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FINNIGAN ION TRAP MASS SPECTROMETER DETECTION LIMITS AND THERMAL ENERGY ANALYZER INTERFACE STATUS REPORT AND PRESENT CAPABILITIES

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Background

A new Finnigan ion trap mass spectrometer was purchased and installed at LLNL. Over a period of several months the instrument was tested under a variety of conditions utilizing a capillary gas chromatography interface which allowed separated organic compounds to be carried directly into the ion source of the mass spectrometer. This direct interface allowed maximum analytical sensitivity. A variety of critical tests were performed in order to optimize the sensitivity of the system under a variety of analysis conditions. These tests altered the critical time cycles of the ionization, ion trapping, and detection. Various carrier gas pressures were also employed in order to ascertain the overall all sensitivity of the instrument.

In addition we have also interfaced a thermal energy analyzer (TEA) to the gas chromatograph in order to simultaneously detect volatile nitrogen containing compounds while mass spectral data is being acquired. This is the first application at this laboratory of simultaneous ultra-trace detections while utilizing two orthogonal analytical techniques.

In particular, explosive-related compounds and/or residues are of interest to the general community in water, soil and gas sampler. Below are highlighted a few examples of the analytical power of this new GC-TEA-ITMS technology.

Sensitivity Studies with the IT-MS

Often the sensitivity of mass spectrometry instruments is reported from the perspective of the manufacturer who may only utilize special chemicals when reporting the sensitivity of their instrument. The objective of these studies were to determine the lower detection limits of the Finnigan-MAT ion trap mass spectrometer using a standard, well known compound. We have chosen naphthalene. It is a common compound which generates an intense molecular ion and few fragments (See Figure 1). Standard solutions of naphthalene were prepared and injected into a DB-5, 30 meter capillary gas chromatographic column which entered directly into the ion source of the mass spectrometer. The gas chromatograph utilized a DB-5 column which was heated as follows: initial temperature, 60°C with 2 min. hold, then a 8°C/min. ramp to 250°C and finally held at the upper temperature for 2 min. The results of these sensitivity studies are seen below.

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Results

A variety of individual experiments were performed with naphthalene in hexane solutions following the scheme outlined in the manufacturing operations manual. The standards were analyzed using the automatic gain control software function and only the region between 125 and 135 amu was scanned. The electron multiplier was set at 2600 volts and the dynode was at 3Kv. The data was recorded in the M/S only mode using the standard electron impact ionization. Naphthalene has a molecular weight of 128 and can clearly be seen in Figure 2 with 2142 counts. The results of the GC-IT/MS analyses indicated that the lower detection limit for naphthalene is 1 pg per injection. At this level of sensitivity, a signal-to-noise ratio of 21:1 was observed (See Figure 2).

Discussion - Sensitivity of the ITMS

The ITMS manufacturer only indicated a lower level of sensitivity of 10 pg without utilizing sophisticated ionization techniques. Under routine analysis we are able to tune the ITMS system to obtain ten times the sensitivity and clearly detect 1 pg of naphthalene with a peak height of approximately 2,000 A/D converter counts and a signal-to-noise ratio of 21:1. At half the sensitivity (500 fg and a signal-to-noise level of 10:1) we may still be able to differentiate the naphthalene from background noise. This level of compound sensitivity becomes important when attempting to see low amounts of material in complex samples. For example a detection level for 1 pg of sample isolated from a 100 mL extract of water, taken up and analyzed by GC-ITMS would be:

$$1 \text{ pg} = 100 \text{ mL} \rightarrow 1 \times 10^{-12} \text{ g} = 100 \text{ mL} \rightarrow 1 \times 10^{-14} \text{g} = 1 \text{ mL}$$

Therefore: Our level of detection is 1 in 10^{14} for water extracts.

If we would extract 1 liter of water our detection ability could be even better because more water has been initially extracted, the target compounds concentrated, and more sample injected into the GC-ITMS.

Therefore, we have shown that the ion trap mass spectrometer is exceeding sensitive to organic compounds and will have a direct impact of the detection of unique compounds in environmental samples.

GC-TEA-ITMS Analysis

Background

In an effort to simultaneously detect nitrogen compounds while performing GC-MS analyses, a thermal energy analysis capability has been added to the IT-MS instrument. This has not been an easy task. It has been determined that because of the great sensitivity of the TEA analyzer, any trace contamination can contaminate the TEA instrument. In addition, the interface which simultaneously allows GC column components to be split for both the IT-MS and the TEA instruments must be carefully designed. Both temperature parameters, flow rates, and interface conditions are most critical for ultra-trace levels of detection.

We now wish to report that most all of the difficulties have been solved concerning the interface between the GC-IT/MS instrument and the TEA analyzer.

Results

The simultaneous acquisition of mass spectral data and TEA nitrogen specific compound information was accomplished by utilizing two PC computers. One acquired the TEA data and the other acquired the IT-MS mass spectral data. The analysis of the sample and data acquisition was easily programmed for both computers to start at the point of GC injection. A considerable amount of new data acquisition software has allowed many TEA-IT/MS experiments to be performed. The results of all of these experiments clearly reveal the utility of GC-TEA-IT/MS analyses.

Some of the initial data clearly can show the importance of the new system. Figure 3A reveals the total ionization plot of a mixture of a number of non-nitrogen and nitrogen containing compounds. (The solvent generates a response either due to nitrogen contamination or pressure surges in the reaction chamber). All are detected at variety of GC-MS retention times. Figure 3B reveals the TEA trace which was acquired simultaneously. In this trace, only nitrogen containing compounds were observed.

Another example is the detection of explosives. Figure 4A represents the total ion chromatograph (TIC) of glycerol trinitrate (NG)/ 1, 2, 3-Propanetriol triacetate (TA), 2, 4, 6-trinitrotoluene (TNT), 1, 2, 3 trinitrobenzone and a trace impurity of dinitrobenzene. (Coincidentally the NG & TA possess almost the exact same retention time on a DB-5 column). The TEA profile of the same explosives is a replica of the TIC as shown in Figure 4B. For every nitrogen containing compound there is a TEA signal. Each of the explosives analyzed are below 1 ng/peak.

One of the major advantages of an GC-TEA-ITMS analysis is the ability to select a nitrogen containing compound in a complex matrix of hydrocarbons. For example, a matrix of hydrocarbons can be time consuming to evaluate for explosives, but with a TEA nitrogen profile one can select the correct peak from the ITC (Figure 5A) by matching the retention times from the TEA nitrogen profile, Figure 5B.

The detection of a CW hydrolysis product, diisopropylaminoethanol can also be performed easily by GC-TEA-ITMS (Figure 6A, 6B). Other applications of the GC-TEA-ITMS include illicit street drug analysis. For example, Figure 7A, 7B are a mixture of methamphetamine, cocain and heroin. Because most illicit drugs contain nitrogen the TEA can direct us to all nitrogen, containing compounds for quick identification of suspect agents. Another example of a CW hydrolysis product is seen in (Figure 6A and 6B).

Conclusions

From the work performed to data, it appears that the GC-TEA-IT/MS system is both sensitive and very specific for the identification and fingerprinting of unique compounds. We are now perfecting the analysis of very complex mixture, refining the software and preparing to analyze other important samples.

FIGURE 1

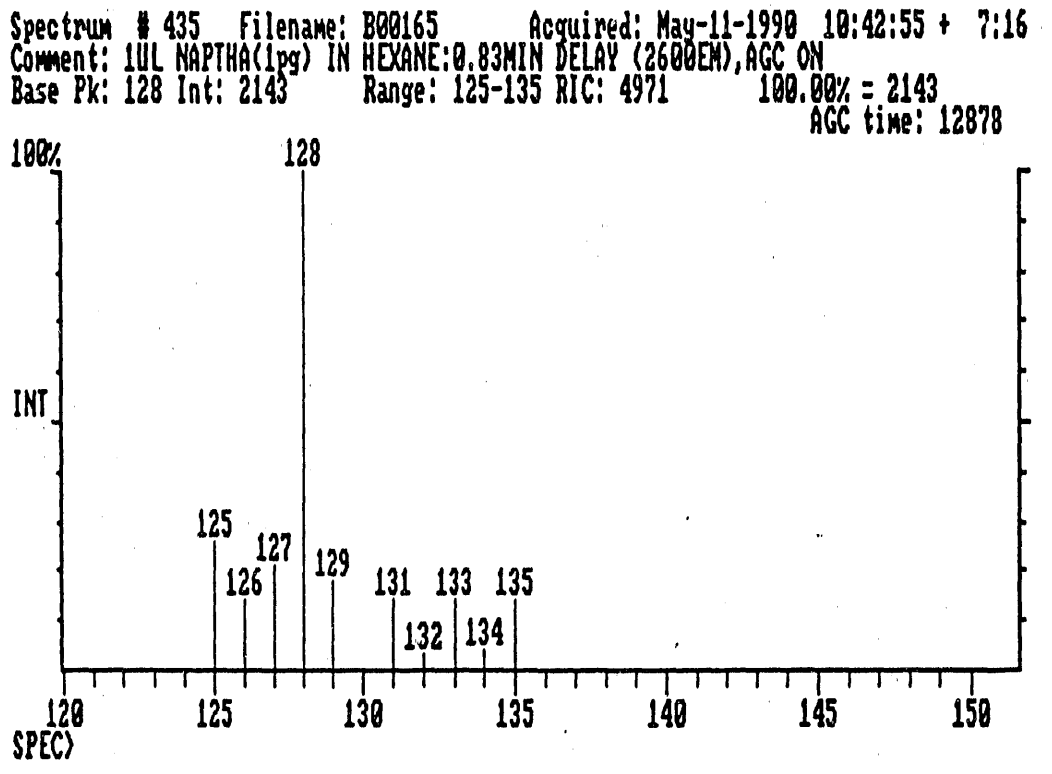


FIGURE 2

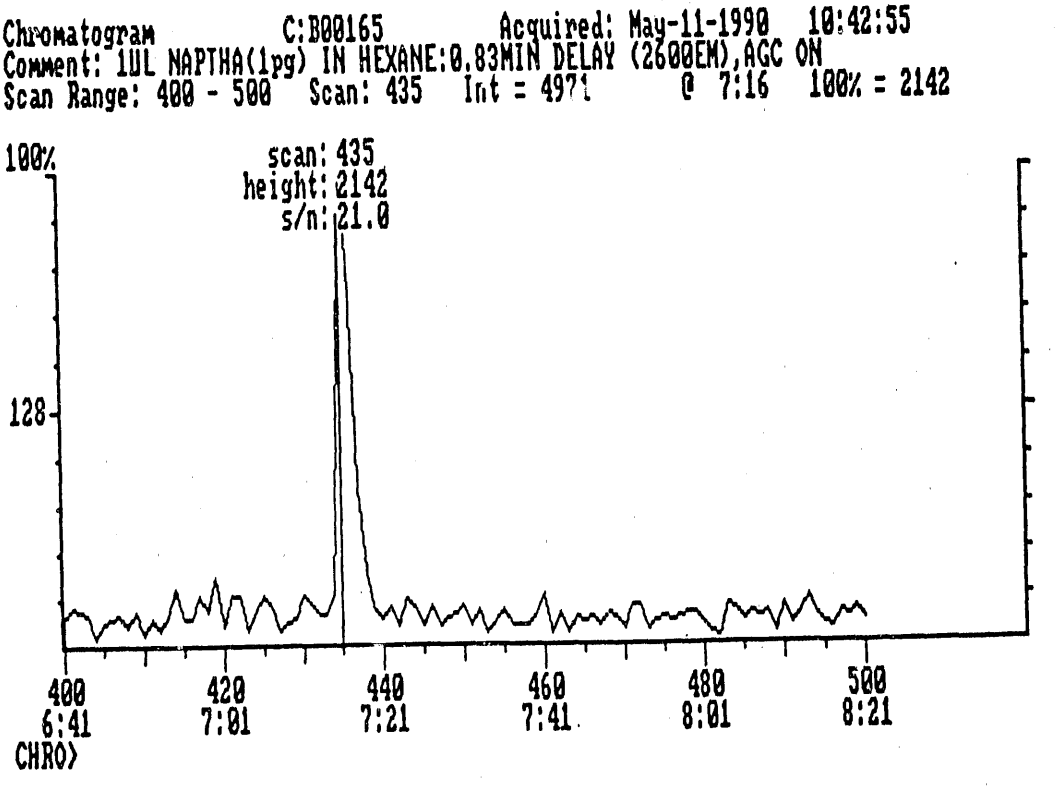


Figure 3A

Chromatogram C:B00337 Acquired: Oct-03-1990 17:59:45
Comment: 1UL TEA/ITMS STD MIX IN ETOH:EM2000,AGC ON,TEA ON
Scan Range: 261 - 1259 Scan: 261 Int = 889 @ 4:22 100% = 35216

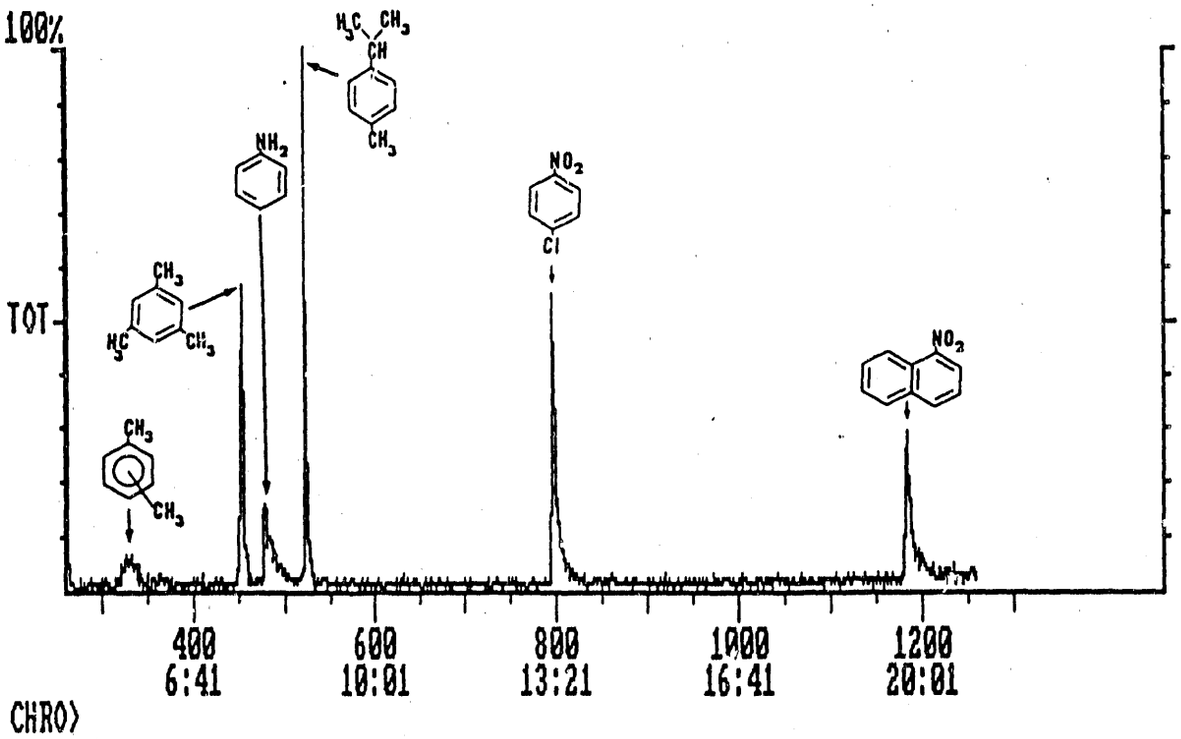


Figure 3B

1uL TEA/ITMS MIX
17:59:39 10/03/90
tea048.DAT

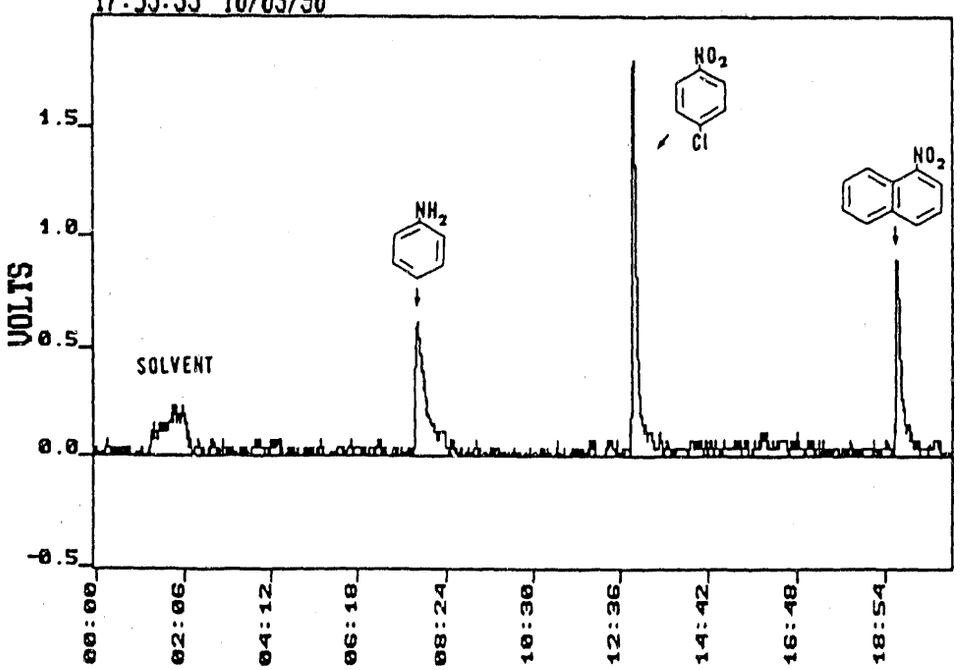


Figure 4A

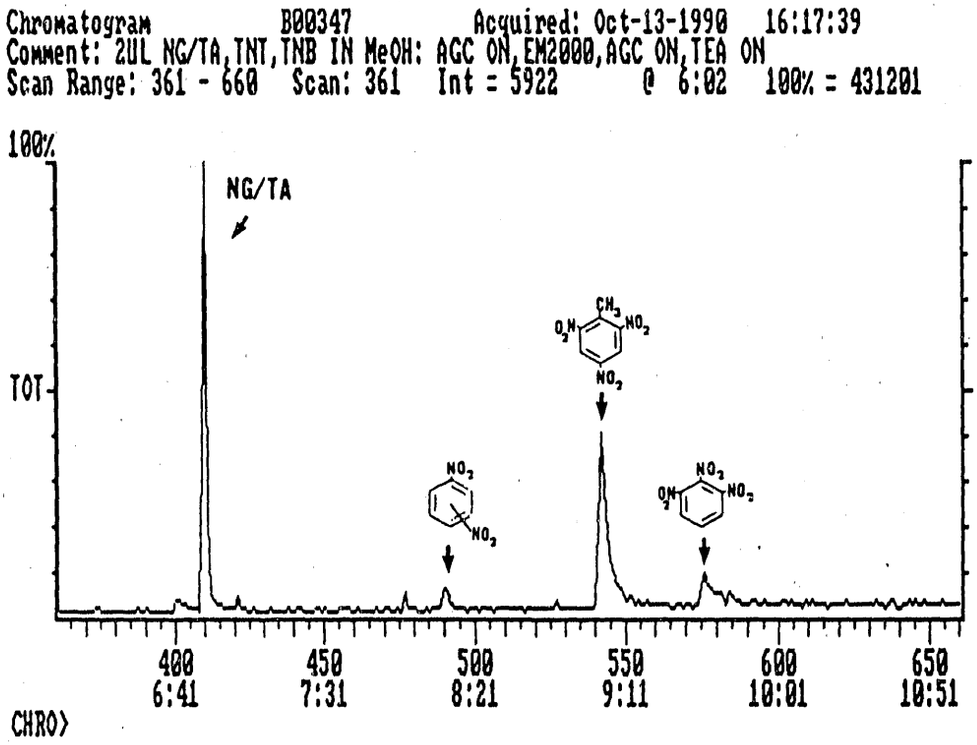


Figure 4B

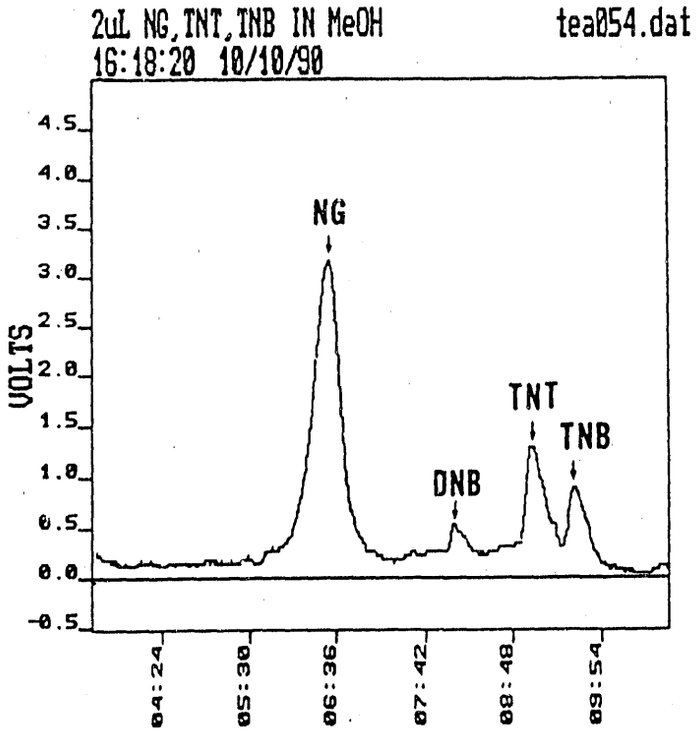


Figure 5A

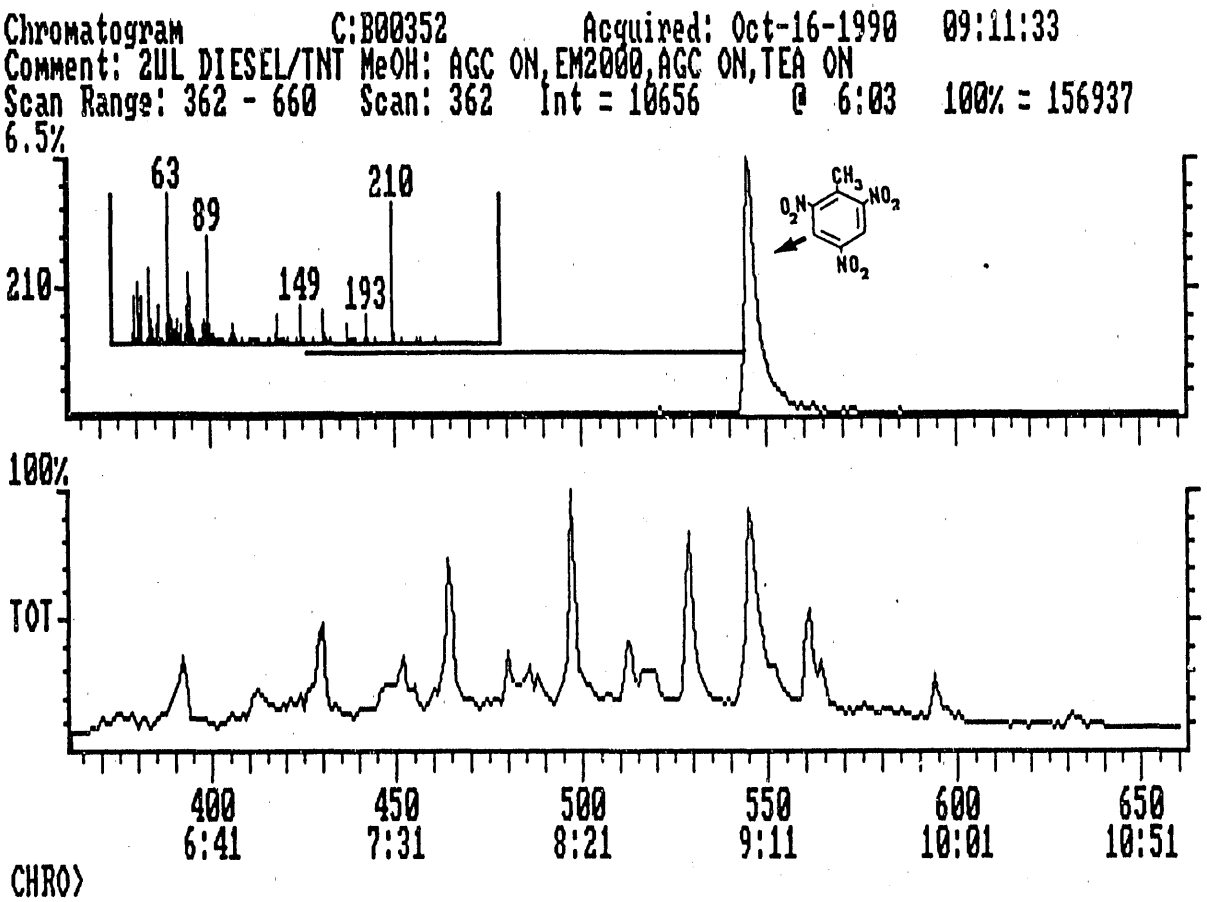


Figure 5B

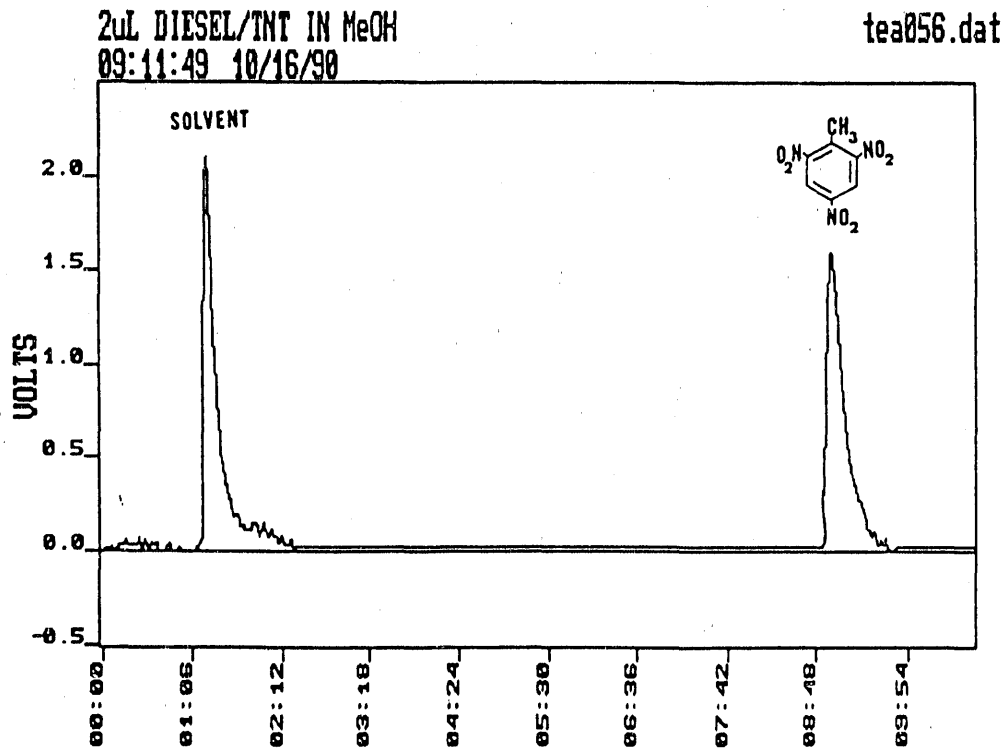


Figure 6A

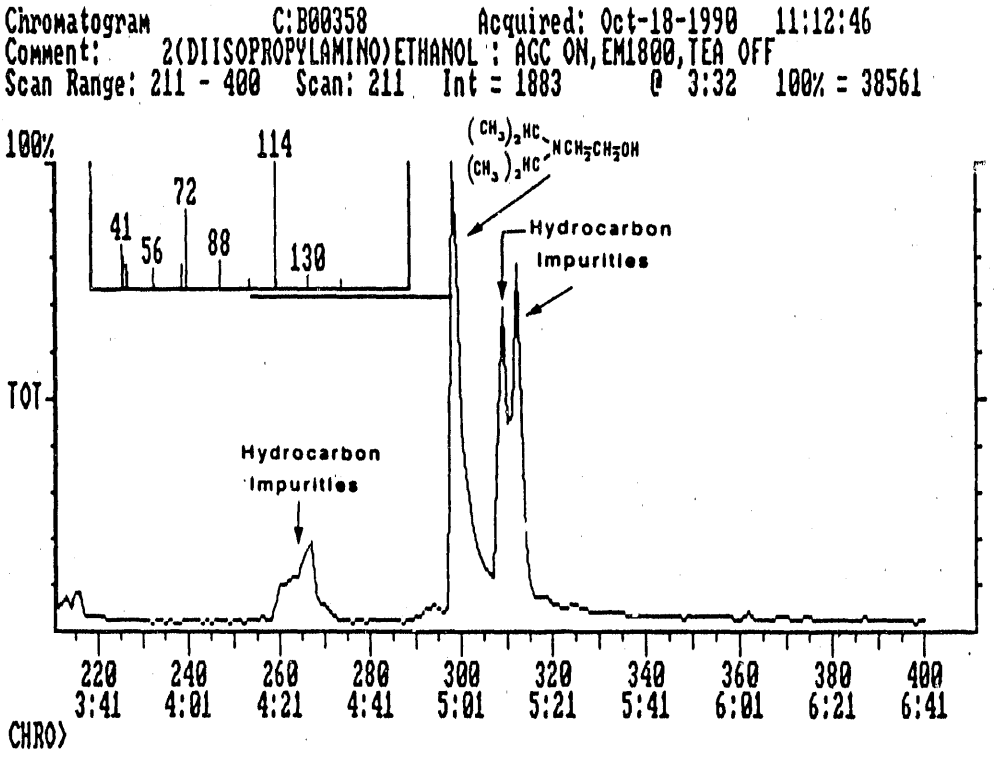


Figure 6B

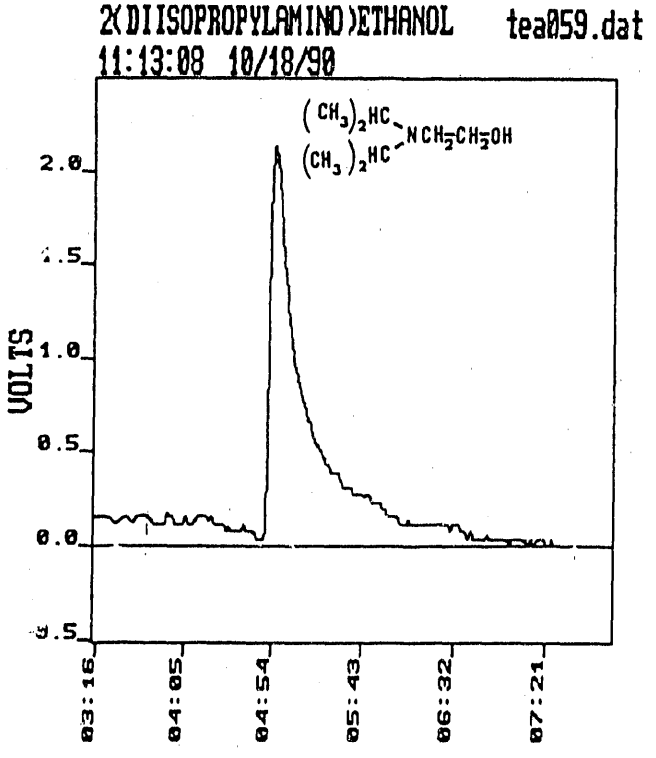


Figure 7A

Chromatogram C:B00356 Acquired: Oct-17-1990 17:37:29
Comment: 2uL DRUG MIX IN ISOPRO/CH2CL2 : AGC ON,EM1800,TEA ON
Scan Range: 361 - 1440 Scan: 361 Int = 6710 @ 6:02 100% = 62167

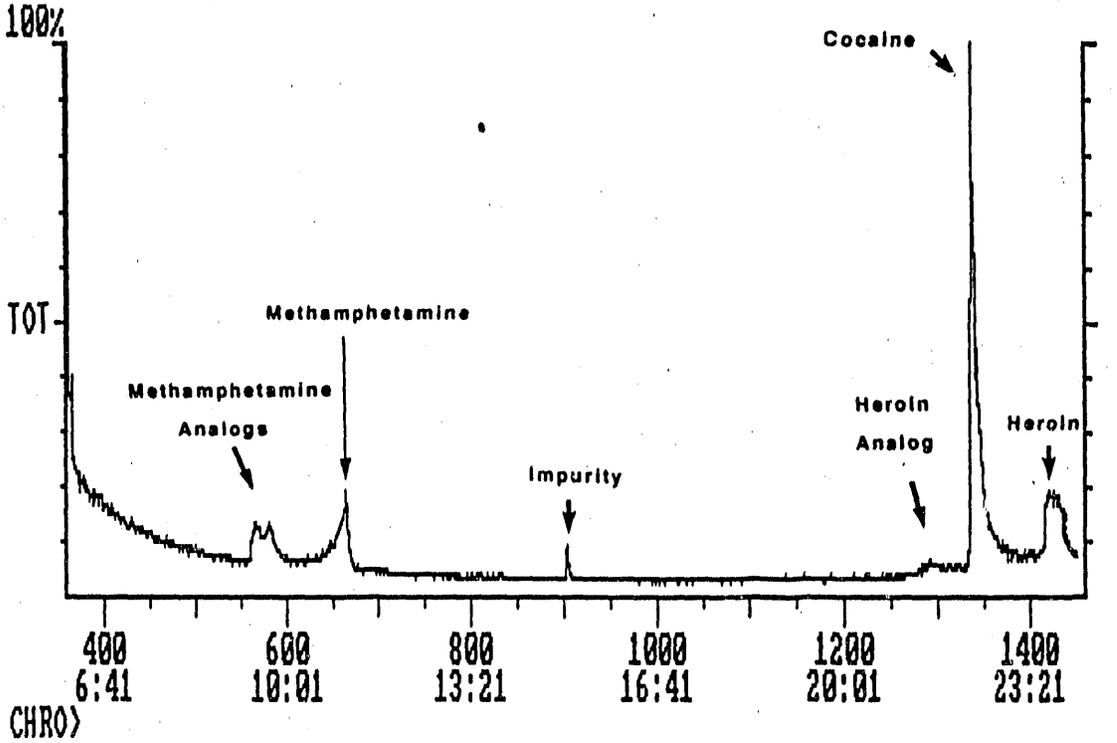
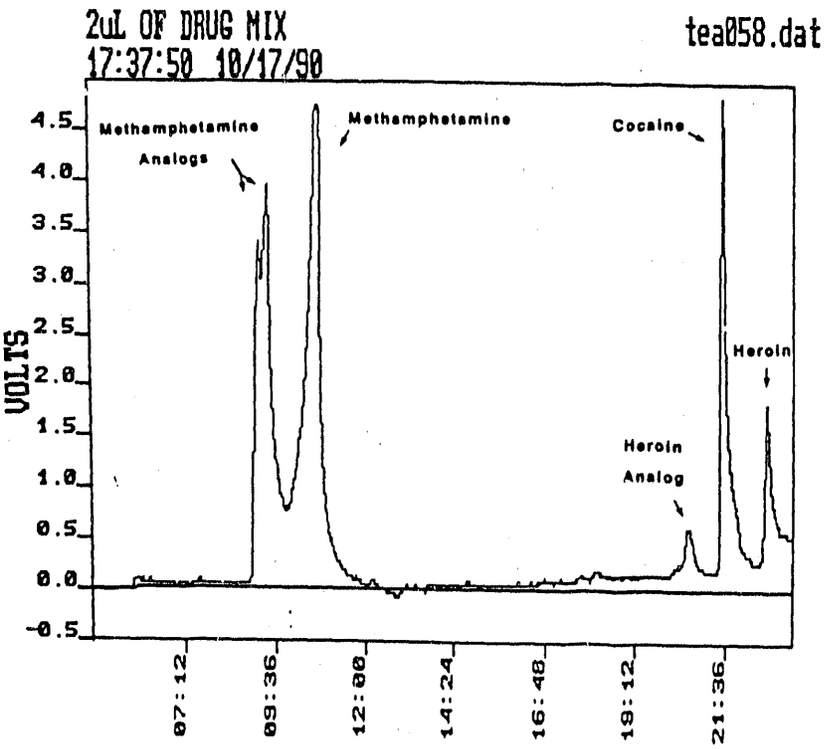


Figure 7B



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