternative detection methods.

Two different approaches were found in the literature concerning alternative methods for the detection of explosives: bulk detection and explosives vapour detection illustrated with a number of examples in both categories. The open literature focusses on mail, luggage and passengers at airports and hardly any attention has been paid to the detection of buried non-metallic mines.

One report has been found dealing with the analysis of vapours emitted from military mines which were <u>not</u> buried[1]. In this study the vapour evolving from several types of intact military mines was analyzed using gas chromatography /mass spectrometry. Although mass spectral identification was lacking, chromatographic data obtained using electron capture detection indicated the presence of TNT in the vapour from the M16 (metallic) anti-personnel mines. The vapour concentration of explosives above buried mines can be expected to be extremely low as a result of a combination of effects: 1. the low vapour pressure of the explosives, 2. retarded vapour penetration through (plastic) casings, 3. adsorption on soil and vegetation, and 4. dilution by wind and absorption by rain and snow.

The main purpose of the present investigations is to establish a required detection limit for existing equipment or for research towards future equipment for the detection of mines. Only TNT, the most often applied explosive is investigated.

A recent paper[2] deals with vapour pressure data for the explosives RDX, PETN, TNT, NG and ammonium nitrate. Since no conclusions could be drawn from these data with respect to TNT vapour concentrations above buried land-mines it was decided to measure the vapour concentrations under simulated conditions. A radiological approach was followed. An amount of ^{14}C-labelled TNT was synthesized and vapour concentrations above TNT, above TNT covered with plastic and above TNT covered with plastic and a layer of soil were determined by measuring the amount of radioactivity.

METHODS

Synthesis And Purification Of [Methyl-^{14}C] TNT:

[Methyl-^{14}C] TNT was synthesized according to the literature[3,4] starting from ^{14}C-CO_2 via nitration of [methyl-^{14}C] toluene in 7 subsequent steps (Amersham International, UK, custom preparation). The reaction scheme is depicted in FIGURE 1.

Purification of the product was accomplished by dissolution in ethanol, treatment with activated charcoal and crystallization at 0 °C.

The resulting product was analyzed by thin-layer chromatography on Merck silica gel 60 F254 HPTLC plates, using light petroleum/acetone (2:1) (System A) or light petroleum/ ethyl acetate (4:1) (System B) and by reversed-phase chromatography on Whatman ODS KC18 TLC plates using methanol/water (9:1) (System C). The thin-layer radio chromatograms were analyzed for the

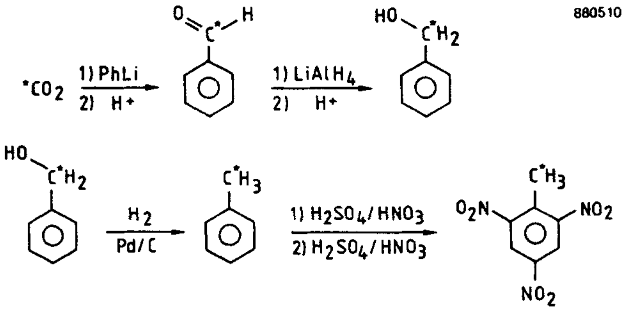

FIGURE 1

The Synthesis Of [Methyl-^{14}C] TNT Starting From $^{14}CO_2$.

(* indicates radioactive label)

distribution of radioactivity with a Berthold LB 2723 thin layer scanner, equipped with an LB 6280 gasflow counter using argon/methane (9:1) as counting gas.

The final product proved to be >99% pure as determined by thin-layer chromatography in all the above-mentioned eluent systems. The reaction product co-eluted with pure inactive TNT. Its identity was established by mass spectrometry (FIGURE 2).

The specific activity was 1.82 GBq/mmole (51.8 mCi/mmole). The total activity was 925 MBq (25 mCi).

TNT Vapour Concentration Measurements:

For the measurements a glass vessel was constructed, equipped with a magnetic stirring device in order to obtain a well mixed atmosphere throughout the whole vessel. The TNT sample was placed above the stirring device in a small cup. A perforated teflon or stainless steel shield was used to prevent direct radiation to come from the sample to be detected by the counting tube.

In the upper part of the vessel the counting tube was mounted. This (Philips PW 4350) Geiger-Mueller tube was connected with a Berthold BF 2302 high voltage supply and a Berthold BF 2304 scaler/rate meter.

In case of the experiments at 50 ^{o}C, the entire vessel was placed in a water bath, the temperature of which was controlled thermostatically.

Gas inlet and outlet connections were used for taking air samples by withdrawing air through a sampling device, using a vacuum

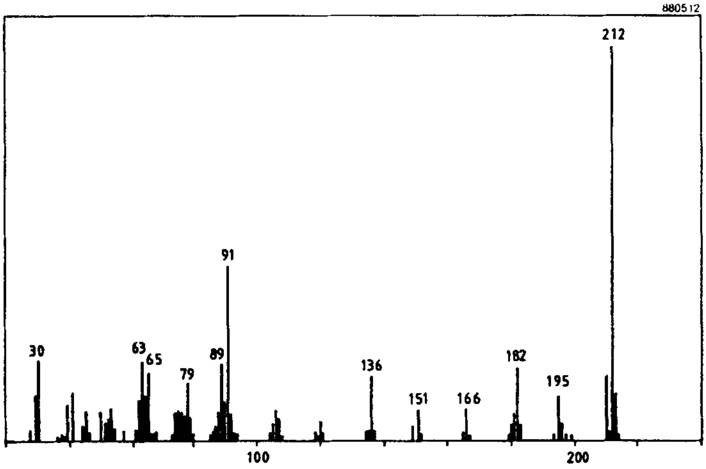

FIGURE 2

Mass Spectrum Of [Methyl-^{14}C] TNT.

pump. Two sampling procedures have been applied: adsorption on 50 mg of Tenax in a column (4.8 cm x 2.5 mm diameter) during 10-20 min or absorption in 5 ml MIC (methyl isobutyl carbinol = 2,2-dimethyl butane-3-ol). In both cases a second tube or absorber was placed behind the first one acting as a back-up. The flow was about 1 l/hour.

In the case of Tenax tubes the adsorption efficiency of the first tube were found to be 90-99%, depending on the TNT vapour concentration. TNT was desorbed from the Tenax by eluting with acetonitrile. It was found that large amounts of eluent were needed in order to desorb TNT. Both adsorption and desorption efficiencies differed considerably from the literature values[5].

In the case of absorption of TNT in MIC the efficiency of the first bubbler proved to be 80-94%. Samples of both the acetonitrile extracts and the MIC absorption solutions were added to a scintillation solvent (Packard Picofluor) and the amount of radioactivity was measured (Packard Minaxi Tri-Carb 4000 series liquid scintillation counter).

RESULTS AND DISCUSSION

TNT vapour concentration measurements:

In order to understand more about evaporation phenomena above buried mines it was decided to start with vapour pressure measurements above TNT without any coverage to check literature values, to test the equipment and to become acquainted with analytical procedures and the evaluation of the results.

After some time an equilibrium situation and a constant counter signal are expected when an amount of TNT is placed in the measuring system. However, even after very long periods of time (>200 hours), the signal failed to become constant.

It was concluded that, apart from the evaporation process, one or more other processes occur. The TNT vapour will most probably adsorb on all parts of the measuring system including the counter tube window, the glass walls and the teflon shield. Thus the adsorbed vapour adds to the counter signal. As the amount of vapour being adsorbed increases steadily also the signal increases. In fact the transport of TNT from the source to other parts of the system is measured even when the vapour equilibrium already exists.

FIGURE 3 shows the results of the above-mentioned experiment. After 190 hours the mica counter tube window was covered with an aluminium foil, preventing the vapour to further contaminate the counter tube. Aluminium has a lower affinity for TNT and therefore the slope of the signal decreased but it was still not constant.

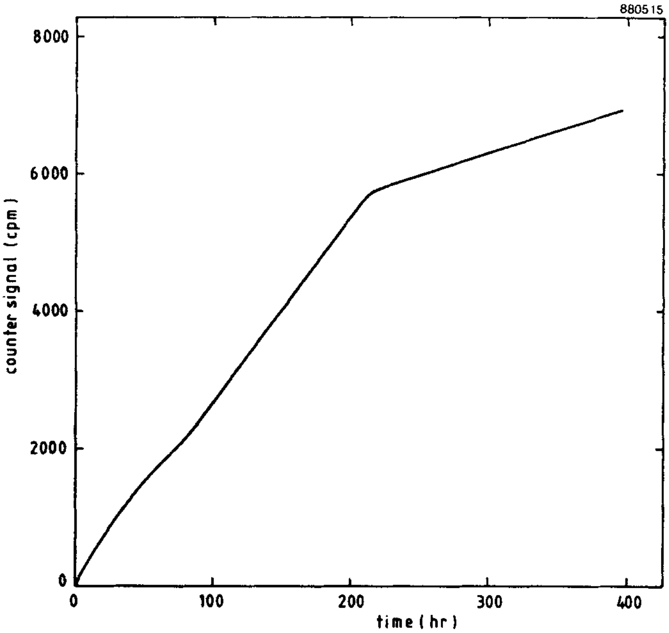

FIGURE 3

Counter Signal As A Function Of Time Before And After (190 hours) The Application Of An Al Foil.

In a second experiment (FIGURE 4) the counter tube was protected with the foil from the start. In order to study temperature effects after 95 hours the temperature was raised to 50 °C resulting in a dramatic increase of the slope of the curve from 3.8 cpm/hour to 83 cpm/hour. This probably is caused by both the higher amount of vapour present in the system and by the acceleration of the transport of TNT to the counter tube and other parts of the system. The slope decreased to its initial value (4.0 cpm/hour) when the temperature was lowered to 20 °C again. The ratio of the slopes (22) does not equal the ratio of the vapour concentrations (55) as is calculated from literature data[2], again indicating more than one phenomenon contributing to the counter signal.

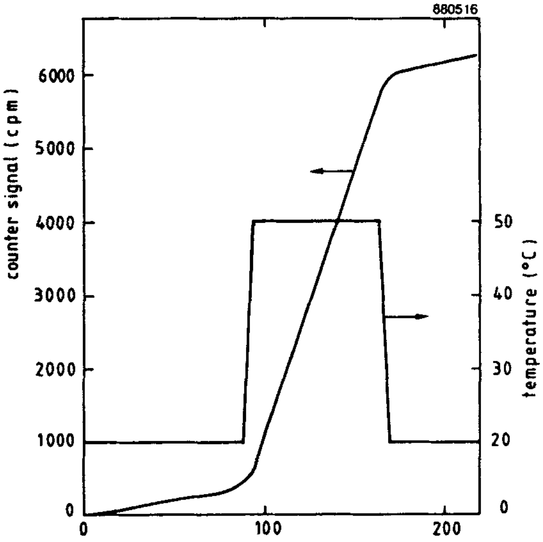

FIGURE 4

Counter Signal vs Time Following The Indicated

20-50-20 °C Temperature Profile.

Measurements at 20 °C were poorly reproducible. The mean of 9 data indicated a vapour concentration of 11 +/- 8 ppb (ref. 3: 4.6 ppb). At 50 °C sampling proved to be very difficult as the vapour had to pass a cold spot in the connector tubings at which large amounts were adsorbed.

In general, sampling caused a dip in the count rate vs. time curve. The initial slope is re-established after 15-20 hours at 20 °C and after 7-10 hours at 50 °C. These two recovery times might give an indication of the evaporation rate.

In all experiments it was assumed that the radiation measured was originating from ^{14}C-labelled TNT and that neither autoradiolysis had taken place nor by-products of the TNT were responsible for the radiation. In order to prove this assumption vapours adsorbed on Tenax were analyzed by High Performance TLC after extraction with acetonitrile. They co-eluted with pure TNT as is observed in FIGURE 5. Mass spectrometry proved the chemical nature of the sample as well.

In the following experiment the TNT sample was covered with a 0.45 mm thick layer of PVC. The slope of the counter signal was now reduced to 90% of the slope without PVC. After 85 hours the experiment was stopped. At that time the atmosphere contained 5 ppb TNT while the PVC contained 4.8 μg TNT/g, the glass wall 16 pg TNT/mm^2 and the teflon shield 112 pg TNT/mm^2 as measured by desorption and counting.

In the next experiment the TNT sample was covered with the same layer of PVC and buried under a 6 cm thick layer of a clay-type soil. The slope, as compared with a non-covered sample decreased to 63% of the slope.

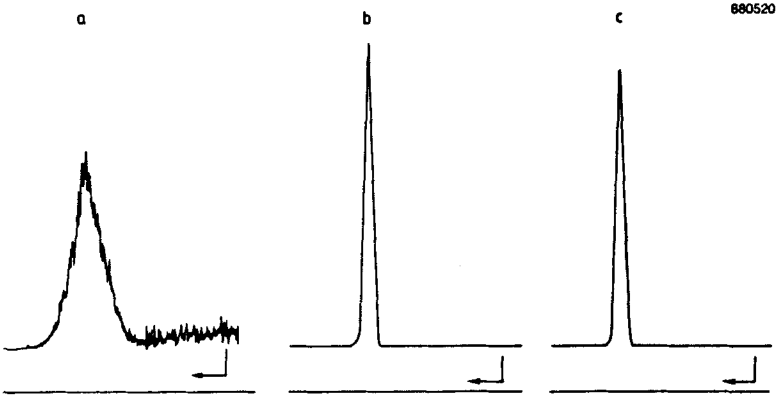

FIGURE 5

Thin-layer Radio Chromatograms Of Absorbed TNT (a), Pure TNT (b) And TNT From Sample Container (c).

In FIGURE 6 a break-through of TNT through the layer of soil is observed. As a reference another experiment is shown in which TNT without any coverage is observed. The counter tube was positioned in a by-pass of the system preventing direct radiation from the TNT sample as well as from the walls to enter the counter tube. After 350 hours the air showed a concentration of only 0.15 ppb TNT which is very low as compared to the concentration of 11 ppb above TNT as such and 5 ppb above TNT sealed in PVC. From the curve in FIGURE 6 break-through was observed after 50-60 hours. The slope was now reduced to only 9% of "uncovered" slope. It was observed that the soil of the break-through experiment contained radioactivity throughout the entire layer.

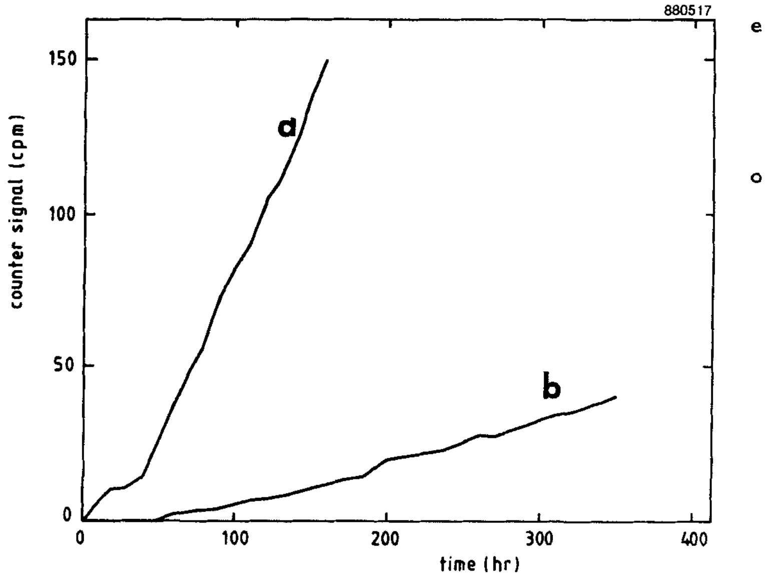

FIGURE 6

Counter Signal vs Time Above TNT Covered With 0.45 mm PVC And 6 cm Of Soil (a) And Without Coverage (b).

<u>Extrapolations to real minefields:</u>

With respect to the main objective of this study to set a detection limit for detectors of vapours of explosives the following calculations have been made. In our case the amount of TNT was 10 mg buried under soil with a surface area of 10 cm^2. The capacity of the TNT source expressed in weight per area is 10 g/m^2. A real size minefield (1000 m x 400 m) comprises 700 anti-tank mines containing 2-3 kg TNT each and about 4200 anti-personnel mines containing about 0.1 kg TNT each. When assuming that mines are buried under the same 6 cm thick layer of soil as in the model experiments, the capacity of the source is about 5 g/m^2, which is half of the model experiment capacity.

In the model experiment after 75 hours, a steady-state increase of the TNT concentration resulted in a concentration of 0.15 ppb TNT in 650 cm^3 of air after 350 hours, accompanied by TNT deposited on the glass wall and on the teflon shield. The total evolution of TNT from the ground was calculated to be 0.27 ng/hour through 10 cm^2, yielding 270 $ng/hour.m^2$.

A schematic view of the minefield is shown in FIGURE 7.

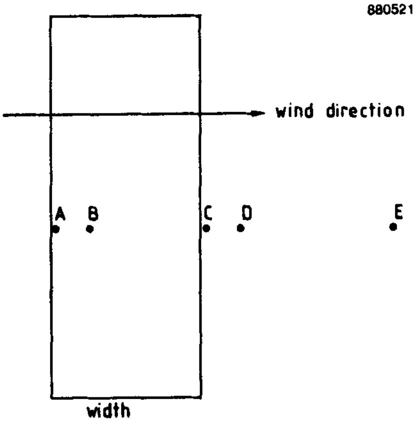

FIGURE 7

Schematic View Of Minefield With Sampling Points.

Assuming a wind speed of 5 m/s perpendicular to the length of the field TNT concentration profiles were calculated as presented in TABLE 1 for neutral weather conditions. Sampling points were assumed inside the field at 10 and 100 meters from the upwind edge (points A and B) and outside the field at 10, 100 and 500 meters from the downwind edge (points C, D and E). The results are given for a width of 10, 100 and 400 meters.

From these figures an impression is obtained of the actual concentration above a minefield and outside. At the edge in the downwind direction concentrations are highest and their value is a function of the distance the wind travels along the minefield during which TNT vapours are being picked up. These concentrations are not easily measured at the moment. Pre-concentration by a factor 1000 seems to be inevitable.

TABLE 1

Calculated TNT Concentrations Inside And Outside Minefields Of Different Size (various widths, length 1 km).

Width (m)	Concentration inside (ppt)		Concentration outside (ppt)		
Distance (m)	A (10)	B (100)	C (10)	D (100)	E (500)
400	0.004	0.034	0.049	0.020	0.008
100	0.004	a	0.034	0.010	0.003
10	a	a	0.004	0.001	0.0003

a = nonexisting sampling point

CONCLUSIONS

In order to obtain quantitative and qualitative information about TNT vapours escaping from buried non-metallic military mines containing TNT, a number of model experiments have been performed using ^{14}C-labelled TNT.

The vapour pressure at room temperature was found to be 11 +/- 8 ppb compared to a literature value of 4.6 ppb. When burying TNT sealed in PVC under a 6 cm thick layer of soil break-through of TNT vapours was observed after 50-60 hours while a TNT vapour concentration of 0.15 ppb in a closed system was measured after 350 hours.

Extrapolating these measurements to a real minefield situation are not easily made as for example the shelf life of the mine and the time the mine has been buried in the ground have to be taken into account. Estimated concentrations are in the sub-ppt range both inside and in the neighbourhood of the field.

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