

# DEVELOPMENT OF AN INFRARED SPECTROPHOTOMETRIC METHOD FOR THE ANALYSIS OF JET FUEL USING A LOOP CALIBRATION TECHNIQUE

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Naval Health Research Center Detachment  
Environmental Health Effects Laboratory  
EHEL-07-02

March, 2007

20071116228

# Neurobehavioral Effects of Sodium Tungstate Exposure on Rats and Their Progeny

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June 30, 2007

**NAVY HEALTH RESEARCH CENTER DETACHMENT**

**DEVELOPMENT OF AN INFRARED SPECTROPHOTOMETRIC METHOD FOR  
THE ANALYSIS OF JET FUEL USING A LOOP CALIBRATION TECHNIQUE**

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**March 2007**

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## **PREFACE**

This document contains the development of a jet fuel vapor phase generator for creating vapor phase standards to be used in calibrations. Infrared spectrophotometric and gas chromatographic calibrations using these vapor phase standards were discussed.

The work was performed as part of a study on the effects of whole body exposure to Jet A aerosol and vapor.

The opinions contained herein are those of the authors and are not to be construed as official or reflecting the view of the Department of the Navy or the Naval services at large.

## ABSTRACT

A whole body inhalation study of combined jet fuel vapor and aerosol necessitated the development of a method for preparing vapor standards from the neat fuel. Due to the complex mixture of components in jet fuel, and the selective partitioning between aerosol and vapor, a novel method was needed to prepare vapor only standards for the calibration of infrared spectrophotometers and a gas chromatograph. A re-circulating loop system was developed which provided vapor only standards whose composition matched those seen in an exposure system. Comparison of nominal concentrations in the exposure system to those determined by infrared spectrophotometry and gas chromatography were in 80%-99% agreement.

## KEY WORDS AND PHRASES

Jet Fuel, Inhalation, Gas Chromatography, Head Space Analysis, Infrared Spectrophotometry.

## **GLOSSARY OF TERMS AND ABBREVIATIONS**

GC – Gas Chromatography

GC/HS-Gas Chromatography using head space sample introduction

IR – Infrared Spectrophotometry

M<sup>3</sup> – Meter cubed: equals 1000 liters.

HEPA filtration -High efficiency particulate air filtration

Note: Common chemical and measurement abbreviations are not included.

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## INTRODUCTION

Jet fuel is a complex mixture of aliphatic and aromatic hydrocarbons (Dietzel et al., 2005). When aerosolized it partitions into a biphasic mixture of aerosol particles and vapor components with the relative concentrations of each phase being determined by the temperature of the mixture. The vapor portion consists mainly of highly volatile lower molecular weight compounds and portions of the less volatile middle and heavy molecular weight compounds. The aerosol droplets consist mainly of middle and heavy molecular weight compounds. Typically, jet fuel studies are conducted by analyzing the total fuel concentration - both aerosol and vapor fraction combined. This can be done by collecting grab samples on carbon tubes with subsequent carbon solvent extraction and gas chromatographic analysis (Dietzel et al, 2005, Pfaff et al, NIOSH 1550) or collection of grab samples in a head space vial analyzed by gas chromatography (GC/HS), or by using a heated transfer line to move the sample from an exposure system to a gas chromatograph/total hydrocarbon analyzer (Mattie et al.) for cyclic monitoring. These methods do not permit continuous monitoring but rather rely on samples collected and analyzed at various time points.

The purpose of the proposed study was to use infrared spectrophotometry (IR) as an alternative method to gas chromatography to allow for continuous monitoring of the jet fuel vapor component during exposure. For a jet fuel study, 4 chambers needed to be monitored simultaneously. As a back-up system and alternative technique, a method for measuring the vapor concentration of jet fuel by Gas Chromatography using head space sample (GC/HS) was developed. Both methods required vapor standards for calibration purposes. IR analysis required the production of vapor only standards for calibration as aerosols must be removed prior to passing through its gas cell. Likewise, vapor only standards were required for the head space gas chromatographic method for direct comparison with the IR.

To create vapor phase jet fuel standards required a method which would allow for quantitatively generating the vapor phase of the jet fuel while removing the aerosol portion from the analysis stream. Such a generation system was developed for making jet fuel vapor calibration standards in a closed loop, re-circulating air system.

The volume of the loop system was determined in a two step process. First, the response of the IR to known concentrations in milligrams per liter (mg/L) of Hexane was determined using standard bag methodology. Second, known masses (mg) of hexane were introduced into the closed loop system and the concentration (mg/L) resulting was determined from the IR response. Dividing the mass (mg) added to the loop by the concentration (mg/L) measured from the IR response gives the volume of the system in liters (L).

GC/HS analysis of the jet fuel vapor created in the closed loop system showed these vapors qualitatively matched the composition of the jet fuel vapor created by the generators being used for the inhalation study and were thus suitable for use as jet fuel

vapor standards. These standards were used to calibrate both the GC/HS system and the long path gas cells on IR spectrophotometers used for the study.

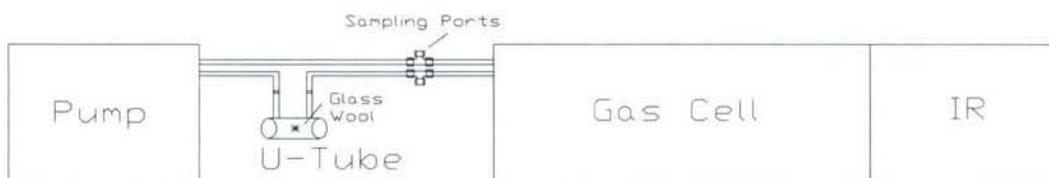
Nominal chamber concentration in mg/L was determined from the pumping rate of jet fuel in milligrams per minute (mg/min) by the generator system divided by the total flow rate in liters per minute (L/min) through the chamber. Inter-comparison of chamber concentrations determined by GC and IR versus nominal values ranged from 80-99%.

## METHODS

### Loop Calibrator Description

The loop calibration system (Figure 1) used a metal bellows pump (Model MB21, Metal Bellow Pump, Sharon, MA. ) to provide the re-circulating air across a puddle of jet fuel contained in a glass U-tube(74000 U tube, Quantasorb, Boynton Beach, FLA) . Both legs of the pump were connected with one quarter inch diameter stainless steel tubing to the input and output ports of a 20-meter gas cell on a Miran 1A (Foxboro, Pittsburg PA) infrared spectrophotometer(IR). The leg attached to the output side of the pump was in two sections to allow for the series insertion of the glass U-tube. A wad of glass wool in the U-tube was used to capture aerosols while allowing vaporized jet fuel to pass.

Figure 1

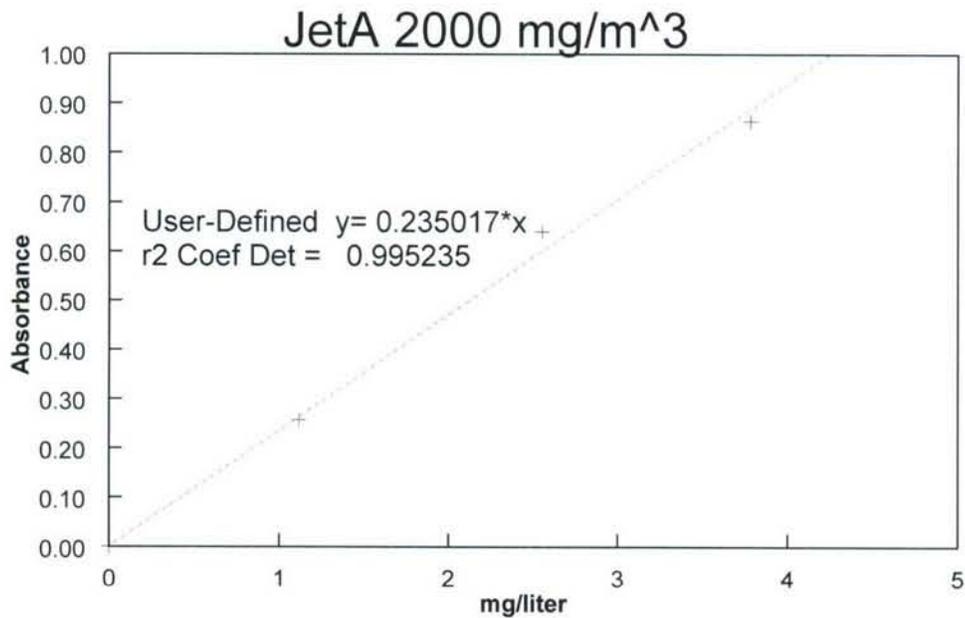


### Jet Fuel Vapor Calibration from the Loop Calibrator

Jet fuel, of known volumes, was injected into the U-tube and the starting weight of the tube was measured (Model AX205, Mettler/Toledo, Columbus OH). The pump re-circulated air through the tube and IR until equilibrium vapor concentration was obtained as determined by the leveling out of the IR response. The tube was re-weighed and the mass of jet fuel vaporized was determined. The mass of jet fuel vaporized in milligrams (mg) divided by the volume in liters (L) of the re-circulating system gave the concentration in milligrams per liter (mg/L). A plot (Figure 2) of average concentration versus IR response in absorbance units was made, and a linear regression was obtained.

Three replicated samples were averaged and used for each point on the plot. Initial background absorbance values were subtracted from the observed absorbance values so that zero vapor was equal to zero absorbance.

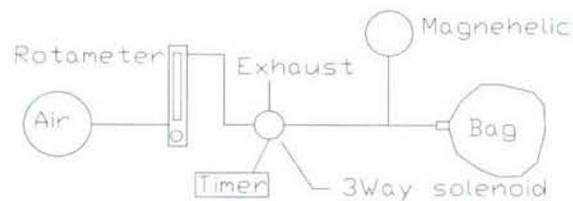
**Figure 2**



### Determination of IR Response to Known Concentrations of Hexane

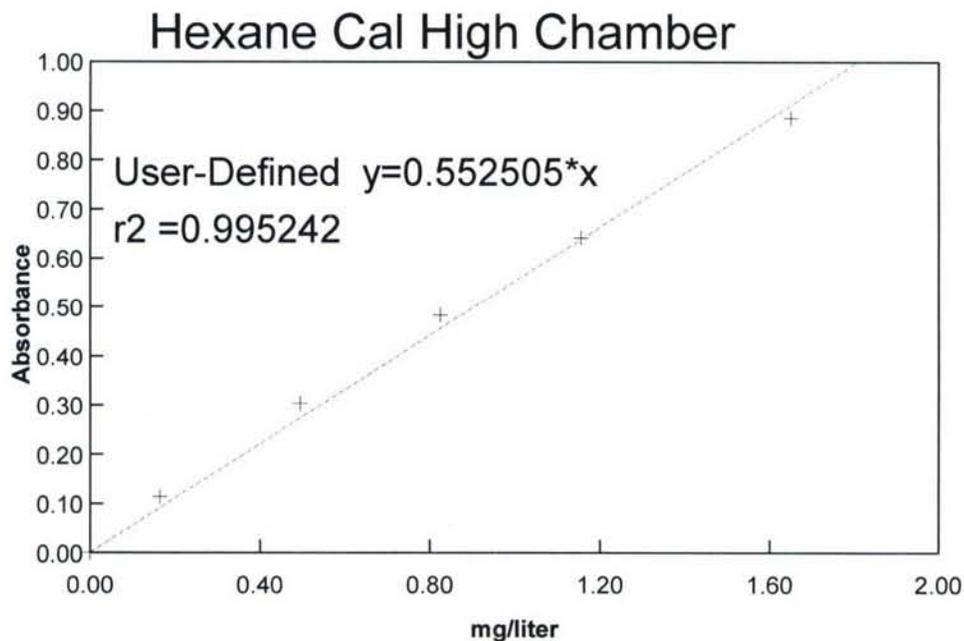
The IR was calibrated using known amounts of hexane added to tedlar bags (SKC, Eighty Four, PA) containing 50 liters of air. (Figure 3).

**Figure 3**



The volumetric air flow rate into the bags was set to 5 liters per minute using a suitably sized, calibrated rotameter ( Model 1050, Matheson Trigas, Montgomeryville, PA), while the pressure drop across the bag's valve was monitored with a Magnehelic pressure gauge (Series 2000, Dwyer Instruments, Michigan City, IN). A grab lab timer (Model 55, Dimco-Gray, Centerville, OH) controlled a 3-way solenoid valve which directed air flow either into the bag or to an exhaust leg. The rotameter flow rate was calibrated using a gillibrator (Gillibrator, Sensidyne/Gillian, Clearwater, FL). Change in flow rate caused by the pressure drop across the bag valve was compensated for by calibrating the rotameter with an inline restrictor valve set to give the same pressure drop as that seen across the bag valve at a given flow rate. A plot of hexane concentration versus IR absorbance was obtained and a linear regression was fitted to the plot (Figure 4).

Figure 4



Three replicated samples were averaged and used for each point, and the background absorbance values were subtracted from the raw IR absorbance values so zero vapor was equal to zero absorbance.

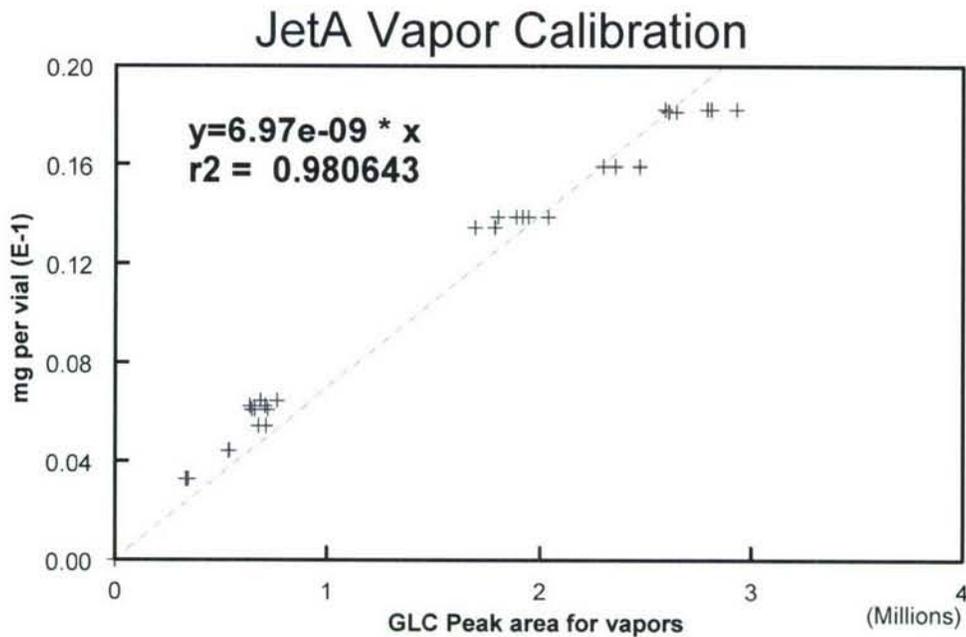
#### **Volume of the Loop Calibrator from IR Response to Hexane**

A known mass (mg) of hexane was introduced into the closed loop system and the concentration (mg/L) determined from the IR response (Figure 4). Dividing the mass (mg) added to the loop by the concentration (mg/L) measured from the IR response gives the volume of the system in Liters (L).

## Head-Space Gas Chromatographic Analysis

A Hewlett Packard gas chromatograph (Model 5890, Series II, Agilent Technologies, Palo Alto, CA) connected to a Tekmar-Dohrmann head space analyzer (Model 7000, Tekmar-Dohrmann, Mason, OH) was used for gas chromatography (GC) analysis of the vapor phase Jet-A in the chambers. A 30 meter fused silica capillary column (25315, Sigma-Aldrich, St. Louis, MO) was temperature programmed from 50°C. to 210°C at 5 deg/min and held at final temperature for 1 minute. Capped 20 ml head space vials were used for sample collection. A gas tight syringe was used to remove 5 ml of air from the sealed head space vial just prior to introducing sample. Another gas tight syringe was used to pull a 5 ml sample from the loop calibrator and to inject it into the head space vial through the same septum penetration as was used for removal of the air. Three vials were collected from the loop for a given calibration point. A plot was made of the total peak area from the GC analysis of these vials versus the concentration of jet fuel in the loop calibrator (Figure 5).

Figure 5



## RESULTS

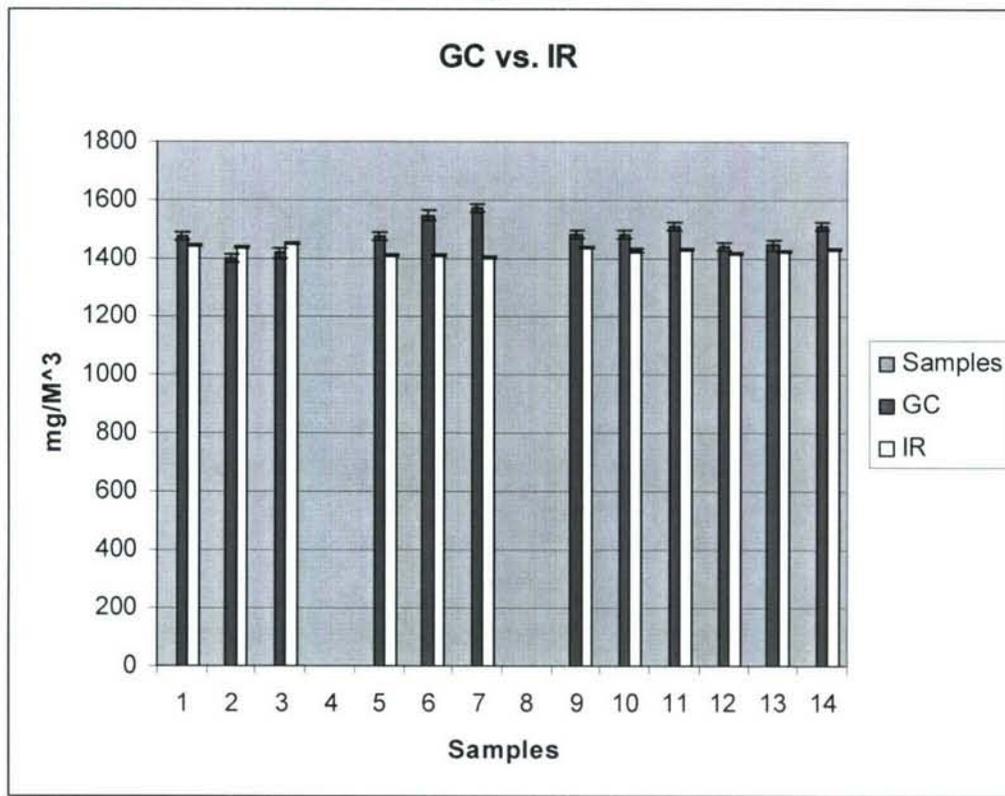
Data collected from an exposure system running at a nominal 2000 milligrams per cubic meter ( $\text{mg}/\text{M}^3$ ) are shown in Table 1 for comparison of values obtained from IR versus GC/HS. Figure 6 shows the data with standard error bars. Samples were taken for GC

analysis from the IR analytical stream just prior to entering the instrument. The GC data was corrected for background by subtracting air samples from a control exposure system. The IR concentrations were corrected for the background by subtraction of air values from the exposure system made just prior to the start of the experiment. An agreement between the IR and GC/HS methods of within 10% was achieved.

**Table 1**

Samples 3 Replications	GC Peak Area	mg/M3 Calculated	mg/M3 IR	Ratio GC/IR
1	1059249.333	1476.59	1445.00	1.02
2	1004220.333	1399.88	1440.00	0.97
3	1017101.333	1417.84	1452.00	0.98
1	1059252.667	1476.60	1410.00	1.05
2	1110254.667	1547.70	1411.00	1.10
3	1129369.667	1574.34	1402.00	1.12
1	1063346.667	1482.31	1439.00	1.03
2	1062192.667	1480.70	1427.00	1.04
3	1085099.667	1512.63	1429.00	1.06
1	1033980	1441.37	1418.00	1.02
2	1037094	1445.71	1423.00	1.02
3	1084029	1511.14	1429.00	1.06
<b>Average</b>	<b>1062099.167</b>	<b>1480.57</b>	<b>1427.1</b>	<b>1.04</b>
<b>Standard Dev</b>	<b>36509.91434</b>	<b>50.89</b>	<b>15.186</b>	<b>0.04</b>

**Figure 6.**



### **STATISTICS**

Calibration plots were analyzed using the math package in SlideWrite Plus for Windows (Advanced Graphics Software, Inc. Encinitas, CA 92024). The curves were fitted using a simple linear regression forced through zero ( $y = mx$ ). The bar graph shows GC/HS and IR jet fuel concentrations and includes the standard error of the mean for each datum.

### **DISCUSSION**

Jet fuel is a complex mixture of aliphatic and aromatic hydrocarbons. When aerosolized it partitions into a biphasic mixture of aerosol particles and vapor components with the relative composition of each phase being determined by the temperature of the mixture, and the vapor pressure of the individual components.

Because of this biphasic behavior, jet fuel can be analyzed either as a whole with both aerosol and vapor portions combined or individually with vapor phase components, and aerosol components analyzed independently.

Analysis of the whole jet fuel requires that the relative ratio of aerosol to vapor be maintained during sampling and analysis. Care must be taken that aerosol is not lost to

the sampling lines. With whole fuel analysis, neat fuel standards can be used for calibration of the instrumentation.

Analysis of the vapor and aerosol components independently requires the creation of vapor only standards, and another method for measuring aerosol concentration. Because of the potential change in ratio of aerosol to vapor with temperature, vapor standards need to be prepared at ambient temperature which matches the temperature at which samples that will be collected from the exposure system.

IR analysis, which allows continuous monitoring, requires preparation of vapor phase only standards as the gas cell on the IR cannot handle aerosols. Inline high efficiency particulate air filters (HEPA) are used to remove the aerosols from the IR sampling line. The molar extinction coefficient is compound specific. Thus, the absorbance seen for a complex mixture such as jet fuel vapor is a composite average of the extinction coefficients and concentrations of all the individual components. This requires that the composition of the vapor standards created for IR calibration be similar to the vapor composition of jet fuel in exposure system.

Likewise, vapor standards for the gas chromatograph needed to be similar in composition to the vapors in the chamber. Several problems can arise with the GC analysis of a complex mixture such as jet fuel. First, baseline separation was not achieved for all the components because of the large number of components in the jet fuel and the analytical conditions used. This can affect area integration which can lead to errors if the standard and sample do not have the same components in the chromatogram. Second, while the flame ionization detector is considered to be a carbon counter, the response is based on the ratio of the total carbon mass divided by the total compound mass, and the relative strength of the bonds within the compound (Tong and Karasek, 1984; Driscoll, 1999) also requiring similar compositions of standards and samples. Third, the concentration of the standards should bracket the expected analytical concentration. Using whole jet fuel, the smallest practical amount of material measurable for the head space vial yielded a calibration curve whose lowest point was above the range of analytical concentrations.

One problem with the loop system was the glass loop. Because of slight temperature changes and/or static electricity the weighing times between samples could be 30 minutes or longer to equilibrium weight. This problem has been resolved by soldering a copper U tube from 1/2 inch copper pipe with end caps for the body, and two lengths of 1/4 inch copper tubing for the legs. The same spacing between the legs as that found in the glass U tube was maintained so as not to require any modification of the system. Glass wool is again used to knock down aerosol, and 12 gauge copper wires inserted into the exhaust leg retain the glass wool.

## **CONCLUSION**

Using the loop method of making vapor standards for the GC and IR yielded an overall agreement in the 90 percent range, while comparisons of the IR to a GC calibrated with whole jet fuel gave only 40 percent agreements in two different experiments. In the present study, using a loop calibration system for generating jet fuel vapors yields standards which give good agreement between head space gas chromatography and infrared spectrophotometry on samples taken from an exposure system., Hence, we have decided that the loop calibration system is a viable method for creating jet fuel vapor standards for calibration of instrumentation.

## REFERENCES

1. Dietzel, K.D., Campbell, J.L., Bartlett, M.G., Witten, M.L., and Fisher, J.W. (2005) Validation of gas chromatography/ mass spectrophotometry method for the quantification of aerosolized Jet Propellant 8. *J. Chromatogr. A* 1093: 11-20.
2. Pfaff, J.K., Tollinger, B.J., Lantz, R.C., Chen, H., Hays, A.M., and Witten M.L. (1996) Neutral Endopeptidase (NEP) and its Role in Pathological Pulmonary Change with Inhalation Exposure to JP-8 Jet Fuel. *Toxicology and Industrial Health*. 12: #1, 93-103.
3. NIOSH method 1550: <http://www.cdc.gov/niosh/nmam/pdfs/1550.pdf>
4. Mattie, D.R., Alden, C.L., Newell, T.K., Gaworski, C.L., and Flemming C.D. (1991) A 90-Day Continuous Vapor Inhalation Toxicity Study of JP-8 Jet Fuel Followed by 10 or 21 Months of Recovery in Fischer 344 Rats and C57BL/6 Mice. *Toxicologic Pathology* 19: #2, 77-87.
5. Tong, H.Y., and Karasek, F.W. (1984) Flame ionization detector response factors for compound classes in quantitative analysis of complex organic mixtures. *Anal. Chem.* 56: 2124-2128.
6. Driscoll, J.N. (1999) Handbook of environmental instruments, gas chromatography chapter. McGraw Hill.