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DETECTION OF 2,4,6-TRINITROTOLUENE VAPOURS IN AIR BY PLASMA CHROMATOGRAPHY

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SUMMARY

Rapid detection and identification of picogram quantities of the vapours of 2,4,6-trinitrotoluene (TNT) and related compounds in air is possible using the technique of plasma chromatography. Operating at atmospheric pressure, the instrument uses either air or nitrogen carrier gas into which the sample is injected directly or through a simple gas chromatographic system. Identification is provided by the characteristic mobility spectra obtained. Both positive and negative mobility spectra for TNT and 2,4-dinitrotoluene are presented and selective detection at ultra-trace levels is demonstrated.

INTRODUCTION

Detection of trace amounts of polynitroaromatic compounds in air, particularly 2,4,6-trinitrotoluene (TNT), is a currently relevant analytical problem. There are a number of laboratory procedures for detection and identification of TNT. These generally involve a preconcentration step from a large air sample followed by such instrumental methods as electron-capture gas chromatography (GC), mass spectrometry (MS), or GC–MS[1]. A GC–MS–computer system specifically designed for monitoring ambient air for such compounds has recently been reported[2]. Because of the complexity of the usual positive ion mass spectra of TNT, its isomers and interfering compounds in air, Yinon and Boettger suggested the use of negative ion mass spectrometry as a viable analytical method[3]. Their data indicated that the base peak for TNT at 6 eV ionizing electrons occurs for the NO_2^- ion at *m/e* 46, where little interference from contaminants occurs. By focusing on this specific, intense ion peak 1 ppm of TNT in air is readily detectable. Although such chromatographic and spectroscopic methods of analysis exist for detection and identification of TNT, a simple and rapid method sufficiently selective and sensitive to detect TNT in ultra-trace concentrations directly in air is quite desireable.

The technique and instrumentation of plasma chromatography appears to

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match these requirements. The plasma chromatograph uses an atmospheric pressure ion–molecule reactor coupled to an ion-drift spectrometer to produce characteristic ion mobility spectra of trace compounds contained in the carrier gas of the plasma chromatograph. Characteristics of the instrumentation and its capability for ultratrace analysis have been described previously[4–6]. Using the plasma chromatographic technique, Wernlund was able to demonstrate selective detection of nanogram and less quantities of TNT in river water[7]. The data presented here on the mobility spectra of TNT are part of a detailed study of polynitroaromatic compounds by plasma chromatography[8]. These results indicate that TNT produces strong positive and negative mobility spectra providing identification of picogram or less quantities in air; quantities well below those existing from the ambient temperature vapour pressure of the compound. With either direct injection of an air sample into the plasma chromatograph, or into a very simple GC instrument using the plasma chromatograph as a detector, a rapid analysis for the TNT content of air can be obtained.

EXPERIMENTAL

Instrumentation

The Beta-VI plasma chromatograph (Franklin GNO Corp., West Palm Beach, Fla., U.S.A.) used in these experiments has been described previously[6]. Ions formed in a flowing carrier gas by a ^{63}Ni source are moved by an electric field through an ion–molecule reactor section toward the drift spectrometer, where separation of the charged species (ions and ion–molecule products) occurs because of their different mobilities as they pass through a counter current flow of an inert nitrogen drift gas. The mobility spectrum produced by the spectrometer can be recorded as a single 20-msec scan from a single injection of ions, or in 1- to 10-min time spans using a variable delay gating technique on a scan grid near the detector, synchronized to the ion injection grid so as to record the sum of sequential ion injections. Unless indicated otherwise in figure and table captions, the experimental parameters used to obtain these data are: carrier gas flow-rate, 100 ml/min; drift gas flow-rate, 400 ml/min; electric field, 250 V/cm; ion injection pulse, 0.2 msec; scan grid pulse, 0.2 msec; recorded scan time, 2 min; pressure, atmospheric (728–745 torr). Either nitrogen or air is used as a carrier gas. All mobility values were obtained using a nitrogen drift gas.

Reagents

The nitrogen used is Linde High Purity (99.996%) and the air is Linde Bone Dry grade. Both gases used for carrier and drift sections of the plasma chromatograph are passed through individual stainless-steel traps of 2.25-l capacity packed with 4–8 mesh Linde molecular sieve 13X. This procedure removes impurities and gives a very low water concentration of approximately 10 ppm. The zone-refined high purity TNT was obtained from Dr. J. W. Harrison, Research Triangle Institute, Research Park, N.C., U.S.A. The 2,4-dinitrotoluene (DNT) is research grade obtained from Eastman, Rochester, N.Y., U.S.A.

Procedure

All samples were prepared as dilute methanol solutions with 10^{-4} g/ml. These were introduced directly into the instrument inlet by dispensing 0.1 μl of solution onto a platinum wire and allowing the solvent to evaporate prior to injection. This procedure gives a sample size of approximately 10^{-8} g.

RESULTS AND DISCUSSION

Using a nitrogen carrier gas, the stable positive reactant species are a series of $(H_2O)_nH^+$ and $(H_2O)_nNO^+$ ions, while only low-energy electrons (approximately 0.5 eV) are seen as the negative species. TNT gives strong, characteristic positive and negative product ion mobility spectra with these reactant species. Because of the nitro groups, TNT is strongly electrophilic and readily undergoes electron capture. This electron-capture behaviour results in the negative mobility spectrum shown in Fig. 1.

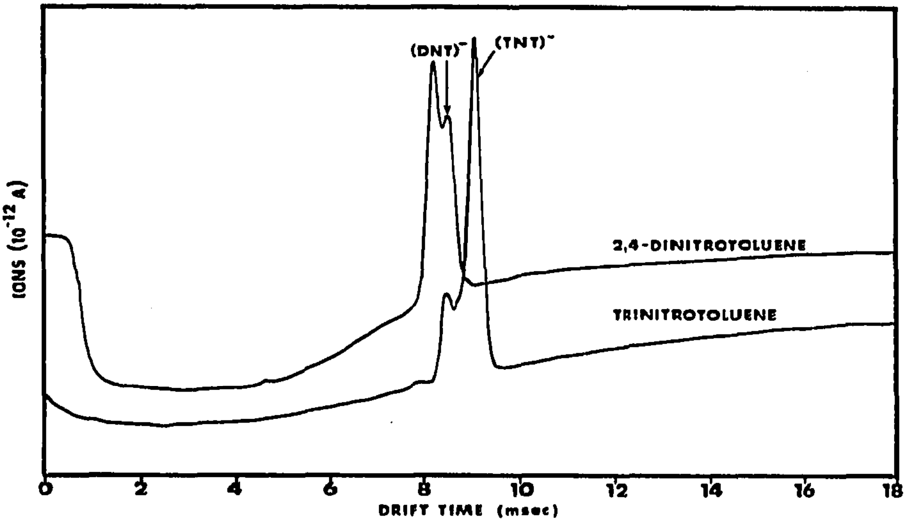

Fig. 1. Negative mobility spectra of TNT and DNT obtained at 193° C with an injected sample of 10^{-8} g. An indication of the initial electron current is seen at zero time, followed by a fall in electron level as a sample is introduced. The changing baseline back toward the original electron level is due to sample depletion during the 2-min scan time employed.

Both associative and dissociative electron capture occur giving the molecular ion, M^-, and $(M-NO_2)^-$. The negative mobility spectrum of DNT, is also shown in Fig. 1. This is an abundant, more volatile impurity usually associated with TNT. Its negative mobility spectrum displays the same electron-capture behaviour, forming two ions. Comparison of the TNT and DNT spectra assists our interpretation of the ions observed by noting the superposition of the $(M-NO_2)^-$ of TNT with the molecular ion of DNT.

While the negative mobility spectrum gives the more intense product ion peaks for detection of TNT, the positive mobility spectrum is equally characteristic and provides an additional identification means. Fig. 2 shows the formation of three product ions in the positive mobility spectrum. The most characteristic ions seen are the MH^+ and $(M+NO)^+$, along with an ion of higher mobility which we attribute to NO_2^+. Again a coincident mobility between the M^- in the negative mobility spectrum

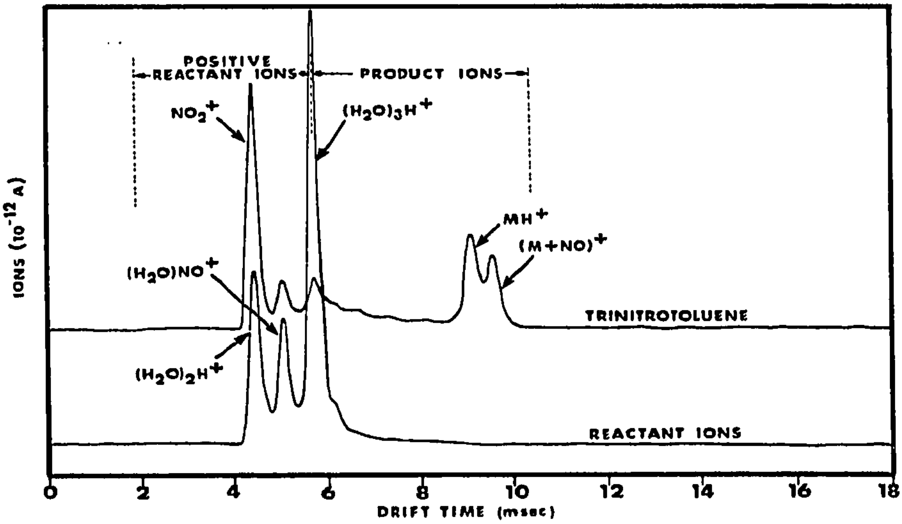

Fig. 2. The positive mobility spectra of both the initial reactant ions and the TNT product ions formed after sample addition. Spectra taken at 193°C.

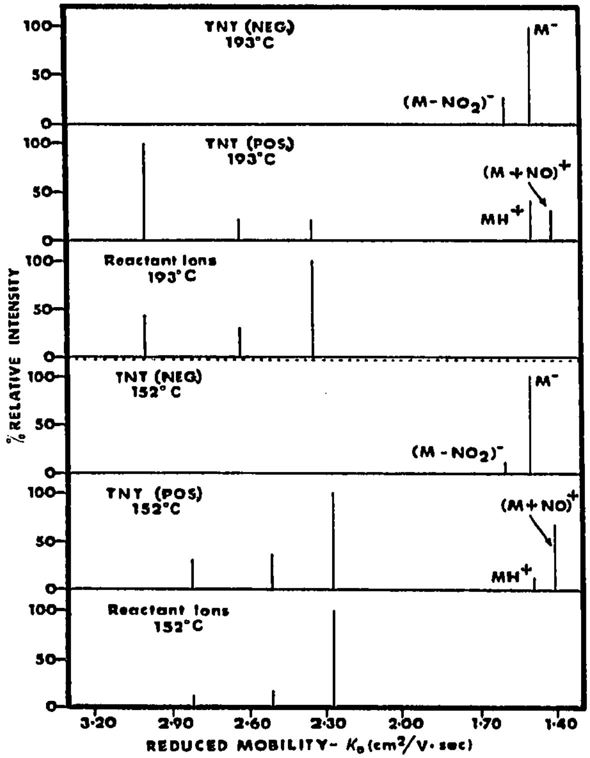

Fig. 3. Normalized mobility spectra of ionic abundance *vs.* K_0 mobility values shown for 152 and 193 °C temperature conditions. The observed change in mobility of the reactant ions and invariance in mobility of the TNT product ions with temperature is characteristic of positive mobility spectra.

and MH^+ in the positive mobility spectrum tends to confirm the identity of these ions. Similar results are obtained for DNT.

The temperature at which the mobility spectra are obtained has the greatest effect on the relative abundance of the ionic species produced. Fig. 3 shows this effect in the 152–193°C range; the higher temperature causing a different relative abundance of $(M-NO_2)^-$ in the negative spectra and $(M+NO)^+$ in the positive spectra.

Detection of TNT in air directly with the plasma chromatograph is facilitated by the use of an air carrier gas. When using air as a carrier gas, the same positive reactant ions are formed as when using a nitrogen carrier gas. The negative species are a mixture of $(H_2O)_nO_2^-$ and electrons, whose relative abundance depends upon temperature[9]. At 197°C the $(H_2O)_nO_2^-$ to electron ratio is less than 1:5. Both these species undergo ion–molecule reactions with the sample to form product ions similar to those obtained with electrons alone. Fig. 4 shows the negative mobility spectra of TNT and DNT obtained with an air carrier gas. These are similar to those seen in Fig. 1 when using a nitrogen carrier gas, which gives electrons as the reactant species, except in this case DNT produces only the dissociated ion $(M-NO_2)^-$, and TNT gives almost equal ratios of molecular and dissociated ions. Mobility data are summarized in Table I.

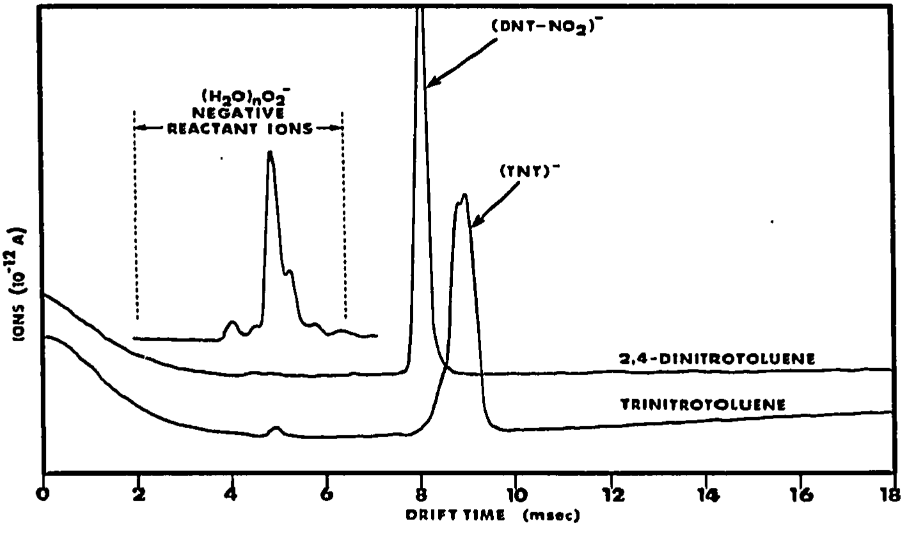

Fig. 4. Negative mobility spectra for TNT and DNT obtained at 197°C using an air carrier gas. The negative $(H_2O)_nO_2^-$ reactant ions prior to sample admission are shown.

Fig. 5 indicates the sensitivity attainable for a sample of air containing TNT either by direct injection of the air sample into the plasma chromatograph or by using the plasma chromatograph as a GC detector. The plasma chromatograph is tuned to the prominent molecular ion peak in the negative mobility spectrum of Fig. 1 and a sample of 10^{-8} g injected. This response peak shows a signal-to-noise ratio greater than 1000, giving a detectability in the picogram range. Since the ambient temperature

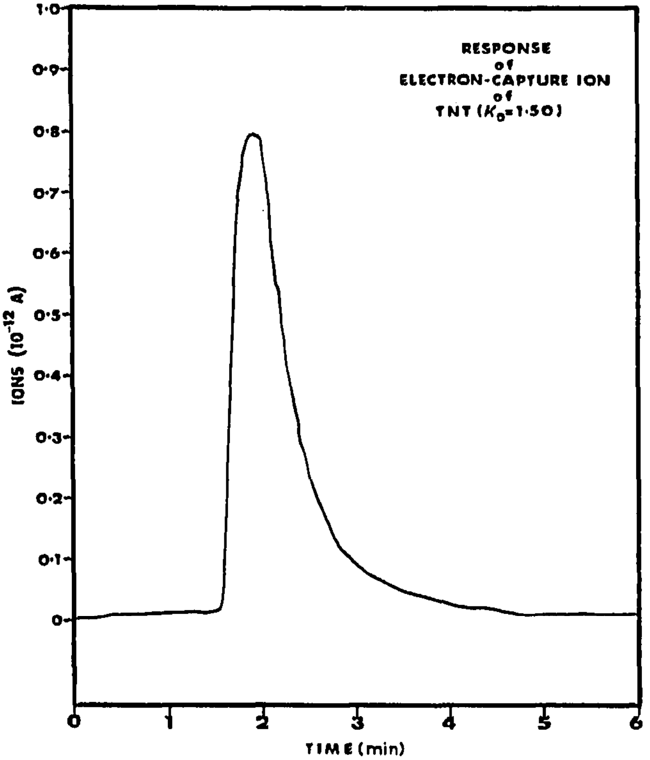

Fig. 5. Response signal generated by the plasma chromatograph at 197°C when tuned to the negative molecular ion peak of TNT and a 10^{-8}-g sample injected.

vapour pressure of TNT produces about 10^{-9} g of vapours per 100 ml of air, this sensitivity appears adequate to detect and identify the TNT present. The response speed indicated by the leading edge of the peak in Fig. 5 is in the few-seconds range; the total 1.8 min duration of the peak being related to the presence of TNT in the instrument during that time.

TABLE I

REDUCED MOBILITY (K_0)* VALUES OF PRODUCT IONS IN NITROGEN DRIFT GAS

Mobility spectrum	*Air carrier gas*		*Nitrogen carrier gas*		*Ions*
	TNT	*DNT*	*TNT*	*DNT*	
Negative	1.50	—	1.50	1.61	M^-
	1.57	1.68	1.60	1.67	$(M-NO_2)^-$
Positive	1.49	—	1.48	1.62	MH^+
	1.42	1.56	1.41	1.55	$(M+NO)^+$

* $K_0 = \dfrac{6.55}{T\tau}\cdot\dfrac{P}{760}\,\mathrm{cm^2\cdot V^{-1}\cdot sec^{-1}}$, where T = temperature (°K); τ = drift time (sec); P = pressure (torr); 6.55 = ion factor incorporating cell length (6 cm), electric field (250 V/cm) and correction to 273°K.

CONCLUSIONS

The plasma chromatograph gives simple, characteristic positive and negative mobility spectra for TNT and other nitroaromatic compounds in air. Sensitivity is in the picogram range, with identification possible by the mobility spectra. The plasma chromatograph can use either an air or nitrogen carrier gas and accept a sample directly from ambient air. The method is relatively insensitive to differing amounts of water vapour and light gases in the atmosphere, since these compounds merely effect the distribution of reactant ions. It is quite possible to design the instrument as a compact, simple monitor of air with a sensitivity greater than demonstrated here by specifically tuning the instrument parameters to respond selectively to the negative molecular ion of TNT.

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REFERENCES

1 C. Merritt, Jr., *Proc. Annu. Conf. Amer. Soc. Mass Spectrom., 21st, San Francisco, May 1973*, ASTM Committee E-14, Philadelphia, Pa., 1973, p. 320.
2 F. W. Karasek, *Res. Develop.*, 24, No. 7 (1973) 53.
3 J. Yinon and H. G. Boettger, *Anal. Chem.*, 44 (1972) 2235.
4 M. J. Cohen and F. W. Karasek, *J. Chromatogr. Sci.*, 9 (1971) 330.
5 F. W. Karasek, *Int. J. Environ. Anal. Chem.*, 2 (1972) 157.
6 F. W. Karasek, O. S. Tatone and D. M. Kane, *Anal. Chem.*, 45 (1973) 1210.
7 R. F. Wernlund, *Quantitation of Plasma Chromatograph Response*, Application Report No. 5, Franklin GNO Corp., West Palm Beach, Fla., April 1973.
8 D. W. Denney, *M. Sc. Thesis*, University of Waterloo, Waterloo, Ontario, Canada, January 1974.
9 F. W. Karasek and D. M. Kane, *Anal. Chem.*, 45 (1973) 576.