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VIRGINIA UNIV CHARLOTTESVILLE DEPT OF CHEMISTRY
CHEMICAL IONIZATION MASS SPECTROMETRY OF NITROAROMATIC VAPORS. (U)
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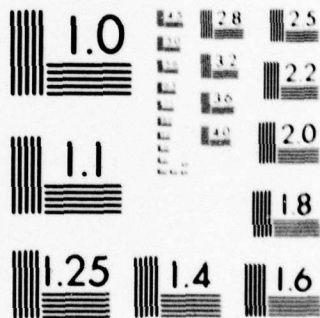
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FINAL TECHNICAL REPORT

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Project Title: Chemical Ionization Mass Spectrometry of Nitroaromatic Vapors

Sponsor: U.S. Army Mobility Equipment R + D Center

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Contract No.: DAAG53-76-C-0086

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Contract Period: 1/21/76 - 9/30/76

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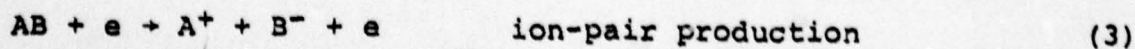
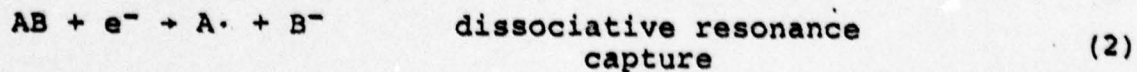
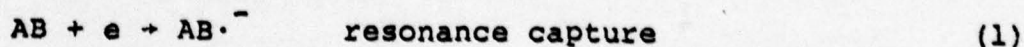
I. AIMS AND OBJECTIVES

- A. Modify a Finnigan Corp. quadrupole mass spectrometer to simultaneously record positive and negative ion chemical ionization mass spectra.
- B. Modify a Finnigan Corp. quadrupole mass spectrometer to accept a Townsend discharge chemical ionization ion source.
- C. Investigate the ionization of various nitroaromatic (including TNT, DNT, and MNT) compounds by negative ion chemical ionization mass spectrometry using a Townsend discharge ion source. Determine chemical ionization spectra in the presence of various reagent gases and at various source temperatures.
- D. Determine the limits of detection for vapors of the above compounds using negative ion chemical ionization mass spectrometry.

All of the objectives of this contract research have been achieved. Results of our research are described in section III.

II. INTRODUCTION

As indicated in several recent reviews (1-4), formation of negative ions by interaction of electrons and sample molecules can occur by three different mechanisms:



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Each of these processes shows a strong dependence on electron energy. Resonance capture affords molecular anions and involves electrons with energies near 0 eV. Dissociative electron capture is observed with electrons in the energy range 0-15 eV, while ion-pair production usually requires electron energies above 10 eV.

Under conventional electron impact conditions (40-80 eV electrons and source pressures in the range 10^{-5} - 10^{-7} Torr), formation of negative ions occurs predominately by the ion pair mechanism. Consequently, the majority of organic compounds afford spectra which are devoid of molecular ions and dominated by structurally insignificant low mass fragment ions such as (O^- , OH^- , CN^- , HC^- , NO_2^- , CNO^- , etc.) (1,5). Sensitivity is also a problem when the EI method is employed. Production of negative and positive ions in a ratio of $1:10^3$ is not uncommon. Despite the above difficulties, negative ion EI mass spectrometry has found limited utility in the analysis of metalloorganic (1), organoboron (6), polynitro (1), polyfluoro (1), organosulfur (1), and organophosphorus (7) compounds. Spectra of these classes of compounds often exhibit both molecular anions and structurally significant fragment ions. Interaction of sample molecules with a small population of low energy electrons produced from electrode surfaces is assumed to be responsible for the generation of molecular anions under the above conditions.

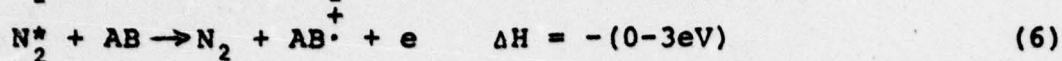
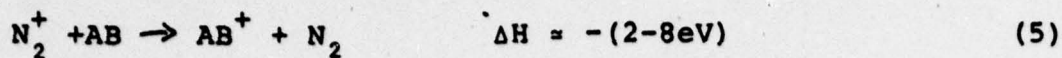
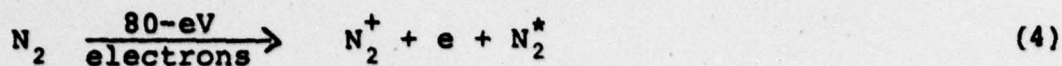
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In an effort to extend the utility of the EI negative ion technique, Bowie has explored the possibility of tagging complex organics with efficient electron capture groups (1). Derivatization of sample molecules in this manner increases the cross section for capture of the small number of thermal electrons in the ion source and also widens slightly the energy range of electrons that can be captured by the sample without inducing fragmentation. Accordingly, the method does enhance the yield of structurally informative anions produced from organic samples. Research in this area has also afforded a wealth of information on the unimolecular fragmentation mechanisms of negative ions. Widespread use of the EI technique in analytical applications is unlikely, however, since much of the ionization still involves interaction of sample with high energy electrons and occurs by the undesirable ion-pair formation mechanism. The above technique is also several orders of magnitude less sensitive than the methodology described in this paper.

Until recently the most useful method of producing negative ion mass spectra was that of von Ardenne (3) who employed a low pressure (10^{-2} Torr) argon discharge to generate a plasma containing positive argon ions and a large population of low energy electrons. This plasma was constricted by a strong magnetic field and allowed to pass into a chamber containing gaseous organic sample. Ionization of the

sample in this Duoplasmatron source occurs predominantly by the resonance capture and dissociative resonance capture mechanisms and the resulting spectra exhibit abundant high mass fragment ions as well as ions characteristic of sample molecular weight. Even though von Ardenne and his coworkers have obtained excellent spectra of hundreds of organic compounds using the above method, the Duoplasmatron ion source has not enjoyed widespread usage. This is in part due to the cost and extensive nature of the modifications required to facilitate attachment of the Duoplasmatron source to commercially available mass spectrometers.

It is important to note that the success of the Duoplasmatron source lies in its ability to generate a large population of near thermal electrons, which are readily captured by many organics without inducing extensive fragmentation. A similar population of electrons is also produced when a mass spectrometer is operated under chemical ionization conditions. In this method a reagent gas such as nitrogen at a pressure of 1 Torr is placed in the ion source and bombarded with high energy electrons (100-500eV) in order to generate reagent ions as shown in Equation 4. Sample molecules are introduced in the usual manner and are ionized by ion-molecule reactions with the reagent ions (Equation 5). As indicated in Equation 4, the formation of each reagent ion is accompanied by the production of a low energy electron. Each ionizing event also removes about 30eV from the bombarding electron (8) which in turn undergoes a number of collisions with neutral



gas molecules. Consequently, the energy of the incident electron beam is reduced to near thermal values also (9). Thus operation of a mass spectrometer under CI conditions affords a mixture of positive reagent ions and near thermal energy electrons. Negative reagent ions can also be generated when the reagent gas molecules themselves are capable of forming stable negative ions by the resonance capture or dissociative resonance capture mechanisms.

Considerable effort has been devoted to exploring the analytical potential of various reagent gases for positive ion CIMS (10-12). This is a direct consequence of the finding that the nature of the CI spectrum produced is dependent on both the nature of the reagent gas and the type of ion molecule reaction used to ionize the sample. Different structural information can be obtained from the same sample by recording several positive ion CI spectra using different reagent gases. Similar results should be obtained in negative ion CIMS studies. Despite this expectation, little research has been conducted on the analytical potential of negative ion CI reagents. Dougherty has reported on the methane and isobutane negative ion CI spectra of polycyclic chlorinated insecticides (13) and aromatic chlorinated pesticides (14) and has also discussed the utility of Cl^- as a CI reagent ion (15). Use of Cl^- and O_2^- in an atmospheric CI source for the analysis of barbituates (16), chlorinated

aromatics (17), and highly acidic compounds (18, 19) has also been reported. The superoxide anion, O_2^- , has been shown to be an excellent reagent for CI analysis of 2,3,7,8-tetrachlorodibenzo-p-dioxin (20), alcohols, and polycyclic aromatic compounds (21).

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A major goal of this contract research was to evaluate the utility of negative ion CIMS for the detection of nitroaromatic vapors in the atmosphere.

Under chemical ionization (CI) conditions the negative ion current obtained from nitroaromatics should exceed the positive ion current by a factor of 10^2 - 10^3 . This means that by using negative ion chemical ionization (NCI) mass spectrometry the limit of detection for nitroaromatics should be more than a hundred times lower than the detection limit currently realized by conventional electron impact and positive chemical ionization techniques. ↗

The enhanced negative ion sensitivity predicted above is based on the assumption that positive and negative ions are destroyed in a CI source at the same rate and by the same process (i.e., diffusion of ions to the ionization chamber walls.)

Formation of positive sample ions under CI conditions requires a collision between positively charged reagent ion and neutral sample molecule. Since this process is diffusion controlled, reactions occurring on every collision usually have rate constants on the order of 10^{-9} molecules cm^{-3} . Formation of negative sample ions by electron capture is also governed by diffusion if the process proceeds with unit efficiency. However, since the mobility of an electron is ca. 100 times greater than that of an ion, the rate constant for resonance electron capture can be more than two orders of magnitude (10^2) greater than typical ion molecule reaction rate constants. We conclude that formation of negative ions by electron capture can be $>10^2$ faster than any ion molecule reaction producing a positive ion. If the rate of sample ion destruction is the same for positive and negative ions, the larger rate of formation of negative ions should be reflected in a 100-1000 decrease in sample size required for negative versus positive ion mass spectrometry.

In order to compare sensitivity in the positive and negative ion mode directly, one of the first objectives of the contract research was to modify a Finnigan quadrupole mass spectrometer so that positive and negative ion mass spectra could be recorded simultaneously. Also since a major goal of the research was to establish

limits of detectability for nitroaromatic vapors in the atmosphere, the utility of air as a CI reagent gas was investigated. Since oxygen rapidly destroys hot metal filaments usually employed to produce an ionizing beam of energetic electrons, the quadrupole mass spectrometer also had to be modified to accommodate a Townsend discharge ion source. The Townsend discharge was to be employed as an alternate source of energetic electrons.

All of the objectives of the contract research have been achieved. Results of our research are described in the following section.

III. RESULTS AND DISCUSSION

A. Simultaneous Recording of Positive and Negative Ion Chemical Ionization Mass Spectra

Simultaneous recording of positive and negative ion CI mass spectra (21) on Finnigan Model 3200 and Model 3300 quadrupole mass spectrometers is accomplished by pulsing the polarity of the ion source potential ($\pm 1-10V$) and focusing lens potential ($\pm 10-30V$) at a rate of 10kHz as illustrated in Figure 1. Under these conditions, packets of positive and negative ions are ejected from the ion source in rapid succession and enter the quadrupole filter. Unlike

the situation in magnetic sector instruments, ions of identical m/e , but different polarity, traverse the quadrupole field with equal facility and exit the rods at the same point. Detection of the positive and negative ion beams is accomplished using two Model 4751 analog continuous dynode electron multipliers (Galileo Electro-Optics Corp., Sturbridge, Mass.) placed side by side at the exit aperture of the quadrupole rods. The potential on the first dynode is maintained at +1200 to +2000 V on one multiplier and -1200 to -2000V on the other. Accordingly, positive ions are attracted to one multiplier and negative ions are attracted to the other. The result is that positive and negative ions are recorded simultaneously as deflections in opposite directions on a conventional light beam oscillograph (LBO). Signals from the positive ion multiplier are handled with standard Finnigan electronics. The negative ion signal is processed by commercially available equipment. This includes a floating coaxial feed through (Ceramaseal Inc., New Labanon Center, N.Y.) and negative ion preamplifier (Extranuclear Laboratories, Pittsburgh, Pa).

In order to obtain a direct comparison of ion currents produced in the positive and negative ion mode using the PPNICI technique, it is necessary to know the relative gain of the positive and negative ion multipliers. This is accomplished in the present study

by inserting a Faraday cup in place of the multipliers and then measuring the positive and negative ion current obtained from an unheated solid probe sample of benzoic acid using 1 Torr methane as the reagent gas. Under the above conditions the ratio of $(M-1)^{-}/(M+1)^{+}$ is 1:4. This experiment is then repeated with the dual electron multipliers in their standard configuration. Equal gain on the multipliers is achieved by varying the voltage applied to each multiplier until the above ion current ratio for benzoic acid is obtained.

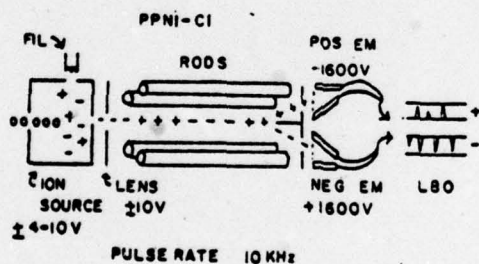


Figure 1. Pulsed positive negative ion chemical ionization (PPNICI) mass spectrometer

FIL = filament, EM = electron multiplier, and LBO = light beam oscillograph

B. Modification of a Finnigan Quadrupole Mass Spectrometer to Accommodate a Townsend Discharge CI Ion Source.

To facilitate use of oxidizing reagent gases, the CI source on the Finnigan 3200 and 3300 quadrupole mass spectrometers was modified to accommodate a Townsend discharge (22). This is accomplished by mounting a discharge tube in the 1/8-inch hole remaining in the ion chamber walls after the conventional electron trap assembly has been removed (Figure 2). Over this hole are placed in the following order; a nickel screen (85% transmission) (Scientific Instrument and Equipment Division, Bendix Corp., Rochester, N.Y.), a hollow cylindrical insulator insulator formed from machinable glass ceramic (Corning Glass Works, Corning, N.Y.), and a cathode machined from stainless steel. These items are assembled with 0-80 screws insulated with sapphire and ceramic spacers. The cathode of the resulting assembly is then connected through a 3-M Ω (2-watt) current limiting resistor to the negative terminal of a 1600-V power supply. This power supply includes 18 type B, 90-V (Eveready No. 490) radio batteries connected in series, a variable voltage control, and an ammeter capable of measuring discharge currents from 1 to 1000 μ A.

For operation of the Townsend discharge as a source of electrons (anode mode) to ionize a reagent gas at 1 Torr, the voltage between the two electrodes is increased to between 800 and 1200 V until the ion current from the source is maximized. Under the above conditions the TD affords 10-30 μ A of electron current, is completely stable, and is unaffected by the pulse frequency applied to the ion source and lens for PPNICI experiments.

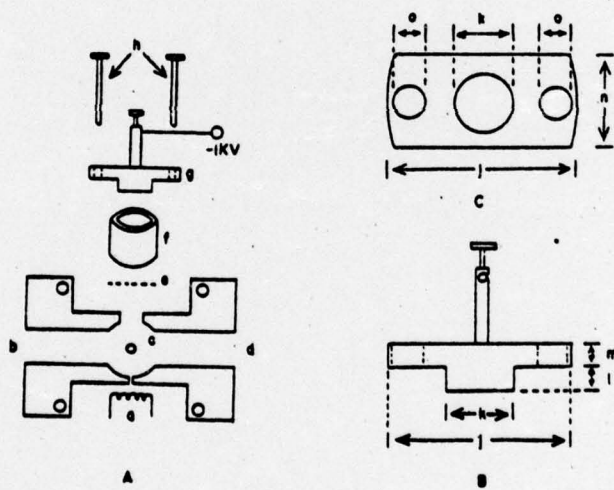


Figure 2. Townsend discharge ion source

(A) Discharge tube components; (B) stainless steel cathode (g) as viewed from the side; and (C) stainless steel cathode as viewed from the bottom; (c) ion source volume; (d) solids probe inlet; (e) 85% transmission Ni screen; (f) hollow glass ceramic cylinder i.d. 3/16 inch, o.d. 1/4 inch, length, 3/16 inch; (h) stainless steel screws 0-80 UNF-2A X 3/8 inch; (j) 9/16 inch; (k) 3/16 inch; (l) 1/16 inch; (m) 1/16 inch; (n) 1/4 inch; (o) 3/32 inch

C. Negative Ion CI Mass Spectra of Nitroaromatic Compounds

Negative ion CI mass spectra of TNT, DNT, and the three isomeric MNT molecules have been obtained using four different gases, methane, nitrogen, oxygen, and air as the CI reagents. Results of these experiments are presented in Tables I and II.

TABLE I

Negative Ion Chemical Ionization Mass Spectra of Nitroaromatic Compounds

Reagent Gas	Compound	MW	M ⁻	% Total Sample Ion Current ^a					Other, %
				(M-1) ⁻	(M-OH) ⁻	(M-NO) ⁻	(M-O) ⁻	NO ₂ ⁻	
1 Torr, CH ₄	TNT	227	37.6	-	13	26.6	6.7	3.8	181(5.8), 167(4.4), 151(2.1)
	2,4 DNT	182	68.9	-	2.7	17.3	6.4	4.7	--
	O-MNT	137	95.7	-	4.3	--	--	--	--
	m-MNT	137	45.2	-	14.4	--	13.5	26.9	--
	p-MNT	137	69.2	-	8.3	--	10.8	11.7	--
1 Torr, N ₂	TNT	227	56.8	1.8	19.9	15.6	--	--	181(1.6), 167(4.3)
	2,4-DNT	182	86.6	1.6	3.8	5.6	2.4	--	--
	O-MNT	137	100	-	--	--	--	--	--
	m-MNT	137	100	-	--	--	--	--	--
	p-MNT	137	100	-	--	--	--	--	--

Table I (cont)

0.8 Torr, O ₂	TNT	227	43.5	29.9	9.8	15.4	1.4	--
2,4-DNT	182	23.9	60.3	-	8.8	5.2	1.8	--
<u>O</u> -MNT	137	49.6	30.0	-	--	5.0	15.4	--
<u>m</u> -MNT	137	53.6	22.6	-	--	3.0	13.4	91(7.4)
<u>p</u> -MNT	137	35.8	65.1	-	--	2.3	5.8	--

1 Torr, Air	TNT	227	66.2	5.0	20	8.8	-	--
2,4-DNT	182	62.5	34.2	1.3	--	2.0	--	--
<u>O</u> -MNT	137	96.8	--	-	--	3.2	--	--
<u>m</u> -MNT	137	95.3	4.7	-	--	-	--	--
<u>p</u> -MNT	137	100	--	-	--	-	--	--

Ion Source Temperature; 110°

TABLE II

HIGH TEMPERATURE NEGATIVE ION CI MASS SPECTRA OF NITROAROMATIC COMPOUNDS

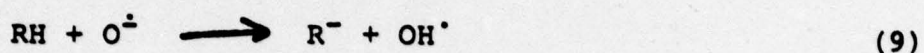
Reagent Gas	Compound	MW	M ⁻	a Total Ion Current ^a					Other m/c (s)
				(M-1)	(M-OH) ⁻	(M-NO) ⁻	(M-O) ⁻	NO ₂ ⁻	
1 Torr, CH ₄	TNT	227	12.1	-	33.2	39.2	-	-	181(7.8), 167(7.7)
	2,4 DNT	182	5.2	-	21.6	34.3	-	29.2	135(9.7)
	p-MNT	137	-	-	-	-	-	100	--
1 Torr, N ₂	TNT	227	15.5	2.8	36.5	37.5	-	5.8	181(1.9)
	2,4 DNT	182	41.0	1.8	15.9	27.2	-	11.4	136(2.7)
0.8 Torr O ₂	TNT	227	16.4	9.4	9.4	13.1	-	51.7	--
	2,4 DNT	182	14.0	43.8	2.8	6.7	-	31.0	136(1.7)

^a Ion Source Temperature, 200°C

Under CI conditions neither methane nor nitrogen form stable negative ions. Production of positive ions from these molecules, however, is accompanied by formation of a population of near thermal electrons which function as "reagent ions" in these two gases. Negatively charged ions from sample-molecules are formed predominately by electron capture in these two reagent gases. Small amounts of OH^- are formed from water as an impurity in the methane and nitrogen but the reaction of this ion with sample is seldom responsible for more than a few percent of the negative sample ion current.

In contrast to the above situation, both air and oxygen afford abundant negatively charged reagent ions under CI conditions. In the case of oxygen at 0.8 torr the following ions appear; O^+ (5.2%), O_2^+ (48%), O^- (3.4%), OH^- (31%), and O_2^- (12.5%). The same ions are formed from air; O^+ (5.2%), O_2^+ (25%), O^- (22%), OH^- (27.5%), and O_2^- (20.3%).

With oxygen or air as the CI reagent formation of negatively charged sample ions can occur by electron capture, charge exchange and/or Brönsted base ion molecule chemistry.



In general the negative ion CI mass spectra of aromatic compounds exhibit high ion currents in the molecular weight region of the spectra. Those fragment ions that do form are highly characteristic of structure and correspond to the loss of small moieties such as OH, NO, O, and NO₂. Very little current is carried by the NO₂⁻ ion which dominates negative ion spectra recorded under conventional EI conditions. In addition to the above ions, formation of an M-1 ion occurs when air or oxygen is employed as the CI reagent. All three of the reagent ions, OH⁻, O⁻, and O₂⁻, in these gases are probably sufficient strong bases to remove protons from the nitroaromatic compounds studied.

Negative ion CI spectra of nitroaromatic compounds were all found to be highly temperature dependent. Increasing the ion source temperature altered the distribution of sample ion current substantially. As shown in Table II spectra of the nitroaromatics recorded

at 200°C all exhibit significantly more fragmentation than those recorded at 100°C. The cross section (sensitivity) for ion formation may also vary considerably with temperature but the necessary experiments to check this have not been performed.

D. Determine the Limits of Detection for TNT Vapors Using Negative Ion Chemical Ionization Mass Spectrometry (NI CIMS).

Method 1 - Gas Chromatography Mass Spectrometry (GCMS)

In the initial experiments to determine the lower limit of detection for TNT vapors by negative ion quadrupole CIMS, samples were introduced to the ion source via a gas chromatograph interfaced directly to the mass spectrometer. Acetone solutions containing known concentrations of TNT were employed in this work. The signal carried by the molecular anion, M^+ , at m/e 227 was sampled continuously by operating the spectrometer in the single ion detection mode and by using a Finnigan PROMIM and Rikadenki recorder to display the signal. The quantity of sample injected into the GC was decreased until the limit of detection ($S/N=2$) was achieved. Other pertinent experimental conditions are listed below.

Temperature - Injector - 275°
Column - 210° (5 ft OV-1, 3%)
Transfer line - 280°
Ion source - 100°
Filament current - 0.2mA at 100eV
Source pressure - 0.86 torr of methane
GC carrier gas - methane
CI reagent gas - methane
TNT retention time - 1.25 min
GC column flow rate = 7ml/min

Using the above methodology a S/N of 3 was obtained when 1pg of TNT was injected onto the GC column.

Method II - Use of a Jet Separator

In a second set of experiments the GC was disconnected and replaced with a standard Finnigan jet separator open to the atmosphere at one end and interfaced to the ion source at the other. The sample consisted of a large mouth jar containing air saturated with TNT vapors. The contents of the jar were sampled by placing the open vessel near the open end of the separator for approximately 1 second.

Additional experimental parameters included:

Separator and Transfer lines	250°	
Ion Source Temperature	100°	
Ion Source Pressure	700 μ	160 μ of air through separator 540 μ of methane added after separator
Monitored ion	m/e 227 (M^+)	for TNT
Recorder	Finnigan PROMIM plus	Rikadenki Recorder

Air saturated with TNT afforded a S/N = 4000 in the above experiment. This result suggests that a level of TNT 2000 times lower than that employed could be detected with a S/N=2. Since saturated TNT in air corresponds to 3 parts TNT in 10^9 parts of air, the lower limit of detection by this method would appear to be 1.5 parts in 10^{12} or 15fg.cc of air.

Method III - Capillary Flow Restrictor

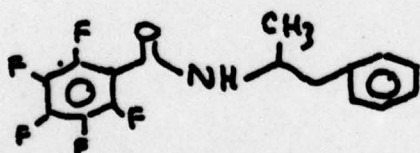
In a third experiment the jet separator was removed and replaced with a 8/1000 inch glass capillary flow restrictor. Flow of air at 1 atm through this glass capillary produced an ion source pressure of 800 μ . Other experimental conditions were identical to

those employed in method II. With the capillary flow restrictor in place, air saturated with TNT afforded a S/N ratio of 2000. This valve extrapolates to a detection limit for TNT of 3 parts in TNT in 10^{12} or 30 fg/cc of air.

GENERAL COMMENTS

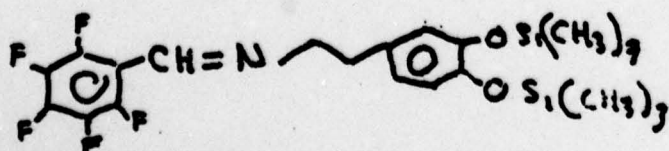
The detection limit of TNT achieved using the jet separator and capillary flow restrictor methods is approximately 50 times lower than that obtained in the GCMS experiment. Irreversible sample absorption in the GC could explain the above discrepancy but the necessary experiments to prove this have not been performed.

It is perhaps worth mentioning that several other compounds have recently been detected at the femtogram level by negative ion GC CIMS. These compounds are shown below along with the lower limit of detection achieved.



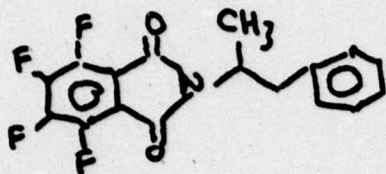
10fg 4/1 S/N

Pentafluorobenzoyl
amphetamine



25fg 4/1 S/N

Pentafluorobenzylidene
dopamine

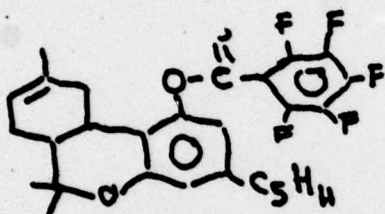


10/g

12/1

S/N

Tetrafluorophthaloyl
amphetamine



20/g

S/N 2/1

Δ^9 -Tetrahydrocannabinol
Pentafluorobenzoate

Since the cross section for formation of a stable negative ion from TNT is equal to that of the above compounds we expect a similar lower limit of detection for TNT, ~~ca.~~ 1 fg/cc of air with a S/N=2 (1 part in 10^{13}), using our present instrument configuration. The level realized to date is 15fg/cc. of air.

Additional Experiments

The above work was carried out on a Finnigan 3300 quadrupole^o mass spectrometer. Finnigan now manufactures a model 4000 instrument which operates with a positive ion sensitivity between 10 and 100 times higher than that obtained on our 3300. This improved performance has been achieved largely by better focusing of the ion beam exciting the ion source and should therefore be independent of the sample ionization step. We therefore anticipate that detection of TNT by negative ion CI on the model 4000 could be observed at 10-100 times lower levels than that measured on the model 3300. On the Finnigan 4000, detection of TNT could possibly be achieved at a level of 1 part in 10^{14} or 10^{-16} g/cc of air. We have recently acquired a Finnigan model 4000 and plan to make the necessary measurements as soon as the instrument has been modified for negative ion CI experiments.

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