ANALYSIS OF THE VAPOR PLUME AT THE END OF THE CREOSOTE WOOD TREATMENT CYCLE

Prepared for:

Koppers Inc.

Prepared by:

Michael R. Corn, P.E.
John Michael Corn, P.E.
Paul J. Marotta, P.E.

AquAeTer, Inc.
Brentwood, Tennessee

MAY 2010

TABLE OF CONTENTS

LIST OF ATTACHMENTS

I. EXECUTIVE SUMMARY

- This report analyzes the chemical constituents that are in the vapor plume arising from an open wood-treating cylinder door at the end of the creosote wood-treating cycle and from creosote-treated wood immediately after the trams have been pulled out of the cylinder. The vapor plume contains greater than 99% water. This finding is based upon vapor plume measurements including: (1) two studies performed to measure the vapor plume emitted from the wood-treating cylinder door opening at the end of a creosote wood-treating cycle; (2) measurements made on creosote-treated wood on trams that have been immediately pulled from the treating cylinder; and (3) laboratory analysis of the constituents in creosote. The conclusions of this report are summarized below.

  The vapor plume arising from an open wood-treating cylinder door at the end of the creosote wood-treating cycle of fresh creosote-treated wood:

  a. Is greater than 99% water;
  b. Of the approximate 1% non-water vaporous material, the compounds include:
     i. PAH's not associated with those identified as potential cancinogens;
     ii. Approximately one-half is naphthalene; and
     iii. Organic compounds from wood.

- Two studies have been performed in which the vapor plume arising from an open wood-treating cylinder door at the end of the creosote wood-treating cycle have been measured. One study was performed by Koppers Company, Inc. at the Susquehanna, Pennsylvania wood treating plant in 1975. The second was conducted on behalf of Koppers Inc. in 2004 at the Guthrie, Kentucky wood treating plant.

- Koppers Company, Inc. found in the Susquehanna study that the vapor plume arising from an open wood-treating cylinder door at the end of the creosote wood-treating cycle is 99.8% water. The remaining 0.2% was comprised of non-carcinogenic PAHs. The highest concentration PAH was naphthalene, at 53% of the total PAHs. The vapor plume contains neither benzo(a)pyrene nor benzene, based on testing done at the Koppers Feather River site, which evaluated emissions from poles immediately pulled from a wood-treating cylinder.

- AquAeTer/Shaw conducted tests at the Koppers Inc. facility in Guthrie, Kentucky in 2004 which similarly found that the vapor plume rising from an open wood-treating cylinder door at the end of the creosote wood-treating cycle contained greater than 99% water vapor. Two tests were conducted: 1) with the treated wood in the wood-treating cylinder; and 2) with no wood in the wood-treating cylinder. AquAeTer measured PAHs and the water content of the collected vapor. Naphthalene was the single highest concentration PAH in the non-water portion. Water vapor was 99% of the emissions where wood was treated in the cylinder.

- Koppers Inc. conducted emission tests at their Feather River facility in California measuring emissions from creosote-treated poles of various ages, including poles that had been immediately removed from the wood-treating cylinder. Naphthalene was the major constituent measured. None of the carcinogenic PAHs, including benzo(a)pyrene, nor the volatile constituent benzene, were detected in the vapor emissions measured off the freshly treated poles. The 5-ringed or higher PAHs of concern would not be expected to be emitted from creosote wood treating operations because of their low vapor pressures and the fact that there is no combustion involved with the treating cylinders.

- Koppers Company, Inc. and Koppers Inc. have conducted personnel monitoring of employees working on the drip pad and in front of the wood-treating cylinder door numerous times since 1978. The vapor plume arising from an open wood-treating cylinder door at the end of the creosote wood-treating cycle does not result in exceedances of the OSHA worker protection standards.

- Freshly harvested wood has about 70% moisture content and air-dried wood has about 50% moisture content. Because water is about 280 times more volatile than naphthalene, water dominates the vapor partial pressure balance and the vapor mass fractions of consitituents in the plume arising from an open wood-treating cylinder door at the end of the creosote wood-treating cycle. Theoretically, and in practice, water vapor is the dominant constituent emitted at the end of a creosote wood-treating cycle when measured at the open door of the wood-treating cylinder or from fresh creosote-treated wood.

- The components of creosote have been measured several times over the years from 1975 to 2006 by Koppers Inc., Koppers Company, Inc., and two nationally recognized laboratories certified by the USEPA. Naphthalene has consistently been one of the constituents with one of the greatest concentrations by mass percent in the liquid creosote. Although naphthalene does not represent the highest mass fraction of the PAHs in creosote, it does represent the highest mass fraction in the vapor. This explains why naphthalene had the greatest concentration measured of any PAH found in the vapor plume arising from an open wood-treating cylinder door at the end of the creosote wood-treating cycle and also from fresh creosote-treated wood.

In conclusion, the vapor plume from both the end of a creosote treating cycle when the wood-treating cylinder door is opened and from the fresh creosote-treated wood is predominantly a water vapor plume containing over 99% water. The primary constituent in the remaining portion of the plume is naphthalene. None of the PAHs that are suspect carcinogens have been detected in this vapor plume, including benzo(a)pyrene.

II. INTRODUCTION

The following report presents the results of studies performed by Koppers Inc., Koppers Company, Inc., and the Creosote Council. Studies and analysis have been conducted of the vapor plume that is visible when the wood-treating cylinder door is opened after the creosote wood treating cycle is completed and from creosote treated ties on trams that have been immediately pulled from the treating cylinder. For the purposes of this report, creosote treated wood on the trams immediately pulled from the cylinder shall mean treated wood that for a period of up to 8 hours following completion of the creosote wood treating cycle continues to be hotter than ambient temperatures.

The vapor plume emanating from the creosote wood-treating cylinder and from the creosote-treated ties that have been immediately pulled from the cylinder contains greater than 99+% water vapor. Of the approximately less that 1% of other constituents in the vapor plume, naphthalene makes up the major fraction of the organic emissions in the water vapor plume. Napthalene is the primary polycyclic aromatic hydrocarbon (PAH) emitted with the water vapor plume when the wood-treating cylinder door is opened.

General information on creosote and water behavior in the environment is presented. Basic information on naphthalene, the major emission (after water vapor) from creosote wood treating, is also presented for comparison. Natural and anthropogenic sources of naphthalene are discussed to highlight the many anthropogenic origins of this common environmental constituent that result in ambient air concentrations of naphthalene of around 5 ug/m^3 (ATSDR, 2005; USEPA, April 1992) in most urban environments. A review of creosote analyses, emissions testing, personnel and ambient air monitoring data is provided to demonstrate that emissions from wood treating processes are not at concentrations above health, safety and regulatory standards, and are generally consistent with background concentrations in the environment.

III. GENERAL INFORMATION ON CREOSOTE AND NAPHTHALENE

A. CREOSOTE

Creosote is a general name used to describe an array of products which include wood creosote and coal tar creosote. This document refers only to coal tar creosote with a CAS registry number 8001-58-9 (Chemical Abstract Service, 2008), which is made up primarily of PAHs. The actual composition of creosote varies somewhat due to differences in the source material, coal. Approximately 155 compounds have been detected in creosote using the current state of the art analytical methods, but only 48 compounds have consistently been shown to be present at concentrations at or above 0.1 wt% (RTI, Feb. 1999).

Creosote is manufactured by the distillation of coal tar, which is obtained through the destructive distillation of coal to produce coke. Coke is a fuel and carbon source necessary to produce steel. Creosote, a distillate of coal tar, must conform to standards established by the American Wood Preservers Association (AWPA, 1995). Historical standards, and the most common standards used today, require that the raw material for creosote be 100% coal tar. AWPA defines two primary creosote specifications, P1/P13 and P2, for use as heavy duty wood preservatives. P2 creosote is the largest volume of creosote used in the U.S. Analyses of data available on creosote chemical make-up, personnel exposure records, emissions testing data, and ambient air testing on and around wood treating facilities have been made (Corn November 2008). These data in their totality demonstrate that the PAHs identified in the RTI analysis are the primary constituents in creosote. Volatiles such as benzene are present only in *de minimis* concentrations. From ambient air measurements made around wood treating facilities, benzene is not distinguishable from normal urban ambient air concentrations at offsite receptor locations.

Vapor Phase Emissions of Creosote Constituents

Creosote is composed of numerous chemicals with varying physical characteristics. All chemicals have different boiling points and therefore enter the vapor phase (evaporate) at varying temperatures. The “normal” boiling point of a chemical is the temperature at which the liquid converts to a vapor at atmospheric pressure. For example, the normal boiling point of water is 212°F. As can be observed from water being heated on a stove, water vapor will be emitted at temperatures lower than 212°F (i.e., before boiling is reached.) The fraction of the material that remains in the liquid state is determined by the temperature of the material and the ambient pressure. As the boiling point is approached, the percentage of the compound in the vapor phase increases. At the boiling point, the chemical will convert from a liquid to a vapor until the entire amount enters the vapor phase. If a boiling pot of water is left on a stove, it will eventually become empty as all of the water converts to water vapor.

Chemicals that evaporate at relatively low temperatures and tend to be present mostly in the vapor phase at ambient pressures are referred to as “volatile”. Comparing the boiling points of chemicals gives an indication of their relative volatility. The boiling point of a chemical is related to its evaporation rate, and therefore the higher the boiling point, the less evaporation will occur at lower temperatures. A large portion of the creosote constituents have high boiling points, and remain as liquids or even solids at room temperature. The boiling points for the chemicals typically found in creosote are presented in Attachment 1 and are compared to benzene and water. It is important to note that creosote is not evaporated, but rather its individual constituents are evaporated individually as a function of the individual mass weight percent and individual volatility of each constituent that make up the creosote mixture (Raoult’s Law of partial pressures).

The vapor pressure of a chemical is another way of expressing when the chemical will change from a liquid to a vapor. The vapor pressure of a chemical is directly related to its evaporation rate; therefore, the lower the vapor pressure, the less the chemical will evaporate. Vapor pressures for the chemicals typically found in creosote are presented in Attachment 1 and are compared to benzene and water. As shown, water has a vapor pressure of 0.46 pounds per square inch, absolute (psia) at 80 degrees Fahrenheit (°F), whereas benzene has a vapor pressure of 1.99 psia. Naphthalene has a vapor pressure of 0.0016 psia. The relative evaporation rates can be calculated, and are dependent on the vapor pressure and the molecular weight of the chemicals. Based on the differences in their properties, water will volatilize into the air approximately 280 times faster than naphthalene. This is one reason why water vapor is the major emission from the door opening.

In a liquid containing multiple chemicals, both the mass weight percent of the chemical in the mixture and the vapor pressure of the individual chemical will dictate the relative concentration of that chemical in the vapor emitted from the liquid. Naphthalene is the predominant vapor emission from creosote because it is present at a higher percentage than most other chemicals found in creosote, and it is one of the most volatile chemicals in creosote. Because naphthalene dominates the creosote emissions, the odor of creosote is characterized by the naphthenic odor commonly associated with mothballs. Even though naphthalene is the major PAH emitted from creosote wood treating operations, the total mass of naphthalene emitted from the door openings is very minimal, as will be presented later.

According to the AWPA standards, creosote used to treat the ties can contain up to 3% water. The wood in the wood-treating cylinder also contains water. As the creosote is reused in the treatment process, water from the wood builds-up in concentration within the creosote. The effect of these water sources on the vapor mass fraction is substantial. The vapor mass fraction of creosote constituents without water present is presented in Attachment 3. The vapor mass fraction of creosote constituents with water present is presented in Attachment 4.

Exposure Standards for Creosote

The Occupational Safety and Health Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH) have published protective standards for worker "permissible exposure limits" (PELs) (NIOSH, September 2005). Time-weighted average (TWA) concentrations for OSHA PELs must not be exceeded during any 8-hour work shift of a 40-hr work week. TWA concentrations for NIOSH are based on exposures for up to a 10-hr workday during a 40-hr week. The TWA PEL used for screening creosote worker exposure is 0.2 milligram/cubic meter (mg/m^3) as coal tar pitch volatiles (CTPV). If the CTPV limit is exceeded, individual PAHs are then evaluated (Burright, D. July 1986). The PAH constituents to be evaluated and the OSHA limits for these PAHs are:

1. Coal Tar Pitch Volatiles (PEL) – PEL = 200 ug/m^3;
2. Phenanthrene - target concentration of 8.892 ug/m^3;
3. Anthracene - target concentration of 0.79 ug/m^3;
4. Pyrene - target concentration of 9.014 ug/m^3;
5. Chrysene - target concentration of 3.27 ug/m^3; and
6. Benzo(a)pyrene - target concentration of 2.49 ug/m^3.

If any of these target concentrations are exceeded, then the OSHA CPTV PEL has been exceeded. The OSHA CPTV limit of 0.2 mg/m^3 is only a screening tool and the individual PAHs must be exceeded to be over the OSHA CPTV PEL.

The OSHA CTPV PEL standard is broadly applied to monitor worker exposure to a variety of substances, including coal tar and its distillates, including creosote and pitch. Coal tar pitch and creosote are separate products. Although the CTPV standard is applied to creosote, this does not mean that creosote contains coal tar pitch. It does not.

Second to water vapor, which has no exposure standards, naphthalene is the major constituent that is emitted from creosote wood treating plants, and exposure standards for naphthalene are presented in a following section.

B. NAPHTHALENE

Naphthalene is a common polycyclic aromatic hydrocarbon. Naphthalene is a component of crude oil, petroleum products (including gasoline and diesel), coal tar, and other organic sources. Naphthalene is used in the manufacture of plasticizers, resins, dyes, pharmaceuticals, insect repellents, and has historically been the main component of mothballs. Naphthalene is released from the combustion of wood, fossil fuels, residential trash, and cigarette smoke. Diesel engines are a big source for naphthalene in the ambient air in the U.S.

Naphthalene has the characteristic odor of mothballs, and has a very low odor threshold, which means it can be detected by the human nose at very low concentrations. It can be detected by smell by most people at an ambient air concentration much lower than that which presents a risk from exposure. Approximately 96% of people can detect naphthalene in ambient air at concentrations ranging from 0.0095 to 0.64 ppm or 50 to 3,350 ug/m^3 with most people being able to detect naphthalene at 199 ug/m^3 (AIHA 1997). The physical and chemical properties of naphthalene are listed in Attachment 5 (NIOSH September 2005; USEPA 1992b).

Exposure Standards for Naphthalene

Both the OSHA (PEL) and the NIOSH (REL) give a TWA of 52,400 ug/m^3 for naphthalene. This worker safety standard is also about 260 times higher than the odor threshold at which most people can smell naphthalene (199 ug/m^3). Therefore, smelling naphthalene is not an indication that one is being exposed to an unsafe level.

The USEPA has developed screening level concentrations based on $1*10^{-4}$ to $1*10^{-6}$ risk-based levels for the general population (ORNL, July 17, 2008). The current ambient air concentration above which the USEPA might consider remedial action for naphthalene is 7.2 ug/m^3. This value was originally 310 ug/m^3 at the $1*10^{-4}$ risk level. The 7.2 ug/m^3 was first suggested in California based on nasal tumors to rats from extreme exposures to rats. This screening level based on a $1*10^{-4}$ risk-based ambient air concentration is very conservative when one looks at the normal cancer incidence rate in the U.S. population of 1 out of every 2 males or $5.0*10^{-1}$ and 1 out of every 3 females or $3.33*10^{-1}$ will develop a cancer in their lifetime. It is also lower than the screening level for benzene of 31 ug/m^3, which intuitively does not make sense since benzene is a known human carcinogen and naphthalene is not a human carcinogen (IRIS 2010).

The old $1*10^{-4}$ risk level of 310 ug/m^3 is quite similar to the rule of thumb used by many state agencies to estimate safe levels for offsite residents around an industrial facility of 100 times less than the OSHA PEL (ADEQ. 1996 revision, reprinted 12/2001). For naphthalene, this ambient air concentration would be 524 ug/m^3. The 7.2 ug/m^3 SL is at the reported U.S. average background concentration for naphthalene of 5 ug/m^3.

IV. CREOSOTE TREATING CYCLE

Wood products are treated in order to extend the life of the wood, sometimes by decades. This reduces the burden on the wood supply as well as produces a product that has longevity in the environment. The creosote wood treating process is described in the following paragraphs.

The creosote treating cycle can include several different treating steps depending on whether freshly harvested wood, meaning greater than 50% moisture content, or dry wood, meaning 50% or less moisture content, is being treated, as depicted in Attachment 6.

A typical railroad crosstie is 7 inches by 9 inches by 8.5 feet long and has a volume of about 3.72 cubic feet. The U.S. Forestry Products Laboratory has published a range of moisture contents for various wood species. In this case, freshly harvested wood means that it has not been dried. Wood typically contains about 70% moisture.

Railroad cross ties are treated to meet a typical creosote retention target of 8 pounds per cubic foot, or about 30 pounds of creosote for each railroad crosstie. The retention target varies by geographic use and by the wood specie treated and is not exact. For instance, cross ties treated for railroads and other end-users in the south are typically treated to a greater retention than those treated for Canadian end-users. The wood species will also limit the creosote retention, since different species will retain different amounts of creosote. In order to force the creosote into the crosstie, an equal volume of water must first be removed from the wood. In order to add 30 pounds of creosote to a standard crosstie, 30 pounds of water or 3.6 gallons of water must first be removed from the pore spaces of each crosstie being treated. The water is removed either by air drying (aging) the crossties in the plant storage yard over about a 4 to 12-month period, or through a process called the Boulton cycle where the water is forced out of the wood in the wood-treating cylinder in a 6 to 8-hour or more period prior to treatment. Both processes prepare the wood for the creosote to replace the removed water volume during the pressure treating cycle and both processes end up removing some amount of water from the wood.

The dried wood is then processed in the wood-treating cylinder by pressurizing the wood-treating cylinder and forcing creosote into the pore spaces of the wood. The wood-treating cylinder during the pressure cycle is typically heated to around 180 to 210ºF to ensure that the creosote is in liquid form, i.e., creosote tends to solidify at ambient air temperatures. When under pressure and the high temperature, additional water will be evaporated from the wood and from the creosote itself.

Once the pressure treating of the wood is completed, the excess creosote is pumped back to the work tanks and a final vacuum is pulled on the wood-treating cylinder. The final vacuum removes vapors within the void space of the wood-treating cylinder and more importantly reduces the surface temperature of the treated wood to around 145ºF. The final vacuum is maintained for about 2 hours, but this may vary from about 1 hour to 4 hours. The surface temperature of the wood measured on the outside of the tram bundles during this final vacuum decreases from about 190°F to around 150°F.

Once the final vacuum is completed, the wood-treating cylinder door is opened to remove the treated wood. As the wood-treating cylinder door opens, a “white vapor plume” is emitted. The plume rises due its thermal buoyancy (higher temperature than ambient air). The vapor plume dissipates quite rapidly, meaning that it is no longer visible within a short distance from the wood-treating cylinder door. This vapor plume partially originates from the residual liquid in the hot wood-treating cylinder (approximately 145°F), but it primarily originates from the treated wood which is still at an elevated temperature (when compared to ambient). Because water is the most volatile constituent in the wood, it is the primary emission (see Attachment 4).

The emissions from the treated wood are greater than 99+% water, with a small fraction of organic constituents including naphthalene. This is because the creosote constituents have much lower vapor pressures than water, as shown in Attachment 7, and as a result they are volatilized at a much lower rate. Test data collected at both Guthrie in 2004 and at Susquehanna in 1975 confirm that the visible plume is primarily water vapor, as presented in Attachment 8. The primary creosote constituent that is released is naphthalene. It is not surprising that the vapor plume is primarily water, since the water is being removed from the wood and creosote during the treatment cycle. Water is much more volatile than the creosote constituents.

When the wood is pulled out of the wood-treating cylinder and onto the drip track, the void space left in the wood-treating cylinder is filled with air coming from outside of the wood-treating cylinder. This results in a substantial dilution of the air inside the wood-treating cylinder. Reloading the wood-treating cylinder with untreated wood forces out a volume of air at least equivalent to the wood and tram volume. This interior air from the wood-treating cylinder, due to the dilution from the outside air that enters the wood-treating cylinder when the trams are extracted from the wood-treating cylinder, is obviously at much lower concentrations of constituents than the hot vapor plume release when the wood-treating cylinder door is initially opened. Once the wood-treating cylinder door is closed, there are no additional emissions from this source until the door is reopened.

If the treated wood was allowed to remain in the wood-treating cylinder, the water vapor plume would still be released from the wood-treating cylinder until the treated wood reached near ambient temperatures and the water vapor condensed. This could take between 12 to 24 hours.

V. VAPOR PLUME ANALYSIS OF WOOD-TREATING CYLINDER DOOR OPENINGS

In 2004, AquAeTer determined that the vapor plume was greater than 99+% water vapor at the Koppers Inc. wood treating facility in Guthrie, Kentucky (See Attachment 7). AquAeTer measured the emissions from the wood-treating cylinder from when the door was first opened, to about 45 minutes following the initial door opening. One of the tests measured emissions from the wood-treating cylinder when wood remained in the wood-treating cylinder.

In 1975, Koppers Company determined that the vapor plume was greater than 99+% water vapor. Koppers Company measured the emissions from ties after they were removed from the wood-treating cylinder at their Susquehanna facility. Tests were run on both covered trams and uncovered trams. While this measurement was not a direct measurement of the door opening, it measured the primary source of the emissions within the wood-treating cylinder. Although the test at Susquehanna and the test at Guthrie were slightly different, they were effectively measuring the same emission source, i.e., the hot treated wood. These two tests are therefore comparable.

In 1990, Koppers Inc. measured air emissions from treated poles at their Feather River Plant in Oroville, California. These data are also used since this dataset contained the best set of speciated PAH data

A. GUTHRIE/SUSQUEHANNA TEST RESULTS

The wood-treating cylinder door emissions testing was completed at the Koppers Guthrie, Kentucky facility in October 2004 (Attachment 7). A custom-made metal cover was placed over the wood-treating cylinder door opening, as shown in Attachments 8, 9 and 10 to collect emissions for sampling. An eight-inch flexible duct was attached to the top of the cover and a fractional hp, 230-cubic feet per minute (cfm) fan was used to pull the vapors through the duct. The air flow was set to just pull the vapors that would normally be emitted without pulling in additional dilutional air nor pull out more vapors than what would normally be emitted This was done by visibly observing the area around the duct placed over the cylinder door opening.

Samples were collected from the duct about every 5 to 10 minutes. Two door opening emissions measurements were made. The first measurement was with the wood-treating cylinder filled with treated wood. The second measurement was from a wood-treating cylinder that went through a treating cycle without any wood in the wood-treating cylinder (empty wood-treating cylinder). Measurements of the naphthalene contained in the vapor plume released when the wood-treating cylinder door is opened are presented in Attachments 11 and 12 and calculations are presented in Attachment 13.

Observations and measurements made during emission testing conducted at the Koppers wood treating facility located in Guthrie, Kentucky in 2004 indicate that approximately 99+% of the air emissions from the wood-treating cylinder consist of water vapor, as presented in Attachment 13. Results from an earlier study performed by Koppers Company, Inc. in 1975 (Williams, May 19, 1975) at the Susquehanna wood treating facility located in Muncy, Pennsylvania demonstrated similar results with the vapor plume from the treated wood calculated at 99.46+% water vapor, as presented in Attachment 14. It is noted that the Susquehanna measurements included total VOC’s and the Guthrie test only included PAH VOC’s.

The naphthalene emissions measured over a 15-minute time period for a door opening at the Guthrie facility are presented in Attachment 13 and the resultant mass release of naphthalene is also calculated in Attachment 13. Calculations are presented in Attachment 13 which derive the water vapor content of the vapor plume emitted during the Guthrie sampling. It should be noted that the following calculations utilize different time periods. Calculation of naphthalene mass emitted assumes a 15 minute timer period to be consistent with the typical time the door is open. A 21 minute time frame is used for the water vapor calculations since the moisture data collected during the test was averaged over this time period. The Koppers Company Susquehanna testing from 1975 is presented in Attachment 14.

Naphthalene concentration, dry bulb and wet bulb temperatures were measured during the Guthrie study. The on-site laboratory calculated the average percent moisture in the vapor plume using the dry bulb and wet bulb temperatures to calculate an absolute humidity. There were four sets of measurements and the average water vapor during the tests was calculated to average 3.6%. The four measurements ranged from 1.9 to 6.4 percent moisture. From Attachment 13, the maximum naphthalene concentration measured was 304.79 nanograms per milliliter, or, 0.30479 mg/L. The time-zero concentration projected from the exponential-curve fit of the data given in Attachment 13 was 0.392 mg/L.

In order to determine the mass percentage of the water vapor compared to the total mass of emitted creosote constituents, the total mass of creosote constituents in the vapor phase was calculated. The naphthalene content in the creosote product itself was measured to be 5.4% by mass. This means that for 100 pounds of creosote, 5.4 pounds will be naphthalene. Creosote as a product is not volatilized, rather its individual components are volatilized. Naphthalene is not a major component of the liquid, but it is the major constituent in the emissions from creosote, ranging from about 50 to 60 percent of the emissions from creosote wood treating. Converting the measured naphthalene concentration first to parts per million using a molar conversion and then to percent yields the mass emitted.

Calculate Mass of Naphthalene in Air/Water Vapor Plume

Under both federal and state environmental regulations requiring industry to permit their air emissions, Koppers must estimate and report emissions of criteria pollutants such as particulate matter (PM), sulfur dioxides (SO_x), nitrous oxides (NO_x), volatile organic constituents (VOCs), and carbon monoxide (CO), and hazardous air pollutants (HAPs), such as, naphthalene, from its wood treating processes. The testing was done to improve the accuracy of the emissions estimates. The results of the testing must be converted to a usable emission factor. This is done in the following way.

The naphthalene concentrations contained in the vapor emissions with respect to time are presented in Attachment 13. The mass of naphthalene released is calculated by determining the area under the curve. The derivation of the formulas are presented in Attachment 13. For the first 21 minutes of door opening, the equation is:

$$\frac{grams\ naphthalene}{charge} = \left(53.53 + \frac{0.255}{t} * \frac{Volume_{void}}{Volume_{cylinder}} * Volume_{wood}\right) * \left(1 - e^{-0.1307 * \frac{t}{3}}\right) \quad (1)$$

where: t = time, in minutes.

There is an upper boundary on the total time limit, although this was not determined during the testing. If the wood-treating cylinder door is left open for more than 35 minutes, care should be taken in using this equation.

This is the equation to calculate the mass of naphthalene emitted from a door opening that does not last longer than 21 minutes. At a facility with a cylinder volume of 5,000 cubic feet (ft^3), a 15-minute door opening and a treated wood volume of 3,500 ft^3, the mass of naphthalene emitted would be 34.2 grams or 0.075 pounds or about 7 teaspoons, which is equivalent to approximately 10 mothballs.

This shows that for a door opening of 15 minutes, only about 7 teaspoons of naphthalene (about 10 mothballs) would be released. Given a typical creosote wood treating facility that treats about 1,000 charges per year or more than 735,000 ties per year, about 75 pounds of naphthalene would be emitted per year from the wood-treating cylinder door openings. An automobile releases about 1 lb of naphthalene for every 1,500 miles driven. So for a typical creosote treating facility, about 7 to 8 cars driving 15,000 miles per year would emit the same mass of naphthalene as the yearly door openings at the wood treating facility producing about 735,000 railroad ties per year.

Previously, the USEPA had estimated the door-opening emission rate at 0.18 lb/hr (USEPA, 1994). Interpolating this value linearly would result in a 15-min door-opening emission rate of 0.045 lb. The measured mass of 0.075 lb emitted during a 15-min door opening at Guthrie is less than what has been traditionally used to estimate door emissions. Therefore, the total naphthalene emissions from most creosote treating plants from door openings will be less than 100 lbs per year or about 0.05 ton per year. This source would be considered insignificant by many states.

Convert Naphthalene Mass to Concentration

The concentration of naphthalene is determined by calculating the mass of naphthalene emitted and dividing by the volume of air leaving the wood-treating cylinder. The mass of naphthalene for a 15-minute door opening is shown above. The concentration is calculated using the following equation:

$$\boldsymbol{C = \frac{34.2\ grams}{210\frac{scf}{min} * 15\ min} * \frac{1{,}000\ mg}{1\ gram} * \left(\frac{1\ ft}{0.3048\ m}\right)^3} \tag{2}$$

The average concentration over the 15-minute door opening would be 73.2 parts per million or 383.4 mg/m^3. This is equivalent to saying that naphthalene is 0.00732% of the total air stream.

Determine Total VOC’s in Releases

In addition to reporting naphthalene, the plant must also report total VOC’s to meet its permit requirements. In order to determine the total amount of VOC’s that are released, one can estimate the ratio of naphthalene to total VOC’s as PAH’s. Naphthalene was measured to be 5.4% in the creosote used during the testing. Based on the RTI analysis, naphthalene at this percentage would be approximately 37.8% of the vapor mass fraction (PAH’s only). The total PAH concentration is then:

73.2 ppm / 0.37769 = 193.8 ppm total VOCs (PAHs)

The total VOCs concentration as PAHs is 193.8 ppm. This is equivalent to saying that VOC’s (including naphthalene) makeup 0.01938 % of the air stream.

B. CALCULATE WATER VAPOR PRESENT FROM GUTHRIE TESTING

As mentioned above, there was a moisture content of 3.6% in the air stream. Therefore, the air stream leaving the wood-treating cylinder was mostly air. If one compares only the VOC’s and water against each other, ignoring the fraction of air, one will find that water makes up greater than 99+% of the constituents in the air as shown in the following equation.

$$\%\ of\ Water\ in\ Constituent\ Mixture = \frac{\%Water\ in\ Air\ Stream}{\%Water\ in\ Air\ Stream + \%\ VOC's\ in\ Air\ Stream}$$

$$\%\ of\ Water\ in\ Constituent\ Mixture = \frac{3.6\%}{3.6\% + 0.01938\%}$$

% of Water in Constituent Mixture = 99.46%

C. CALCULATE WATER VAPOR PRESENT FROM SUSQUEHANNA TESTING

Emissions from the freshly treated wood at the Koppers Company Susquehanna facility were captured by plastic film, allowed to condense, and the water was then collected and volume determined. The following data were derived from the Williams memorandum (May 19, 1975) presented in Attachment 14.

From this test, the maximum Total Organic Carbon (TOC) concentration measured in the condensate collected from creosote treatment vapor from freshly treated poles was 2,200 mg/L or parts per million (ppm). The percent water in the Susquehanna test measurements can be calculated as follows:

(2,200 parts/1,000,000 parts) *100% = 0.22% as VOCs

Water Vapor = 100% - 0.22% VOCs = 99.78% water vapor

D. COMPARISON OF GUTHRIE AND SUSQUEHANNA RESULTS

Both tests showed that the vapor plume leaving the wood-treating cylinder as the door opens consists of greater than 99+% water. Although these tests employed different methods and were conducted 33 years apart, both tests had virtually identical results; that is, at Guthrie, water vapor was measured as 99.46+% water in the vapor plume and at Susquehanna, water vapor was measured as 99.8% water in the vapor plume.

The test personnel for the Susquehanna work noted that naphthalene sublimed (transformed from a vapor to a solid) in some of the test series (covered trams) so that the total naphthalene measured is lower than what was actually emitted. This suggests that the naphthalene emitted would most likely fall out of the vapor plume as a dry deposition as it cools off within a short distance from the wood-treating cylinder. Samples at Guthrie were collected before sublimation could occur, i.e., the temperature was hot enough that sublimation did not occur until after the sample was collected. The two sampling events were slightly different in the collection, but the results were similar.

The naphthalene concentration is highly dependent on when the samples are taken, with the initial samples being the greatest and subsequent samples decreasing in concentration exponentially. The naphthalene concentration in the creosote being used at the Susquehanna test was 6.8% (page 7 of the report) compared to 5.4% naphthalene in the creosote being used at Guthrie during the test there. This indicates that the naphthalene emissions are similar and thus the total mass of the creosote VOCs emitted are similar.

E. FEATHER RIVER EMISSION TESTING

Koppers Inc. conducted air emission testing on fresh treated poles and ties at their Feather River Plant in Oroville, California in 1990 (Smith, 1994). Water vapor was not measured during this test. The testing analyzed for multiple components known to be in creosote as well as benzene. Benzene was not detected at a detection limit of 1.25 milligrams per hour. As expected, the most volatile component of creosote, naphthalene, was also the component with the largest emission rate. Heavier components, such as benzo(a)pyrene, were not detected as an air emission pathway.

VI. CONCLUSIONS

The visible vapor plume that can be seen when the wood-treating cylinder door is opened following the completion of a creosote wood treating charge in the wood-treating cylinder contains greater than 99+% water vapor. This finding is based on two studies performed to measure emissions from the wood-treating cylinder door opening, and data analysis of the constituents in creosote, as well as, measurements made on freshly treated wood at the Koppers Feather River Plant located in Oroville, California. Conclusions from these analyses are summarized as follows:

1. Koppers Company, Inc. in 1975 found that the vapor plume contained 99.8% water. Koppers measured the vapor content collected off covered freshly treated ties that had been extracted from the wood-treating cylinder immediately following the opening of the wood-treating cylinder door. The remaining 0.2% was comprised of non-carcinogenic PAHs. The highest concentration PAH was naphthalene, at 53% of the total PAHs. This naphthalene emission percentage is in good agreement with vapor mass fraction analyses given in Attachment 7. Additional constituents tested included benzene, which was not detected in the condensed water vapor collected.

2. AquAeTer/Shaw conducted tests at the Koppers Inc. facility in Guthrie, Kentucky in 2004. The study results found that the vapor plume contained 99+% water. AquAeTer measured wood-treating cylinder door emissions by placing a cover over the open wood-treating cylinder immediately following the door opening. Two tests were conducted: 1) the first test was conducted with the treated wood in the wood-treating cylinder; and 2) the second test was conducted with no wood in the wood-treating cylinder. AquAeTer measured polycyclic aromatic hydrocarbons (PAHs) and water content of the collected vapor stream coming off the top of the wood-treating cylinder door opening. Naphthalene was the single largest PAH measured in the non-water portion. The naphthalene mass emitted from the wood-treating cylinder was calculated to be only 0.071 pound or about 6 teaspoons of naphthalene during a typical 15-minute door opening, for a cylinder that treats 3,500 cubic feet of wood.

3. For a wood treating facility that treats about 1,000 charges with a total wood volume of about 2.7 million cubic feet of wood per year and which represents about 735,000 cross ties, the total naphthalene emissions from the door openings would be less than 100 lbs per year. This is equivalent to the naphthalene emissions from about 7 to 8 automobiles that are driven about 15,000 miles per year each.

4. Koppers Inc. conducted air emission tests at the Koppers Feather River plant of treated poles of various ages including poles that had been directly pulled from the wood-treating cylinder. Naphthalene was the major constituent measured. None of the carcinogenic PAHs, including benzo(a)pyrene, were detected in the

volatile vapor emissions measured off the freshly treated poles at a method detection limit of less than 1.98 mg/hr. Based on their very low vapor pressures, the five and six-ringed PAHs including benzo(a)pyrene are not expected to be emitted from creosote wood treating operations.

5. Koppers Company, Inc. and Koppers Inc. have conducted personnel monitoring of employees working directly on the drip pad and directly in front of the wood-treating cylinder door since 1978. Vapor emissions from the wood-treating cylinder door do not result in employee exceedances of the OSHA worker protection standards.

6. Freshly harvested wood has about 70% moisture content and air-dried wood has about 50% moisture. Because water is about 280 times more volatile than naphthalene, water dominates the emissions coming from the wood-treating cylinder door openings. Theoretically, water vapor is the dominant emission from the wood-treating cylinder and this was confirmed by the actual vapor emission testing conducted by Koppers Company, Inc. in 1975 and by AquAeTer in 2004.

In conclusion, the vapor plume from both the end of a creosote treating cycle when the wood-treating cylinder door is opened and from the fresh creosote-treated wood is predominantly a water vapor plume containing over 99% water. The primary constituent in the remaining portion of the plume is naphthalene. None of the PAHs listed as suspect carcinogens have been detected in this vapor plume, including benzo(a)pyrene.

VII. REFERENCES

ADEQ. 1996 Revision; reprinted 12/2001.

American Wood Preservers' Association (AWPA). 1995. 2008 AWPA Book of Standards. AWPA, Birmingham, Alabama.

American Industrial Hygiene Association (AIHA). 1989. "Odor Thresholds for Chemicals with Established Occupational Health Standards," Fairfax, Virginia, Reprinted 1997.

ATSDR. 2005. "Toxicological profile for Naphthalene, 1-Methylnaphthalene, and 2-Methylnaphthalene," U.S. Department of Health and Human Services, Public Health Service, Atlanta, Georgia.

Burright, Donald. July 1986. "Coal Tart Pitch Volatiles (CTPV) Coke Oven Emissions (COE) Selected Polynuclear Aromatic Hydrocarbons (PAHs)", OSHA Analytical Laboratory, Salt Lake City, Utah.

Chemical Abstracts Service (CAS). August 5, 2008. "Chemical Abstracts Service Registry", CAS, A Division of the American Chemical Society, Columbus, Ohio, http://www.cas.org.

Corn, Michael R., and C. Brown. September, 2008. Benzene.

Marotta, P.J., In Press. "Koppers Field Test Retort Door – Empty and Full Retort, Naphthalene Mass Rate Results, Guthrie Plant," prepared for Koppers, Inc., Pittsburg, Pennsylvania by AquAeTer, Brentwood, Tennessee.

National Institute of Health, 2005. "Naphthalene CASRN: 91-20-3," National Institutes of Health (NIH), National Library of Medicine (NLM), Toxicology Data Network (TOXNET), Hazardous Substances Data Bank (HSDB). Complete Update on June 24, 2005, Bethesda, Maryland.

National Institute for Occupational Safety and Health (NIOSH). September 2005. NIOSH Pocket Guide to Chemical Hazards. 2006. DHHS (NIOSH) Publication No. 2005-149, Cincinnati, Ohio.

Oak Ridge National Laboratory (ORNL). June 17, 2008. "Regional Screening Levels: Summary Table.", ORNL, Oak Ridge, Tennessee, http://epa-prgs.ornl.gov/chemicals/download.shtml.

Perry, R. H., and D. W. Green. 1997. Perry's Chemical Engineers' Handbook, Seventh Edition, New York, New York.

Research Triangle Institute. February 19, 1999a. "Preliminary Analysis for Koppers Industries, Inc. Coal Tar Creosote P1/P13," prepared for the Creosote Council, Pittsburg, Pennsylvania by RTI, Research Triangle, North Carolina.

Research Triangle Institute. February 19, 1999b. "Preliminary Analysis for Koppers Industries, Inc. Coal Tar Creosote P2," prepared for the Creosote Council, Pittsburg, Pennsylvania by RTI, Research Triangle, North Carolina.

Science Applications International Corporation. December 1993. "Draft Emissions Test Report of the Kerr-McGee Chemical Corporation Forest Products Division Wood Treatment Plant Avoca, Pennsylvania," prepared for the United States Environmental Protection Agency by SAIC, Beaverton, Oregon.

Smith, S. T. August 26, 1994. "Explanation of Treated Wood Air Emissions Estimates from the Feather River Study Data at Koppers' Oroville, CA Plant to the AWPI Air Subcommittee," prepared for AWPI, Fairfax, Virginia, by Koppers, Inc., Pittsburg, Pennsylvania.

USEPA. April 1992b. "Naphthalene," USEPA Technology Transfer Network Air Toxics Web Site, http://epa.gov/ttn/atw/hlthef/naphthal.html.

Williams, P.R. May 19, 1975. "Interoffice Correspondence: Susquehanna Plant Odor Problem", Koppers, Pittsburg, Pennsylvania.

ATTACHMENT 1. BOILING POINTS AND VAPOR PRESSURES OF CHEMICALS TYPICALLY FOUND IN CREOSOTE

CONSTITUENT IDENTITY	MOLECULAR WEIGHT (lbs/lb-mole)	CAS NO.	PROJECTED BOILING POINT (°F)	VAPOR PRESSURE @80°F (psia)
Indane	118.2	496-11-7	350.5	3.33E-02
Indene	116.2	95-13-6	359.6	2.36E-02
Naphthalene	128.2	91-20-3	419.3	5.89E-03
Benzo[b]thiophene	134.2	95-15-8	423.1	5.18E-03
Cresols (isomers)	108.1	1319-77-3	443.2	3.80E-03
Quinoline	129.2	91-22-5	451.3	1.34E-03
2-Methylnaphthalene	142.2	91-57-6	455.1	1.44E-03
2-Methylbenzo[b]thiophene	148.2	1195-14-8	459.7	1.05E-03
Isoquinoline	129.2	119-65-3	463.1	1.54E-03
1-Methylnaphthalene	142.2	90-12-0	466.0	1.66E-03
Biphenyl (Diphenyl, 1,1-Biphenyl)	154.2	92-52-4	479.6	6.13E-04
1H-Indole	117.2	120-72-9	486.3	6.00E-04
1-Ethylnaphthalene	156.2	1127-76-0	497.7	5.40E-04
6-Methylquinoline	143.2	91-62-3	504.8	3.00E-04
2,6-Dimethylnaphthalene	156.2	581-42-0	505.5	3.97E-04
Acenaphthylene	152.2	208-96-8	507.1	1.52E-04
1,3-Dimethylnaphthalene	156.2	575-41-7	514.4	3.29E-04
4-Methylbiphenyl	168.2	644-08-6	515.7	2.80E-04
Acenaphthene	154.2	83-32-9	521.1	3.14E-04
5-Methylchrysene		3697-24-3	531.5	1.84E-09
Dibenzofuran	184.3	132-64-9	539.7	1.09E-03
9H-Fluorene	166.2	86-73-7	551.8	8.59E-05
9,10-Dihydroanthracene	180.2	613-31-0	562.7	2.94E-06
1-Naphthalenecarbonitrile	153.2	86-53-3	600.1	1.61E-05
Benzo(k)fluoranthene	252.3	207-08-9	601.4	4.54E-11
1-Phenylnaphthalene	204.3	605-02-7	603.7	6.57E-06
Dibenzothiophene	184.3	132-65-0	608.0	1.80E-05
Acridine	179.2	290-94-6	618.3	1.11E-06
Phenanthrene	178.2	85-01-8	619.9	1.26E-05
Anthracene	178.2	120-12-7	620.5	1.55E-05
5,6-Benzoquinoline	179.2	85-02-9	629.4	1.07E-06
Benzo(b)fluoranthene	252.3	205-99-2	631.3	2.65E-09
Carbazole (Dibenzopyrrole, 9H-Carbazole)	167.2	86-74-8	634.3	2.56E-06
4H-Cyclopenta(d,e,f)phenanthrene	190.2	203-64-5	634.8	1.42E-06
2-Methylphenanthrene	192.3	2531-84-2	636.5	1.39E-06
1-Methylphenanthrene	192.3	832-69-9	640.5	1.13E-06
Fluoranthene	202.2	206-44-0	700.0	2.61E-06
11H-Benzo(b)fluorene (2,3-Benzofluorene)	216.3	243-17-4	703.4	3.91E-08
Pyrene	202.2	129-00-0	704.4	5.64E-07
2-Phenylnaphthalene*	204.2	612-94-2	551.8	8.59E-05
11H-Benzo(a)fluorene	216.3	238-84-6	711.5	2.84E-08
Benzo-b-anthracene (Naphthacene)	228.3	92-24-0	741.7	6.05E-09
Benzo(g,h,i)perylene	276.3	191-24-2	747.9	4.99E-12
Benz(a)anthracene	228.3	56-55-3	751.1	4.95E-09
Chrysene	228.3	218-01-9	764.3	1.00E-08
Dibenzo(a,h)anthracene	278.4	53-70-3	814.0	8.05E-10
Benzo(e)pyrene	252.3	192-97-2	832.3	6.39E-10
Benzo(a)pyrene	252.3	50-32-8	836.4	5.43E-10
Indeno(1,2,3-cd)pyrene	276.3	193-39-5	896.0	8.02E-14
For Comparison:				
Water	18.0	7732-18-5	212.0	4.67E-01
Benzene	78.0	71-43-2	176.0	1.99E+00

Note: *Assumed that 2-phenylnaphthalene coefficients were the same as 1-phenylnaphthalene.

ATTACHMENT 2 SUMMARY OF METHOD TO-14A (SUMMA CANNISTERS) ANALYSES
STATION 8 - RAIL LINE ALONG WEST CENTRAL BOUNDARY

CONSTITUENT	SAMPLE DATE	SAMPLE ID	REPORTING LIMIT (ppbv)	RESULT (ppbv)	RESULT (ug/m^3)	SCREENING LEVEL (ug/m^3)	WIND DIRECTION
Benzene	8-Aug-00	8-S-8/8	0.05	0.21	0.67	0.25	
	9-Aug-00	8-S-8/9	0.069	0.21	0.67		
	10-Aug-00	8-S-8/10	0.19	0.31	0.99		
Toluene	8-Aug-00	8-S-8/8	0.062	2.3	8.67	400	
	9-Aug-00	8-S-8/9	0.086	0.74	2.79		
	10-Aug-00	8-S-8/10	0.23	1.1	4.15		
Ethylbenzene	8-Aug-00	8-S-8/8	0.095	0.18	0.78	1,100	
	9-Aug-00	8-S-8/9	0.13	0.23	1.00		
	10-Aug-00	8-S-8/10	0.35	< 0.35	< 1.52		
1,3- and 1,4-Dimethylbenzenes (m,p-Xylenes)	8-Aug-00	8-S-8/8	0.17	0.31	1.35	730	
	9-Aug-00	8-S-8/9	0.24	0.33	1.43		
	10-Aug-00	8-S-8/10	0.64	< 0.64	< 2.78		
1,2-Dimethylbenzene (o-Xylene)	8-Aug-00	8-S-8/8	0.06	0.11	0.48	730	
	9-Aug-00	8-S-8/9	0.084	0.11	0.48		
	10-Aug-00	8-S-8/10	0.22	< 0.22	< 0.96		
Naphthalene	8-Aug-00	8-S-8/8	0.31	4.2	22.02	3.1	
	9-Aug-00	8-S-8/9	2.6	38	199.21		
	10-Aug-00	8-S-8/10	1.2	9.9	51.90		

NOTES:

Screening Level - USEPA Region 6 Human Health Screening Levels for Ambient Air (Residential Scenario)

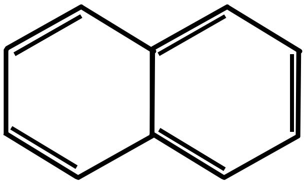
8-S-8/9 - This sample was reanalyzed at a greater dilution as the initial analysis found naphthalene to be present at a level (15.6 ppbv) above the upper limit of the calibration range.

TABLE 4. CALCULATION OF VAPOR PERCENTAGE FROM KOPPERS P2 CREO

CONSTITUENT IDENTITY	MOLECULAR WEIGHT (MW) (lbs/lb-mole)	CAS NO.	MEAN WEIGHT in Creosote (mass fraction)	VAPOR MASS (fraction)
Water	18.0		**0**	0.00E+00
1-Ethylnaphthalene	156.2	1127-76-0	0.0048	4.33E-03
2-Methylbenzo[b]thiophe	148.2	1195-14-8	0.0003	4.19E-04
Isoquinoline	129.2	119-65-3	0.0020	4.61E-03
Anthracene	178.2	120-12-7	0.0290	1.01E-03
1H-Indole	117.2	120-72-9	0.0025	2.53E-03
Pyrene	202.2	129-00-0	0.0520	9.85E-05
Cresols (isomers)	108.1	1319-77-3	0.00075	5.09E-03
Dibenzofuran	184.3	132-64-9	0.0338	4.72E-02
Dibenzothiophene	184.3	132-65-0	0.0115	4.74E-04
1-Methyl-9H-fluorene	180.2	1730-37-6		0.00E+00
Benzo(g,h,i)perylene	276.3	191-24-2	0.0005	2.59E-11
Benzo(e)pyrene	252.3	192-97-2	0.0038	1.46E-08
Indeno(1,2,3-cd)pyrene	276.3	193-39-5	0.0011	1.51E-12
Perylene	253.3	3697-24-3		0.00E+00
4H-Cyclopenta(d,e,f)phe	190.2	203-64-5	0.0145	6.39E-05
Benzo(b)fluoranthene	252.3	205-99-2	0.0088	6.64E-08
Fluoranthene	202.2	206-44-0	0.0595	4.20E-04
Benzo(k)fluoranthene	252.3	207-08-9	0.0035	1.61E-09
Acenaphthylene	152.2	208-96-8	0.0031	9.45E-04
Chrysene	228.3	218-01-9	0.0165	7.92E-07
2,3,5-Trimethylnaphthale	170.3	2245-38-7		0.00E+00
11H-Benzo(a)fluorene	216.3	238-84-6	0.0088	1.15E-06
1,2-Benzodiphenylenesul	184.3	191-24-2		0.00E+00
11H-Benzo(b)fluorene (2	216.3	243-17-4	0.0108	1.90E-06
2-Methylphenanthrene	192.3	2531-84-2	0.0063	2.69E-05
Benzo[c]thiophene	134.2	270-82-6	0.0019	0.00E+00
Acridine	179.2	290-94-6	0.0020	7.47E-06
Indan	118.2	496-11-7	0.0008	2.78E-02
Benzo(a)pyrene	252.3	50-32-8	0.0053	1.76E-08
Dibenzo(a,h)anthracene	278.4	53-70-3	0.0004	1.86E-09
Benz(a)anthracene	228.3	56-55-3	0.0050	1.35E-07
1,3-Dimethylnaphthalene	156.2	575-41-7	0.0063	3.70E-03
2,6-Dimethylnaphthalene	156.2	581-42-0	0.0045	3.15E-03
1-Phenylnaphthalene	204.3	605-02-7		0.00E+00
2-Phenylnaphthalene	204.2	53-70-3	0.0004	1.86E-09
9,10-Dihydroanthracene	180.2	613-31-0	0.0030	2.97E-05
4-Methylbiphenyl	168.2	644-08-6	0.0010	5.04E-04
1-Methylphenanthrene	192.3	832-69-9	0.0058	2.04E-05
Acenaphthene	154.2	83-32-9	0.0638	3.37E-02
Phenanthrene	178.2	85-01-8	0.1178	3.62E-03
5-Methylchrysene	252.3	3697-24-3	0.0006	4.30E-09
5,6-Benzoquinoline	179.2	85-02-9	0.0025	8.66E-06
1-Naphthalenecarbonitril	153.2	86-53-3	0.0018	7.57E-05
9H-Fluorene	166.2	86-73-7	0.0490	8.53E-03
Carbazole (Dibenzopyrro	167.2	86-74-8	0.0163	1.20E-04
1-Methylnaphthalene	142.2	90-12-0	0.0230	5.46E-02
Naphthalene	128.2	91-20-3	0.0743	5.61E-01
Quinoline	129.2	91-22-5	0.0085	1.91E-02
2-Methylnaphthalene	142.2	91-57-6	0.0523	1.19E-01
6-Methylquinoline	143.2	91-62-3	0.0006	3.51E-04
Naphthacene	228.3	92-24-0	0.0163	5.24E-07
Biphenyl (Diphenyl, 1,1-	154.2	92-52-4	0.0130	1.35E-02
Indene	116.2	95-13-6	0.0029	8.37E-02
Benzo[b]thiophene	134.2	95-15-8		0.00E+00
TOTALS			0.7520	1.0000E+00

TABLE 4. CALCULATION OF VAPOR PERCENTAGE FROM KOPPERS P2 CREO

CONSTITUENT IDENTITY	MOLECULAR WEIGHT (MW) (lbs/lb-mole)	CAS NO.	MEAN WEIGHT in Creosote (mass fraction)	VAPOR MASS (fraction)
Water	18.0		**0.03**	9.77E-01
1-Ethylnaphthalene	156.2	1127-76-0	0.0048	1.01E-04
2-Methylbenzo[b]thiophe	148.2	1195-14-8	0.0003	9.77E-06
Isoquinoline	129.2	119-65-3	0.0020	1.08E-04
Anthracene	178.2	120-12-7	0.0290	2.35E-05
1H-Indole	117.2	120-72-9	0.0025	5.91E-05
Pyrene	202.2	129-00-0	0.0520	2.30E-06
Cresols (isomers)	108.1	1319-77-3	0.00075	1.19E-04
Dibenzofuran	184.3	132-64-9	0.0338	1.10E-03
Dibenzothiophene	184.3	132-65-0	0.0115	1.11E-05
1-Methyl-9H-fluorene	180.2	1730-37-6		0.00E+00
Benzo(g,h,i)perylene	276.3	191-24-2	0.0005	6.04E-13
Benzo(e)pyrene	252.3	192-97-2	0.0038	3.40E-10
Indeno(1,2,3-cd)pyrene	276.3	193-39-5	0.0011	3.51E-14
Perylene	253.3	3697-24-3		0.00E+00
4H-Cyclopenta(d,e,f)pher	190.2	203-64-5	0.0145	1.49E-06
Benzo(b)fluoranthene	252.3	205-99-2	0.0088	1.55E-09
Fluoranthene	202.2	206-44-0	0.0595	9.80E-06
Benzo(k)fluoranthene	252.3	207-08-9	0.0035	3.77E-11
Acenaphthylene	152.2	208-96-8	0.0031	2.20E-05
Chrysene	228.3	218-01-9	0.0165	1.85E-08
2,3,5-Trimethylnaphthale	170.3	2245-38-7		0.00E+00
11H-Benzo(a)fluorene	216.3	238-84-6	0.0088	2.69E-08
1,2-Benzodiphenylenesul	184.3	191-24-2		0.00E+00
11H-Benzo(b)fluorene (2	216.3	243-17-4	0.0108	4.43E-08
2-Methylphenanthrene	192.3	2531-84-2	0.0063	6.27E-07
Benzo[c]thiophene	134.2	270-82-6	0.0019	0.00E+00
Acridine	179.2	290-94-6	0.0020	1.74E-07
Indan	118.2	496-11-7	0.0008	6.49E-04
Benzo(a)pyrene	252.3	50-32-8	0.0053	4.10E-10
Dibenzo(a,h)anthracene	278.4	53-70-3	0.0004	4.33E-11
Benz(a)anthracene	228.3	56-55-3	0.0050	3.14E-09
1,3-Dimethylnaphthalene	156.2	575-41-7	0.0063	8.62E-05
2,6-Dimethylnaphthalene	156.2	581-42-0	0.0045	7.36E-05
1-Phenylnaphthalene	204.3	605-02-7		0.00E+00
2-Phenylnaphthalene	204.2	53-70-3	0.0004	4.33E-11
9,10-Dihydroanthracene	180.2	613-31-0	0.0030	6.92E-07
4-Methylbiphenyl	168.2	644-08-6	0.0010	1.18E-05
1-Methylphenanthrene	192.3	832-69-9	0.0058	4.77E-07
Acenaphthene	154.2	83-32-9	0.0638	7.86E-04
Phenanthrene	178.2	85-01-8	0.1178	8.45E-05
5-Methylchrysene	252.3	3697-24-3	0.0006	1.00E-10
5,6-Benzoquinoline	179.2	85-02-9	0.0025	2.02E-07
1-Naphthalenecarbonitril	153.2	86-53-3	0.0018	1.76E-06
9H-Fluorene	166.2	86-73-7	0.0490	1.99E-04
Carbazole (Dibenzopyrro	167.2	86-74-8	0.0163	2.80E-06
1-Methylnaphthalene	142.2	90-12-0	0.0230	1.27E-03
Naphthalene	128.2	91-20-3	0.0743	1.31E-02
Quinoline	129.2	91-22-5	0.0085	4.45E-04
2-Methylnaphthalene	142.2	91-57-6	0.0523	2.78E-03
6-Methylquinoline	143.2	91-62-3	0.0006	8.18E-06
Naphthacene	228.3	92-24-0	0.0163	1.22E-08
Biphenyl (Diphenyl, 1,1-	154.2	92-52-4	0.0130	3.14E-04
Indene	116.2	95-13-6	0.0029	1.95E-03
Benzo[b]thiophene	134.2	95-15-8		0.00E+00
TOTALS			0.7520	1.0000E+00



NAPHTHALENE

STRUCTURE
$C_{10}H_8$

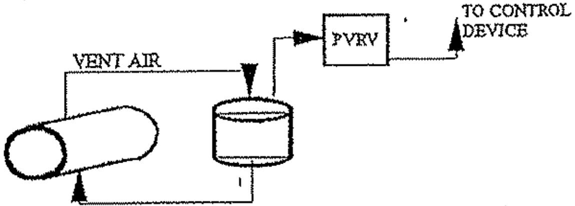
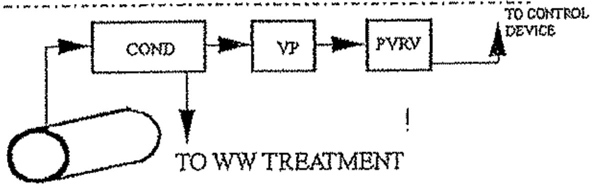
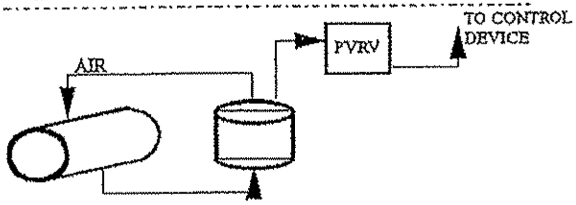
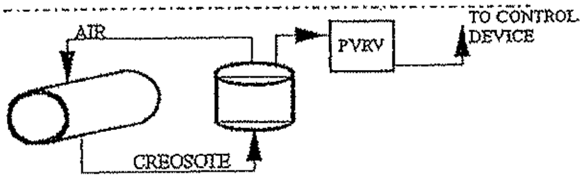
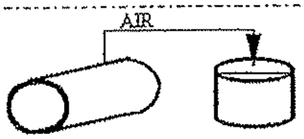
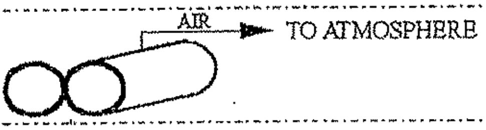
SYNONYMS:	Mothballs, tar camphor
CAS No:	91-20-3
PHYSICAL & CHEMICAL PROPERTIES	
Boiling Point:	217.9 °C
Molecular Weight:	128.2
Vapor Pressure:	8.5E-02 mm Hg at 25 °C
Melting Point:	80.2 °C
DISSOCIATION CONSTANTS	
Henry's Law Constant:	4.40E-04 atm-m^3/mol
Density:	1.162 g/cm^3 at 20 °C
Vapor Density:	
Water Solubility:	31 mg/L at 25 °C
Log Octanol/Water Coefficient:	3.3
K_{ow}:	1,995

AquAeTer *optimizing environmental resources* ◆ water, air, earth

ATTACHMENT 5

PHYSICAL AND CHEMICAL PROPERTIES OF

NAPHTHALENE

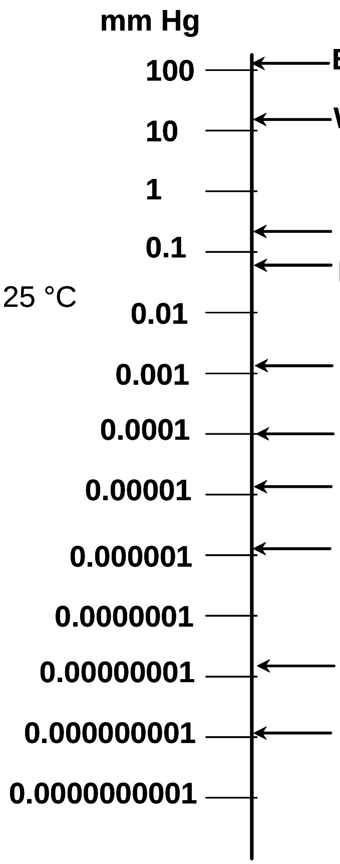
PROCESS STEP	TIME	PURPOSE	SETUP	EMISSIONS
CLOSE DOOR	30 SEC.			NONE
INITIAL AIR	0.25 MIN.	REPLACE CELLS WATER WITH AIR		NONE
FILL	0.25 HR.	BOIL OUT WATER		
VACUUM	12-14 HRS.	BOIL OUT WATER		
1st PUMP BACK	0.25 HR.	ADD AIR		
PRESSURIZATION	2-4 HRS.	TREATING WOOD		NONE
DEPRESSURIZE (2nd PUMP BACK)	0.25 HR.	EMPTY TANK		
FINAL VACUUM	2-4 HRS.	PREVENT DRIPPING		TO WORK TANK
OPEN DOOR	15 MIN.			

ATTACHMENT 6 Treatment Cycle

VOLATILITY INDEX

Water Vapor

All vapor pressures at 25 °C



Benzene, 100.84 mm Hg

Water Vapor, 23.74 mm Hg

Phenol, 0.35 mm Hg

Naphthalene, 0.085 mm Hg

Acenaphthene, 0.0025 mm Hg

Phenanthrene, 0.00012 mm Hg PCP, 0.00011 mm Hg

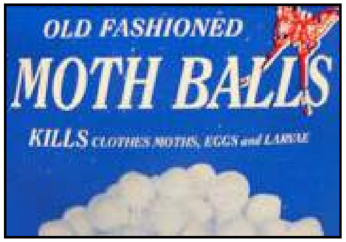
Fluoranthene, 0.0000521 mm Hg

Pyrene, 0.000006004 mm Hg
Anthracene, 0.00000267 mm Hg

Benzo(a)pyrene, 0.00000006 mm Hg

2,3,7,8-TCDD, 0.0000000015 mm Hg

Benzene (gasoline)



Moth Balls
(naphthalene)

Benzo(a)pyrene
(Asphalt)

AquAeTer

CLIENT:
LOCATION:
PROJECT/FILE:

optimizing environmental resources | water, air, earth

ATTACHMENT 7
COMPARISON OF VAPOR PRESSURES

CLIENT:
LOCATION:
PROJECT/FILE:

AquAeTer

optimizing environmental resources | water, air, earth

ATTACHMENT 8

RETORT DOOR COLLECTION COVER

AquAeTer

CLIENT:
LOCATION:
PROJECT/FILE:

optimizing environmental resources | water, air, earth

ATTACHMENT 9

COLLECTION COVER FITTED OVER RETORT DOOR

CLIENT:
LOCATION:
PROJECT/FILE:

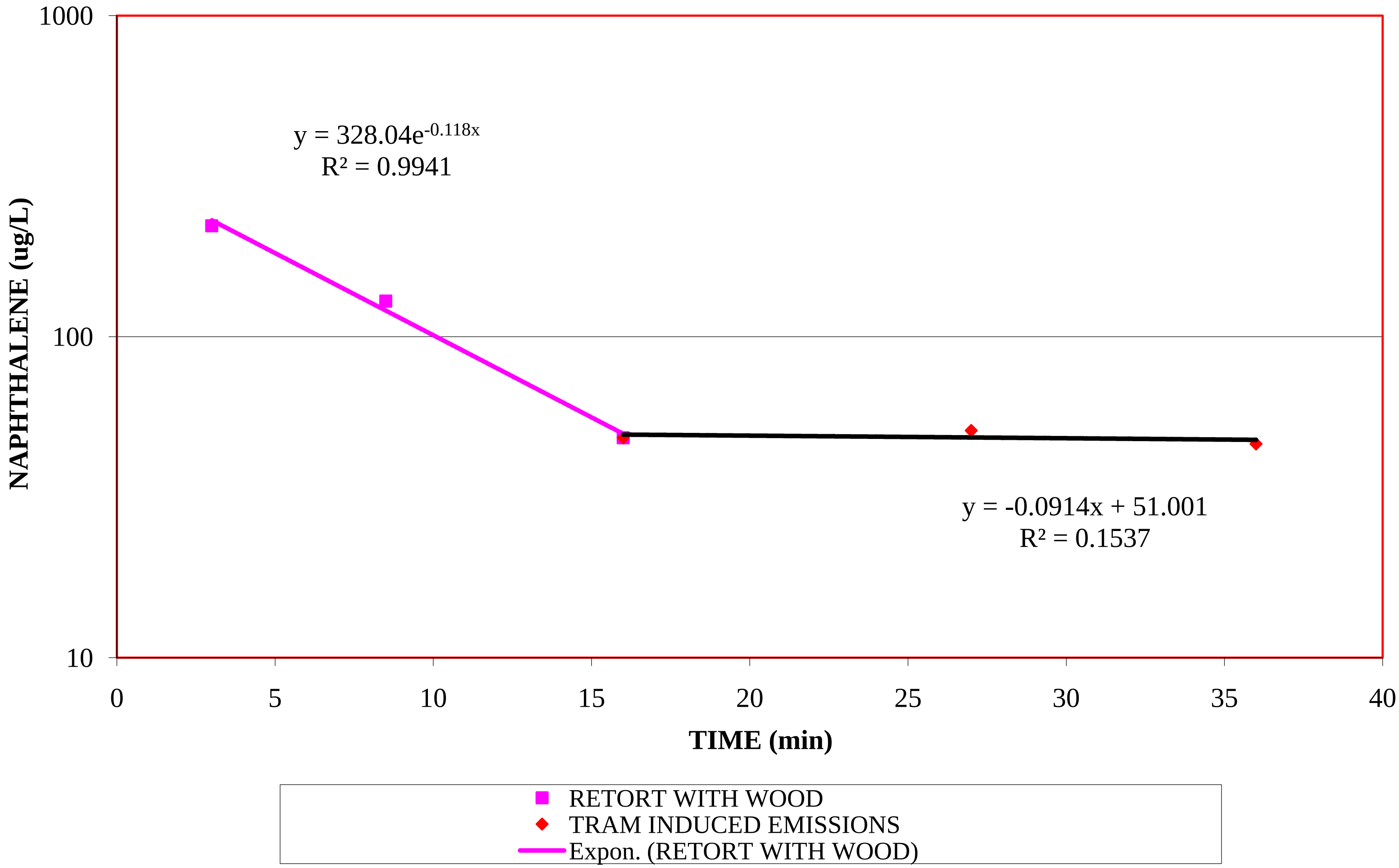
AquAeTer

optimizing environmental resources | water, air, earth

ATTACHMENT 10

RETORT DOOR COLLECTION COVER

ATTACHMENT 8. VAPOR EMISSIONS WITH WOOD IN RETORT



AquAeTer

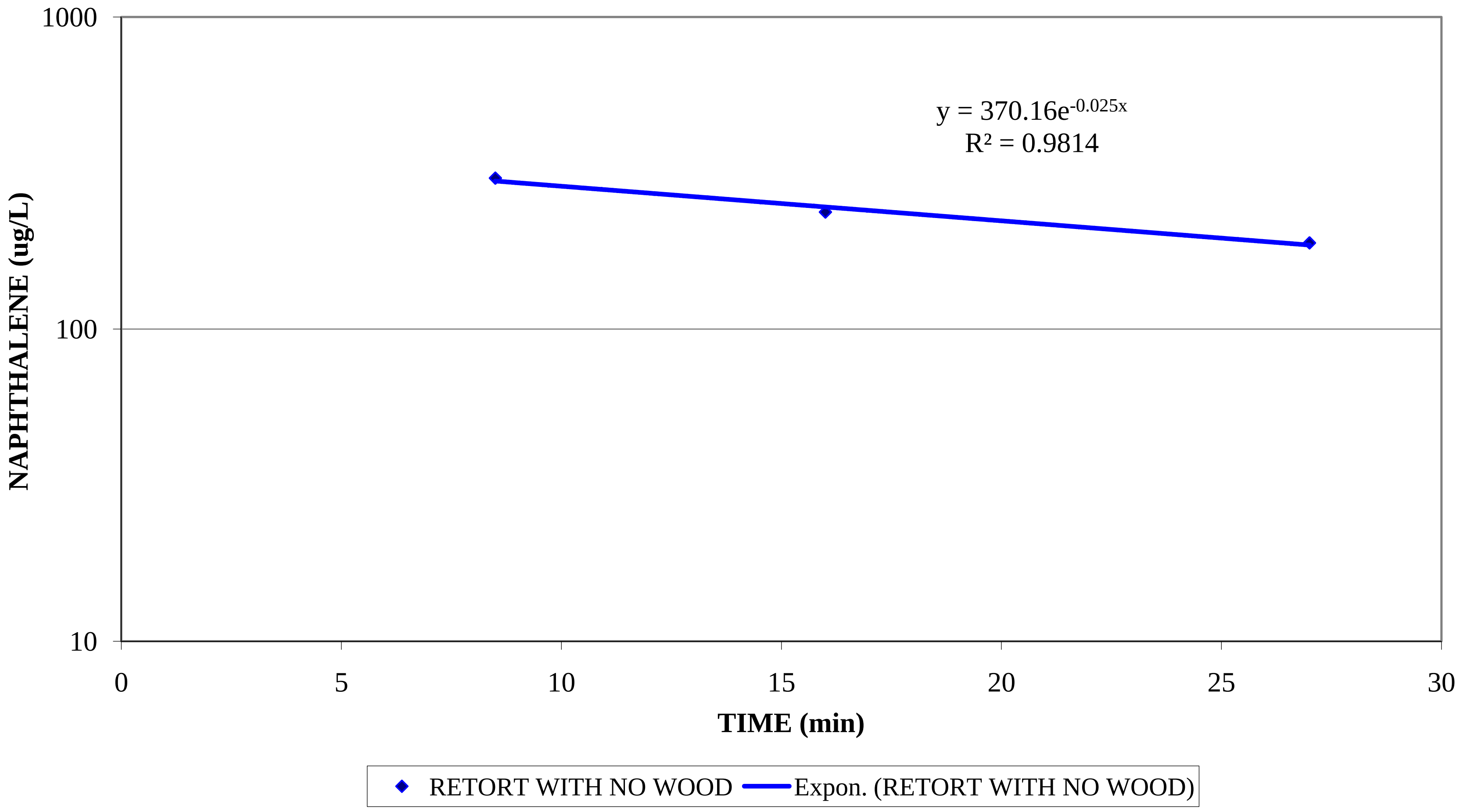
CLIENT:
LOCATION:
PROJECT/FILE:

optimizing environmental resources | water, air, earth

ATTACHMENT 11

VAPOR EMISSIONS WITH WOOD IN RETORT

ATTACHMENT 9. NAPHTHALENE EMISSIONS FROM RETORT WITH NO WOOD



AquAeTer

CLIENT:
LOCATION:
PROJECT/FILE:

optimizing environmental resources | water, air, earth

ATTACHMENT 12.

NAPHTHALENE EMISSIONS FROM RETORT WITH NO WOOD

FIELD STUDY OF PAH AIR EMISSIONS FROM CREOSOTE WOOD-TREATING CYLINDER DOOR OPENINGS

CONDUCTED AT KOPPERS INC.
GUTHRIE, KENTUCKY FACILITY

PREPARED FOR:

KOPPERS INC.
PITTSBURGH, PENNSYLVANIA

PREPARED BY:

Michael R. Corn, P.E. (KY)
Paul J. Marotta, P.E. (KY)
AquAeTer, Inc.
Brentwood, TN

MAY 2010

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

ACKNOWLEDGEMENT

In Cooperation with:
Leah Blinn, P.E.
Arijit Pakrasi, Ph.D., P.E.
Shaw Environmental, Inc.
Pittsburgh, PA

Thomas A. Zordan, Ph.D.
Zordan Associates, Inc.
Pittsburgh, PA

1 INTRODUCTION

AquAeTer, Inc located in Brentwood, Tennessee and Shaw Environmental located in Pittsburgh, Pennsylvania were requested by Koppers Inc. located in Pittsburgh, Pennsylvania to conduct confirmatory air emissions tests on cylinder door openings. A visible white plume is emitted when the door is opened to remove treated ties and insert new ties for treatment. Air emissions testing had been conducted in the past on these emissions at the Koppers Susquehanna, PA wood treating facility in 1976 and at the Burke-Parsons-Bowlby wood treating facility located in Dubois, Pennsylvania.. The emissions testing results at the Burke-Parsons-Bowlby facility was used by the USEPA for estimating naphthalene emissions from door openings as part of their Maximum Achievable Control Technology (MACT) analysis of the creosote industry.

AquAeTer and Shaw conducted these tests on October 6, 2004. This report gives the methodology employed and the results of these tests. The results were reported in a Vapor Report prepared by AquAeTer for use in legal proceedings.

BACKGROUND

The process of treating wood with creosote results in volatile organic compound (VOC) air emissions. A major constituent of the VOC emissions is naphthalene, which is a listed hazardous air pollutant (HAP). Wood treating facilities are required to estimate the VOC and HAP emissions to determine the applicability of various regulatory requirements such as the Superfund Amendments and Reauthorization Act (SARA), Clean Air Act (CAA), and most importantly the Title V Operating Permit provisions. Determination of the applicable permitting mechanism (such as Title V Major Source or Minor Source Operating permits), is based on the quantity of pollutant emitted. Due to differences in the requirements and focus of the Major and Minor Source permits, it is important to determine air emissions from a facility using as much measured data as possible.

A VOC Major Source is typically defined as a facility that emits equal to or greater than 100 tons per year of conventional pollutants including VOCs. A facility meeting or exceeding this threshold would be required to obtain a Title V Operating Permit and would be referred to as a Major Source. Facilities emitting less than 100 tons per year of VOCs would be considered a Minor Source and be permitted as such. If one or more of the VOC constituents is a listed HAP, then the threshold for Major Source determination has a HAP component, also. The Major Source designation for HAPs is the emission of greater than 10 tons per year of any single HAP, or, 25 tons per year of total HAPs. Typically, naphthalene is the predominant HAP in the liquid creosote that represents the highest HAP emission. Naphthalene is the only significant PAH that is emitted and emissions of naphthalene determine whether the wood treating facility is a Major or Minor Source with respect to the 10 tons per year for the single HAP threshold.

Historically, the creosote wood treating industry has estimated the emissions of naphthalene from the wood treatment operations using the emission factors developed for the American Wood Preservers Institute (AWPI), which are documented and organized in a spreadsheet format for use in emission estimate calculations. The spreadsheet is referred to in the industry as the AWPI Model. The AWPI Model is structured to calculate emissions from groups of sources including work tanks, storage tanks, treating cycles, cylinder door openings, equipment fugitives, and treated wood storage yard emissions. The emission factors within the AWPI Model are based on actual field testing performed in several wood treatment plants conducted in the 1980s and 1990s, published emission factors contained in documents such as the U.S. Environmental Protection Agency (USEPA) Compilation of Air Pollutant Emissions Factors, AP-42, and synthetic organic chemical manufacturing industry (SOCMI), engineering calculations and updates by the Texas Commission on Environmental Quality (TCEQ), and the creosote constituents analyses conducted by Research Triangle Institute (RTI) in Research Triangle, North Carolina.

In 2004, Koppers re-evaluated the emissions factor and calculation procedures for estimating emissions of naphthalene from the wood treating cylinder door used in the AWPI Model. The emission factor used by the USEPA to estimate emissions from the Kerr-McGee Avoca, Pennsylvania creosote treating facility was originally developed from photoionization detector (PID) measurements taken from the steam plume of a cylinder door opening at a Burke-

Parsons-Bowlby Corporation wood treating facility located in Dubois, Pennsylvania. The PID readings were converted to a VOC emission factor of 5.917 lbs/hr. Mr. Eugene Crumpler of the USEPA located in Durham, North Carolina converted the VOC emissions to a naphthalene emission rate of 0.045 lb naphthalene per 15-minute door opening. Since speciated data for PAHs were not obtained for the door-opening emissions testing conducted at the BPB Dubois facility, Koppers requested that these data be quantified by re-testing cylinder door emissions under controlled conditions. Naphthalene emissions measurements from the wood treating cylinder door opening process were the focus of this study.

Testing of the emissions from wood treating cylinder door openings was conducted on October 6, 2004 at the Koppers Guthrie, Kentucky facility. The site is located at 198 Fairground Road, Todd County, Guthrie, Kentucky 42234. This report describes the procedures used in the 2004 cylinder door emission tests and the findings, test results, and conclusions from the tests.

SCOPE OF WORK

The scope of work included measuring polycyclic aromatic hydrocarbons (PAHs) emissions from the cylinder-door openings which is comprised of the cylinder door opening at the completion of wood treating process, removing the treated wood charge from the cylinder, and finally reloading the cylinder with untreated wood to re-start the cycle. The purpose of the study was to obtain speciated emission data to be used to develop an emission factor for the entire time period for the cylinder door-opening based on the measurement of emissions from key points during the door-opening. A process flow diagram for the door opening time period and the time intervals during the door opening when emissions were measured is illustrated in Figure 1. To measure representative emissions from the entire door-opening period, three sampling events were performed.

The first sampling event was designed to measure emissions from the door opening following completion of a typical wood-treating cycle. The cylinder door was opened and a hood constructed of steel and plywood was placed over the cylinder opening. The vapor released from the interior of the open treating cylinder was collected by the hood and funneled up through a sampling duct. The sample duct was fitted with a small electrically-powered fan sized to draw the vapor out of the collection hood without pulling in additional surrounding air. The addition of surrounding air would have diluted the vapor concentration in the sample duct. Samples were drawn from the sample duct every five to ten minutes for a total of 45 minutes and tested for semi-volatile organic compounds (SVOCs). Flow measurements were made at the beginning and end of the sampling event. Sampling and analytical methods are described in more detail in a later section of this report.

The second sampling event was designed to determine emissions from the cylinder door opening on a cylinder containing no wood to simulate the emissions from an empty cylinder. Emissions from the empty cylinder occur in the time period directly following the removal of the treated wood from the cylinder and during the introduction of a new charge for treatment. This sampling event involved duplicating the previous sampling process but without wood, and included filling and heating creosote in the cylinder similarly to a treating cycle process. Again, the cylinder door was opened and the collection hood was placed over the cylinder door allowing the vapor released from the treating cylinder to be funneled through a sampling duct. This would be considered a conservative emission estimate since the cylinder would have additional void space for collection of vapors during the heating process and after the creosote had been pumped back to the work tanks (about twice the void space as when the wood is in the cylinder. Since the emissions measured in this case do not include the dilution/mixing effect of removing the treated wood from the cylinder, the results are considered to be conservatively high.

The third and final sampling event involved taking a sample of the cylinder vapor directly from the vacuum system at the end of the empty-cylinder event to simulate the conditions in the cylinder prior to the introduction of untreated wood. This information was then used to estimate the naphthalene emissions released as the fresh charge of wood is placed into the cylinder displacing the volume of creosote vapor equal to the wood and trams. Here again, the emissions measured in this case do not include the dilution/mixing effect of removing the treated wood from the cylinder prior to introduction of untreated wood, and the results are considered to be conservatively high.

This report presents the sample collection methodology including techniques and equipment, data collected, photographs, calculations, assumptions, and other information used to develop emission factors for future air emission estimates.

2 INVESTIGATION PROCEDURES

AquAeTer, Inc. provided the test plan development, sampling equipment designs, and technical oversight for the air emissions measurements during the test period in October 2004. Shaw Environmental, Inc. (Shaw) provided a mobile laboratory, air emission test equipment, and technicians to collect and analyze the samples. Koppers facility personnel constructed the treating cylinder hood enclosure and sampling duct/manifold for sample collection, and provided operational support to facilitate normal manufacturing process conditions required for the sampling events.

SAMPLING SETUP

To sample the emissions from door openings, a removable partial enclosure was designed and constructed with steel and plywood. The enclosure was sized to match the treating-cylinder door flange so that when the cylinder door was opened, the partial enclosure could be placed over, and partially cover the open treating cylinder door area. The enclosure was set in front of the open treating cylinder prior to opening the door. Once the door was opened, a fork truck was used to set and hold the enclosure tightly against the treating cylinder door flange to minimize any vapor leakage during the sampling event. A ten-inch diameter flexible duct directed the vapor flow from the enclosure to a six-inch diameter steel sample duct. An adequate straight length of sample steel duct fitted with sample ports was provided to conform to the flow measurement requirements of USEPA Method 1 (Sample and Velocity Traverses for Stationary Sources). A flow control damper and electric powered in-line fan were attached to the sample duct downstream from the sample ports. Photographs of the enclosure and sample duct are provided in Appendix 1.

The enclosure directed the vapor emissions to the exhaust duct where samples were obtained at sequential time intervals. Additionally, measurements of the volumetric flow rate through the sampling duct were made utilizing a straight circular duct (pipe) with sample ports and calibrated pitot tube instrumentation per USEPA Method 1. The sampling system was designed such that the enclosure and sampling duct neither impeded nor enhanced the flow of emissions from the cylinder so that representative samples would be obtained. This was visibly confirmed during the testing. If the sample flow rate is too high, surrounding air will be pulled into the sample duct and dilute the sample. If the sample flow rate is too low, the concentration of the sample will not be affected, however, the calculated emission mass flow rate will be understated since all of the escaping vapor will not be accounted for and vapors would have been emitted from the bottom of the open cylinder door area. This balance was observed directly during sampling by noting the flow of vapor out of the cylinder into the enclosure (vapor line on enclosure) during the testing event (see Photograph 8, page A1-4). Emissions (visible steam vapor) were directed into the cylinder door enclosure and to the sampling train using a low-flow rate fan (see Photographs 9 and 10, page A1-5). The sample duct flow rate could be adjusted manually using an in-line damper control.

SAMPLE COLLECTION AND ANALYSIS

Sample Collection

Vapor emissions from the treating cylinder were directed from the door-opening enclosure to the sample duct as described previously. These emissions include water vapor and SVOCs associated with the creosote preservative mixture. The emission samples were collected using a low-volume sampling pump and Tedlar™ bags over a 45-minute cycle as shown below. Initially, the sampling method considered for use was USEPA SW-846 Method 0010 for SVOCs using a Modified Method 5 Sampling Train. The Tedlar™ bag sample method was selected for use in this study to obtain sample concentration as a function of time as well as giving the sampling team a method to collect a sample of a primarily water vapor emission. Method 5 would have only provided one integrated mass emission rate, and not the actual emission rate as a function of time. The emissions sampling was conducted over a total of 45 minutes. Samples were collected at the following times (5 Total Samples):

Time = -10 to 0 minutes (Background);
Time = 0 to 5 minutes;
Time = 5 to 15 minutes;
Time = 15 to 25 minutes; and
Time = 25 to 35 minutes.

Samples were drawn into 1-Liter Tedlar™ sample bags and provided to the on-site mobile laboratory for analysis. This procedure was completed for two cases: 1) empty-cylinder (no trams or wood); and 2) full-cylinder (with trams fully loaded with wood). One additional bag sample (approximately 5-minute sample) was taken from the vacuum system at the end of the empty-cylinder case to calculate the emissions resulting when a new charge of untreated wood is pushed into the cylinder.

Sample Analysis

Tedlar™ bag samples were analyzed in accordance with the procedures provided in Appendix 5 using a modified purge and trap method with gas chromatography-mass spectrometry (GC-MS) detection for naphthalene. A chemical quality assessment report for the laboratory operation is also included in Appendix 5. Laboratory data results are attached in Appendix 3.

All door opening and vacuum system sampling events occurred on October 6, 2004 as described in the Field Notes (Appendix 4), and summarized in Table 1. Wood surface and wet/dry bulb temperatures were recorded during the testing for qualitative purposes. Samples of the liquid creosote used during the emissions sampling event were collected by facility personnel and sent by Shaw to an off-site laboratory for chemical analysis. This data allowed correlation of the measured emission rate with the concentration of specific constituents in the creosote used during the sampling event. The creosote analytical data are included in Appendix 6.

3 FINDINGS AND CALCULATIONS

OBSERVATION OF CYLINDER DOOR SAMPLE COLLECTION

Vapor emissions from the cylinder, measured by placing a hood over the cylinder with an exhaust duct to direct/funnel the vapor plume through, were measured by Shaw on October 6, 2004. Calculations for tram volume, cylinder volume, cylinder displacement volume, and a depiction of the cylinder with the charge inside are included in Appendix 2, Calculations. The emission measurements and various volume calculations are used to estimate a cylinder door emission factor as presented below. Photographs of the cylinders and loaded charges are included in Appendix 1 (pages A1-6 and -7).

The vapor flow pattern observed during sampling was complex as expected. Following the cylinder door opening, the approximately 150ºF internal wood/cylinder temperature caused the vapor inside the cylinder to be buoyant and provided the driving force for the vapor to rise. This vapor consists primarily of water vapor and to a lesser extent the PAHs associated with the creosote. The rising vapor exiting the top of the cylinder vessel was replaced with cooler (more dense) ambient outside air which flowed into the bottom of the vessel. That is, as the steam plume exited the cylinder, fresh replacement air flowed into the bottom of the cylinder to provide an equilibrium pressure in the open cylinder. This quasi-steady state flow pattern appeared to remain constant throughout the test. As mentioned previously, the vapor flow rate out of the cylinder must balance with the ambient air into the cylinder with the sample enclosure in place. This simulates the actual flow conditions and avoids dilution of sample with excess dilution air.

The vapor-condensation trace line evident on the inner surface of the enclosure just below the mid-line indicates that the vapor plume flow rate was at the desired balance point (see Appendix 1, Photograph 8, page A1-4). An increased sample flow from the cylinder would have moved the condensation line into the upper part of the enclosure and resulted in sample dilution. Reducing the sample flow rate would have resulted in a loss of vapor mass from the bottom half of the open cylinder door which was not enclosed. The concentration measurement would have been approximately correct; however, the sample flow rate would be too low and the resulting mass emission rate would be biased low.

SAMPLE ANALYSIS RESULTS

Analytical data generated from the analysis of the Tedlar™ bags for cylinder door openings and vacuum system sampling are included in Appendix 3. The initial background sample taken prior to the full cylinder sampling event between 0554 and 0604 AM resulted in a non-detect result for background naphthalene. The second background sample taken prior to the empty cylinder sampling event resulted in a concentration of 12.4 nanograms per milliliter (ng/mL) naphthalene. This measurement was just above the Method Detection Limit (MDL) of 6.56 ng/mL. The naphthalene concentrations measured from the sample duct ranged from 46.35 to 304.79 ng/mL. Since these concentrations were significantly greater than the measured background, no correction for background was made. This assumption yields a higher naphthalene emission factor since any correction for background concentration would reduce the net concentration number used to calculate the emission factor. For example, the sample duct concentration is always greater than sample duct concentration minus the background concentration.

FLOW RATE MEASUREMENT AND CALCULATION

Flow rates used in the emission factor calculation are based on USEPA Method 1 results. The measurements and calculations of these volumetric flow rates are provided in Appendix 2. Appendix 2a includes the calculation of velocity measurement traverse points based on the sample duct (pipe) dimensions. Appendix 2b includes the velocity, barometric pressure, and temperature measurements along with the volumetric flow rate calculations in dry standard cubic feet per minute (dscfm). Flow rate data is summarized in Appendix 2c. Velocity measurements were taken at the start and end of both the ful-treating cylinder and empty-treating cylinder sampling events for a total of four volumetric flow-rate calculations. For the full cylinder event, the volumetric flow rate was calculated to be 210 dry standard cubic feet per minute (dscfm) at the start of the sampling and 211 dscfm at the end. Flows calculated for the second, cylinder empty, sampling event were 234 dscfm at the start and 241 dscfm at the end, which reflects the greater gas content due to no wood being in the cylinder.

4 INTERPRETATION OF DATA

ALTERNATIVE EMISSION CALCULATION METHODS

Two alternative emission factor derivations are presented in this section. Both utilize the same data set described in the previous sections and both give very similar total emissions from the door openings. The first derivation assumes a linearization of the measured emission rate data as a function of time as shown in Figure 2. The linearization includes extrapolation to time zero for both the full cylinder with-wood and the empty cylinder without-wood cases. An arithmetic average of these emission rate data points was calculated. The second derivation utilizes the higher emission rate empty cylinder without-wood case data, and fits it to a first order exponential equation as shown in Figure 3. The first order relationship was selected since the emission rate should approximate a natural decay over time. As can be seen, the R squared value is greater than 0.90 indicating that the selected exponential decay equation fits the data points very well. The emission rate is then derived by integrating the concentration exponential equation as a function of time. In both derivations, the emissions estimated for the fresh charge of wood entering the cylinder, starting the next treating cycle, are added to provide a complete door opening cycle emission factor. These derivations are described in greater detail in the following sections.

LINEARIZED NAPHTHALENE EMISSION FACTOR

Results of the naphthalene emissions measurements from the empty cylinder and full cylinder cases and associated calculations are illustrated in Figure 2. Emissions are quantified in units of grams per minute (g/min) and are plotted as a function of time in minutes. Emission rate calculations which form the basis for Figure 2 are provided in Appendix 7. The emission rates are calculated by multiplying the air flow times the sample concentration as demonstrated on page A7-11. Both the empty cylinder and full cylinder curves demonstrate similar emission decay trends as a function of time. Time zero emissions are determined by extrapolation since placement of the emissions measurement device took a few minutes following the opening of the door. The empty cylinder line is extrapolated to 41 minutes to provide a time range consistent with the full cylinder event as shown on page A7-1.

The vacuum system sample, taken at the end of the empty cylinder case, yielded a naphthalene concentration of 154.39 ng/mL. This value appears reasonable compared to the range of measured concentrations from the other sampling events. As will be seen in the second derivation, this concentration value correlates very well with the concentration versus time equation for the without-wood case.

The naphthalene emission factor for the entire door opening cycle incorporates all of the data previously described. The supporting calculations for the following discussion are presented in Appendix 7. An overall average emission rate of 1.10 g/min was calculated from both sets of data as shown on pages A7-2 and A7-11. This rate multiplied by the total number of minutes the door is open yields the first part of the emission factor accounting for emissions from the cylinder, with or without wood.

The second component of the emission factor is derived from the measured vacuum vent naphthalene concentration and the calculation of the total displacement volume of the untreated wood and tram. The emissions are calculated to be 0.0044 g/cubic foot of displacement volume. Displacement volume was calculated to be 2,810 cubic feet and the total volume of the treating cylinder is 5,003 cubic feet which yields a displacement percentage of 56 percent as shown on page A7-3. The emission factor for this component is calculated to be 0.0025 g naphthalene per cubic foot of treating cylinder volume per year as shown on page A7-4.

Assuming that the displacement percentage is a reasonable approximation for most treating cylinders, then, a general emission factor can be derived as follows:

$$\text{Door Emissions} = \left[1.10T + \left[0.0025 * V\right]\ \right] * N = \frac{g}{year}\ \text{Naphthalene, or,} \frac{lb}{453.6\, g\ year}\ \text{Naphthalene}$$

Where: T = Total Door Opening Time (minutes);

V= Total Cylinder Volume (cubic feet); and

N = Number of charges per year.

An example calculation using this equation is provided on page A7-6. Based on a total door opening time of 30 minutes, cylinder volume of 5,003 cubic feet and 730 charges per year (approximately 2,000,000 cubic feet of treated wood per year), 73.2 pounds or 0.04 ton of naphthalene would be emitted as a result of the door opening cycle per year.

EXPONENTIAL NAPHTHALENE EMISSION FACTOR

The actual mathematical relationship expected for the decay of PAH concentrations emitted from the door openings is expected to be an exponential decay, although this analysis requires a greater degree of mathematical derivation. Results of the naphthalene emissions measurements from the full cylinder with-wood case are illustrated in Figure 3 along with an exponential curve fit for the initial period. The final period of the measurement was fit using a linear equation. Emissions are quantified in units of concentration as a function of time (nanograms per milliliter). The concentration measured as a function of time is proportional to the emission rate as a function of time since the volumetric flow rate through the sampling train was maintained approximately constant throughout the test. The curve fit includes the final vent sample concentration at approximately 45 minutes which demonstrates that the naphthalene concentration decay measured at the door opening is consistent with the interior cylinder concentration.

Derivation of Emission Factor

The derivation for the emission factor is provided on pages A7-7 through A7-9, and results in the equation to calculate emissions from the open door:

$$\frac{grams\ Naphthalene}{charge} = \left(53.53 + \frac{0.255}{t} * \frac{V_v}{V_c} * V_w\right) * \left(1 - e^{-0.1307 * \frac{t}{3}}\right)$$

where: t = total door opening time, minutes;

V_v = void volume in the cylinder, ft^3;

V_c = cylinder volume, ft^3 and,

V_w = wood volume, ft^3.

An example calculation using this equation is provided on page A7-10. Based on a total door opening time of 30 minutes, cylinder volume of 5,000 cubic feet, wood volume of 3,500 cubic feet and 730 charges per year (approximately 2,555,000 cubic feet of treated wood per year), 73.4 pounds or 0.037 ton of naphthalene would be emitted as a result of the door opening cycle per year.

APPENDIX 1

PHOTOGRAPHS

1. Cylinder door emissions capture structure.

2. Cylinder door emissions capture structure.

3. Placing cylinder door enclosure.

4. Placing cylinder door enclosure.

5. Sample collection from cylinder door opening.

6. Setting the cylinder door enclosure.

7. Placing cylinder door enclosure.

8. Vapor line on inside of enclosure.

9. Sample collection from cylinder door opening.

10. Sample collection device.

11. Example of emissions from cylinder with door open and a full charge.

12. Example of pulling a treated charge from cylinder.

13. Example of emissions from empty cylinder.

14. Example tram configuration.

15. Vacuum pump sample location.

16. Analytical trailer lab.

17. Analytical trailer lab.

APPENDIX 2

CALCULATIONS

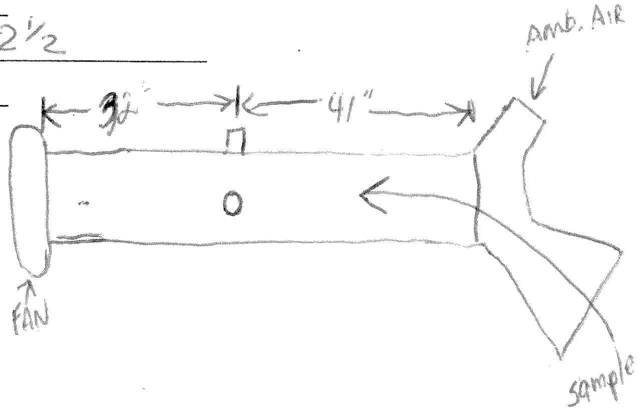
2a. Calculation of Traverse Point
2b. USEPA Method 1 Flow Rate Data
2c. Flow Rate Data

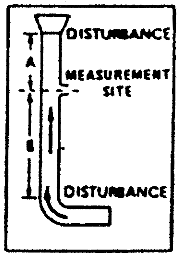
Appendix 2a.
Calculation of Traverse Point

Shaw™ The Shaw Group Inc.

TRAVERSE POINT LOCATION FOR CIRCULAR DUCTS

Plant: Koppers
Date: 10-5-04
Sampling location: Retort Door
Inside of far wall to outside of nipple: 8½
Inside of near wall to outside of nipple (nipple length): 2½
Stack inside diameter (i.d.) , inches: 6
Distance downstream from flow disturbance (Distance B):
41 inches/equivalent diameter = 6.8 dd
Distance upstream from flow disturbance (Distance A):
32 inches/equivalent diameter = 5.3 dd
Calculated by: J. Neese





SCHEMATIC OF SAMPLING LOCATION

Traverse Point No.	Fraction of Stack i.d.	Stack i.d.	Product of Columns 2 & 3 (to nearest ⅛ in.)*	Nipple Length (in.)	Traverse Point Location From Outside of Nipple (Sum of Columns 4 & 5)
1	.067	6	.40 (½)	2½	3
2	.250	↓	1½	↓	4
3	.750		4½		7
4	.933		5⅝ (5½)		8

* The first and last points must be no closer than 1 in. from the stack wall for stack diameters >24 in. or no closer than 0.5 in. from the stack wall for stack diameters ≤24 in.

Appendix 2b.
USEPA Method 1 Flow Rate Data

validated 11/1/90

Shaw™

Shaw E & I, Inc.

VELOCITY DETERMINATION

PLANT :	Koppers
SAMPLE LOCATION :	Retort Door
RUN NUMBER :	KRD-V-1

DATE :	10/6/2004	**BAROMETRIC PRES., in. Hg :**	30
TIME(24-HR) :	731	**STATIC PRES., in. H2O :**	-0.24
OPERATOR(S) :	LB/JN		
PERCENT MOISTURE :	2.9	**PITOT TUBE, Cp :**	0.84
STACK AREA, SQ. IN. :	28.30	**PERCENT CO2 :**	0.0
NO. OF TRAVERSE PTS. :	8	**PERCENT O2 :**	21.0

TRAVERSE PT. NO.	VELOCITY HEAD, in. H2O	STACK TEMP., deg. F
1	0.120	109
2	0.107	109
3	0.115	110
4	0.125	110
5	0.088	110
6	0.103	112
7	0.120	112
8	0.138	113
	0.115	**111**

VELOCITY DETERMINATION

Shaw E & I, Inc.

PLANT :	Koppers
SAMPLE LOCATION :	Retort Door
RUN NUMBER :	KRD-V-2

DATE :	10/6/2004	**BAROMETRIC PRES., in. Hg :**	30
TIME(24-HR) :		**STATIC PRES., in. H2O :**	-0.24
OPERATOR(S) :	LB/JN		
PERCENT MOISTURE :	6.4	**PITOT TUBE, Cp :**	0.84
STACK AREA, SQ. IN. :	28.30	**PERCENT CO2 :**	0.0
NO. OF TRAVERSE PTS. :	8	**PERCENT O2 :**	21.0

TRAVERSE PT. NO.	VELOCITY HEAD, in. H2O	STACK TEMP., deg. F
1	0.120	108
2	0.120	108
3	0.110	111
4	0.130	113
5	0.100	113
6	0.120	109
7	0.130	115
8	0.150	116
	0.123	**112**

Shaw™
Shaw E & I, Inc.

validated 11/1/90

VELOCITY DETERMINATION

PLANT : Koppers
SAMPLE LOCATION : Retort Door

Run No:	KRD-V-1	KRD-V-2	AVERAGE
STACK PRESSURE, in Hg :	29.98	29.98	**29.98**
STACK TEMP., deg. F :	111	112	**111**
MOLECULAR WEIGHT, DRY :	28.84	28.84	**28.84**
MOLECULAR WEIGHT, STACK :	28.52	28.15	**28.52**
AVG. SQRT. VELOCITY HEAD :	0.34	0.35	**0.34**
VELOCITY, fps :	19.81	20.65	**19.81**
ACTUAL CUBIC FEET/ MINUTE :	234	244	**234**
DRY STANDARD CUBIC FEET/ MINUTE :	210	211	**210**

AVERAGE FLOW RATE RUN#1 TO RUN#2:	211 dscfm
AVERAGE FLOW RATE RUN#2 TO RUN#3:	211 dscfm

validated 11/1/90

VELOCITY DETERMINATION

Shaw E & I, Inc.

PLANT :	Koppers
SAMPLE LOCATION :	Retort Door
RUN NUMBER :	5-10 Minute

DATE :	10/6/2004	**BAROMETRIC PRES., in. Hg :**	29.98
TIME(24-HR) :		**STATIC PRES., in. H2O :**	-0.23
OPERATOR(S) :	LB/JN		
PERCENT MOISTURE :	3.1	**PITOT TUBE, Cp :**	0.84
STACK AREA, SQ. IN. :	28.30	**PERCENT CO2 :**	0.0
NO. OF TRAVERSE PTS. :	8	**PERCENT O2 :**	21.0

TRAVERSE PT. NO.	**VELOCITY HEAD, in. H2O**	**STACK TEMP., deg. F**
1	0.140	111
2	0.130	114
3	0.150	115
4	0.160	116
5	0.130	110
6	0.130	111
7	0.150	114
8	0.150	115
	0.143	**113**

validated 11/1/90

Shaw™
Shaw E & I, Inc.

VELOCITY DETERMINATION

PLANT : Koppers
SAMPLE LOCATION : Retort Door
RUN NUMBER : 10-20 Minute

DATE :	10/6/2004	**BAROMETRIC PRES., in. Hg :**	29.98
TIME(24-HR) :		**STATIC PRES., in. H2O :**	-0.218
OPERATOR(S) :	LB/JN		
PERCENT MOISTURE :	1.9	**PITOT TUBE, Cp :**	0.84
STACK AREA, SQ. IN. :	28.30	**PERCENT CO2 :**	0.0
NO. OF TRAVERSE PTS. :	8	**PERCENT O2 :**	21.0

TRAVERSE PT. NO.	VELOCITY HEAD, in. H2O	STACK TEMP., deg. F
1	0.134	84
2	0.142	92
3	0.142	99
4	0.159	105
5	0.134	103
6	0.134	108
7	0.150	111
8	0.167	114
	0.145	**102**

Shaw E & I, Inc.

validated 11/1/90

VELOCITY DETERMINATION

PLANT : Koppers
SAMPLE LOCATION : Retort Door

Run No:	5-10 Minute	10-20 Minute	AVERAGE
STACK PRESSURE, in Hg :	29.96	29.96	**29.96**
STACK TEMP., deg. F :	113	102	**113**
MOLECULAR WEIGHT, DRY :	28.84	28.84	**28.84**
MOLECULAR WEIGHT, STACK :	28.50	28.63	**28.50**
AVG. SQRT. VELOCITY HEAD :	0.38	0.38	**0.38**
VELOCITY, fps :	22.19	22.13	**22.19**
ACTUAL CUBIC FEET/ MINUTE :	262	261	**262**
DRY STANDARD CUBIC FEET/ MINUTE :	234	241	**234**

AVERAGE FLOW RATE RUN#1 TO RUN#2: 237 dscfm

AVERAGE FLOW RATE RUN#2 TO RUN#3: 241 dscfm

Appendix 2c.
Flow Rate Data

KOPPERS FIELD TEST
CYLINDER DOOR - FLOW RATE DATA

NAPHTHALENE

Scenario A: Tram Inside of Retort Background Air Concentration

Date	Time	Measured NAPH Conc ng/mL
10/5/2004	0554-0604	0.00

Scenario A: Tram Inside of Retort

Date	Time	Time (min from door opening (t=0)) start	end	Volumetric Flow Rate cfm	Volumetric Flow Rate scfm	Measured NAPH Conc ng/mL
10/6/2004	0731-0736	6	11	234	210	129.07
10/6/2004	0736-0746	11	21	234	210	48.43
10/6/2004	0746-0756	21	31	244	211	51.01
10/6/2004	0756-0806	31	41	244	211	46.35

MDL =6.56 ng/mL

Scenario B: Empty Retort Background Air Concentration

Date	Time min	Time min	Measured NAPH Conc ng/mL
10/6/2004	1323-1333	NA	0.00

Scenario B: Empty Retort

Date	Time min	Time (min from door opening (t=0)) start	end	Volumetric Flow Rate cfm	Volumetric Flow Rate scfm	Measured NAPH Conc ng/mL
10/6/2004	1339-1344	1	6	262	234	143.09
10/6/2004	1344-1349	6	11	262	234	304.79
10/6/2004	1349-1359	11	21	261	241	237.19
10/6/2004	1359-1409	21	31	261	241	188.90

KOPPERS FIELD TEST
FLOW SUMMARY

Test	Flow	
	acfm	**dscfm**
Cylinder Door Full Tram		
0-5 min	234	210
25-35 min	244	211
Cylinder Door Empty		
0-5 min	262	234
25-35 min	261	241

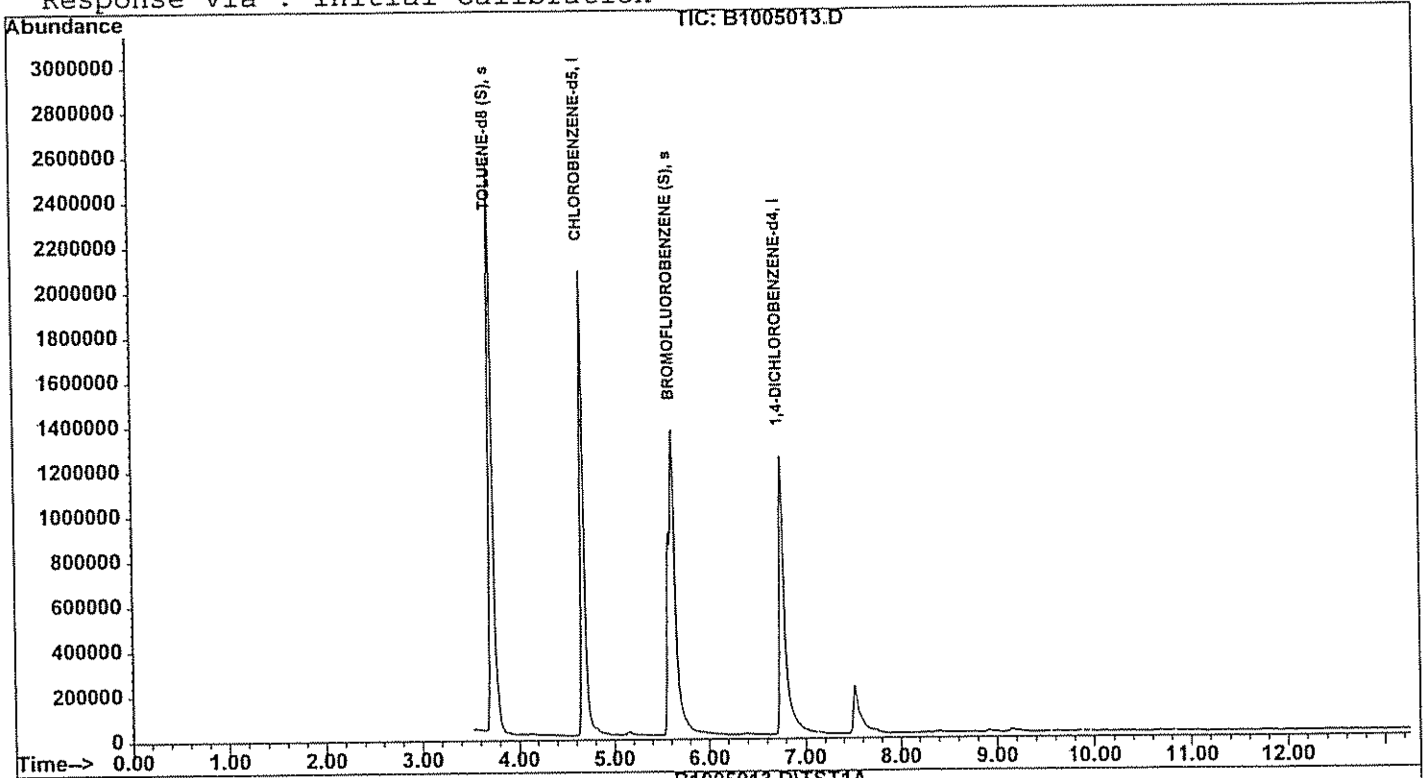
APPENDIX 3

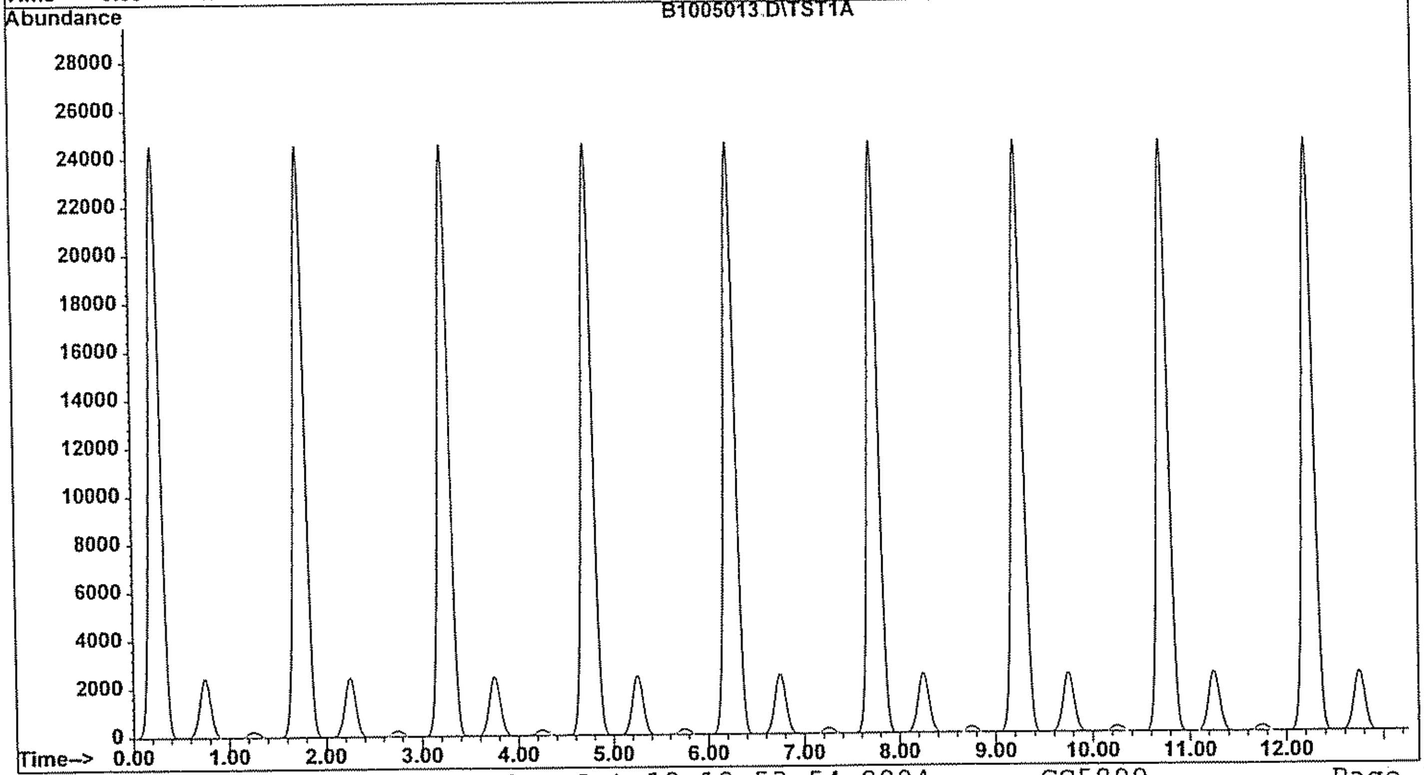
LABORATORY DATA

```
                         Quantitation Report    (QT Reviewed)

Data File : C:\HPCHEM\1\DATA\B100504\B1005013.D            Vial: 3
Acq On    :  5 Oct 2004   6:57 pm                       Operator:
Sample    : Background retort  AB104                    Inst     : GC/MS Ins
Misc      : 10ml from 10L bag                           Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 16:31 19104               Quant Results File: KOPPERS.RES

Quant Method : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
Title        : 8260 Volatiles
Last Update  : Mon Oct 04 13:13:05 2004
Response via : Initial Calibration
DataAcq Meth : KOPPERS

Internal Standards                   R.T. QIon  Response  Conc Units Dev(Min)
-----------------------------------------------------------------------------
  1) CHLOROBENZENE-d5                4.69  117 16686992    50.00 ppb    -0.06
  3) 1,4-DICHLOROBENZENE-d4          6.77  150 10275279    50.00 ppb    -0.06

System Monitoring Compounds
  2) TOLUENE-d8 (S)                  3.73   98 22577971    49.54 ppb    -0.06
  Spiked Amount      50.000   Range  75 - 125    Recovery    =   99.08%
  4) BROMOFLUOROBENZENE (S)          5.63   95  8462818    51.78 ppb    -0.08
  Spiked Amount      50.000   Range  75 - 125    Recovery    =  103.56%

Target Compounds                                                   Qvalue
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100504\B1005013.D          Vial: 3
Acq On    :  5 Oct 2004   6:57 pm                      Operator:
Sample    : Background retort  AB104                   Inst     : GC/MS Ins
Misc      : 10ml from 10L bag                          Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 16:31 19104                Quant Results File: KOPPERS.RES

Method         : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
Title          : 8260 Volatiles
Last Update    : Fri Oct 08 18:37:49 2004
Response via   : Initial Calibration
```

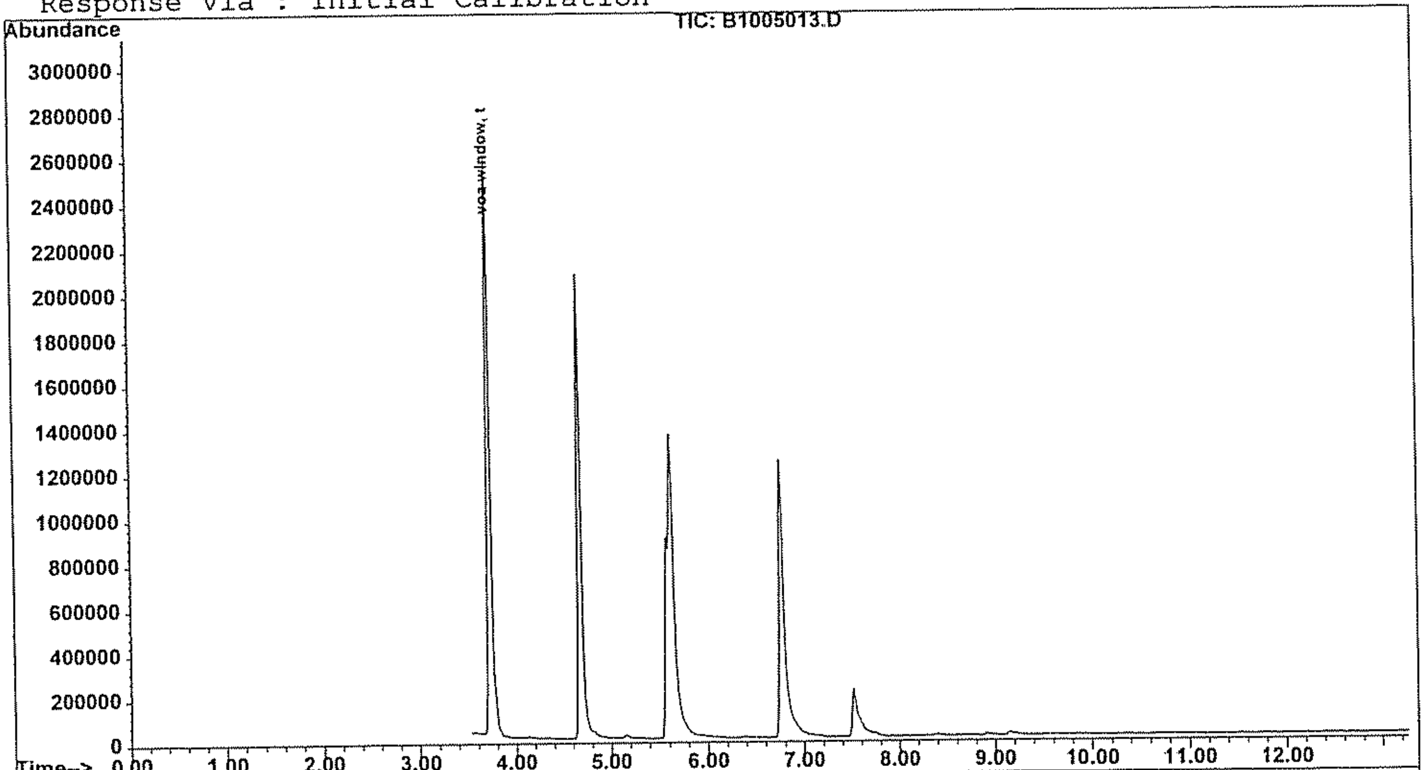


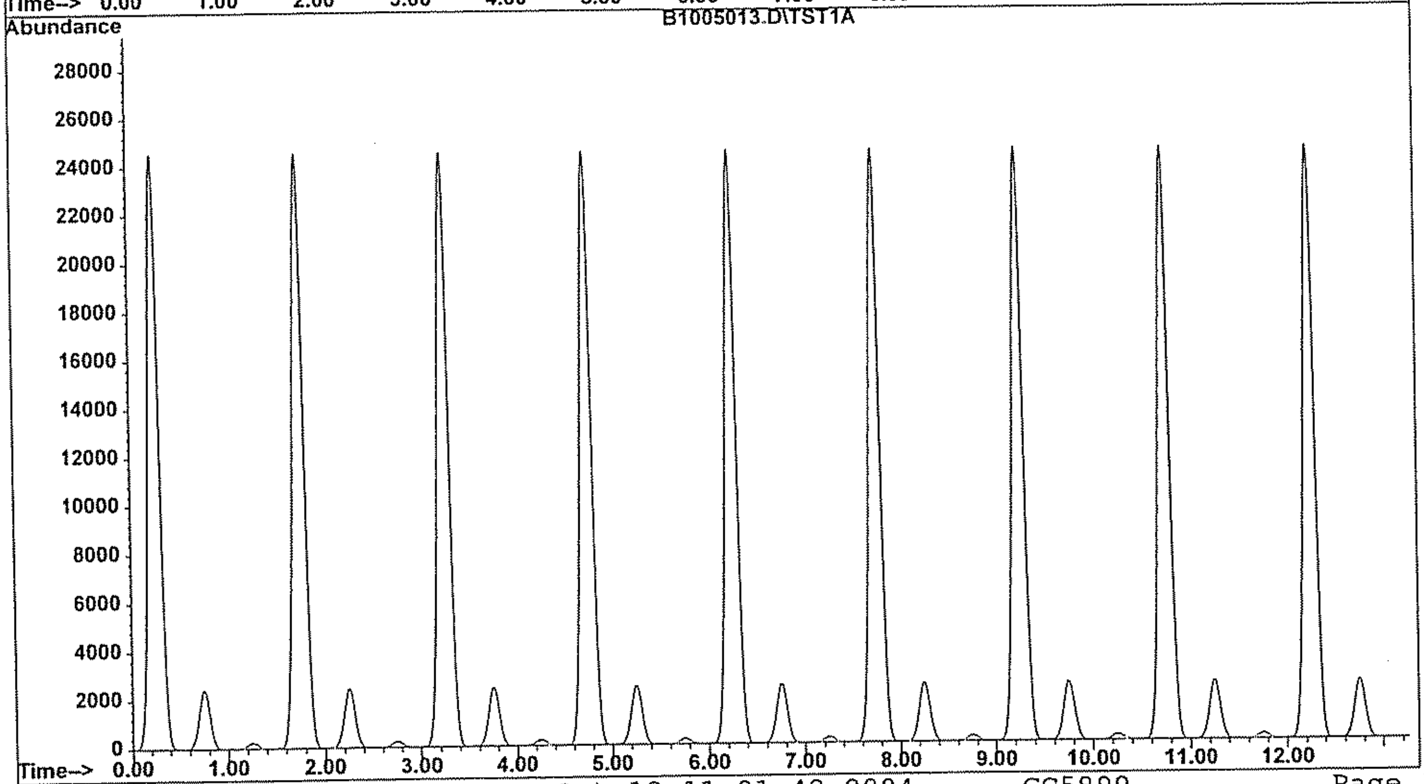


```
                          Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100504\B1005013.D         Vial: 3
  Acq On    :  5 Oct 2004   6:57 pm                    Operator:
  Sample    : Background retort  AB104                 Inst     : GC/MS Ins
  Misc      : 10ml from 10L bag                        Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 16:32 19104              Quant Results File: WINDOW.RES

  Quant Method : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
  Title        : koppers volatile window
  Last Update  : Wed Oct 06 18:41:15 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS

Internal Standards                   R.T. QIon  Response  Conc Units Dev(Min)
-----------------------------------------------------------------------------

System Monitoring Compounds

Target Compounds                                                    Qvalue
  1) voa window                      3.73  TIC 258680082m   10.17 ng on

-----------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100504\B1005013.D          Vial: 3
Acq On    :  5 Oct 2004   6:57 pm                     Operator:
Sample    : Background retort  AB104                  Inst     : GC/MS Ins
Misc      : 10ml from 10L bag                         Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 16:32 19104            Quant Results File: WINDOW.RES

Method        : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
Title         : koppers volatile window
Last Update   : Fri Oct 08 18:40:27 2004
Response via  : Initial Calibration
```

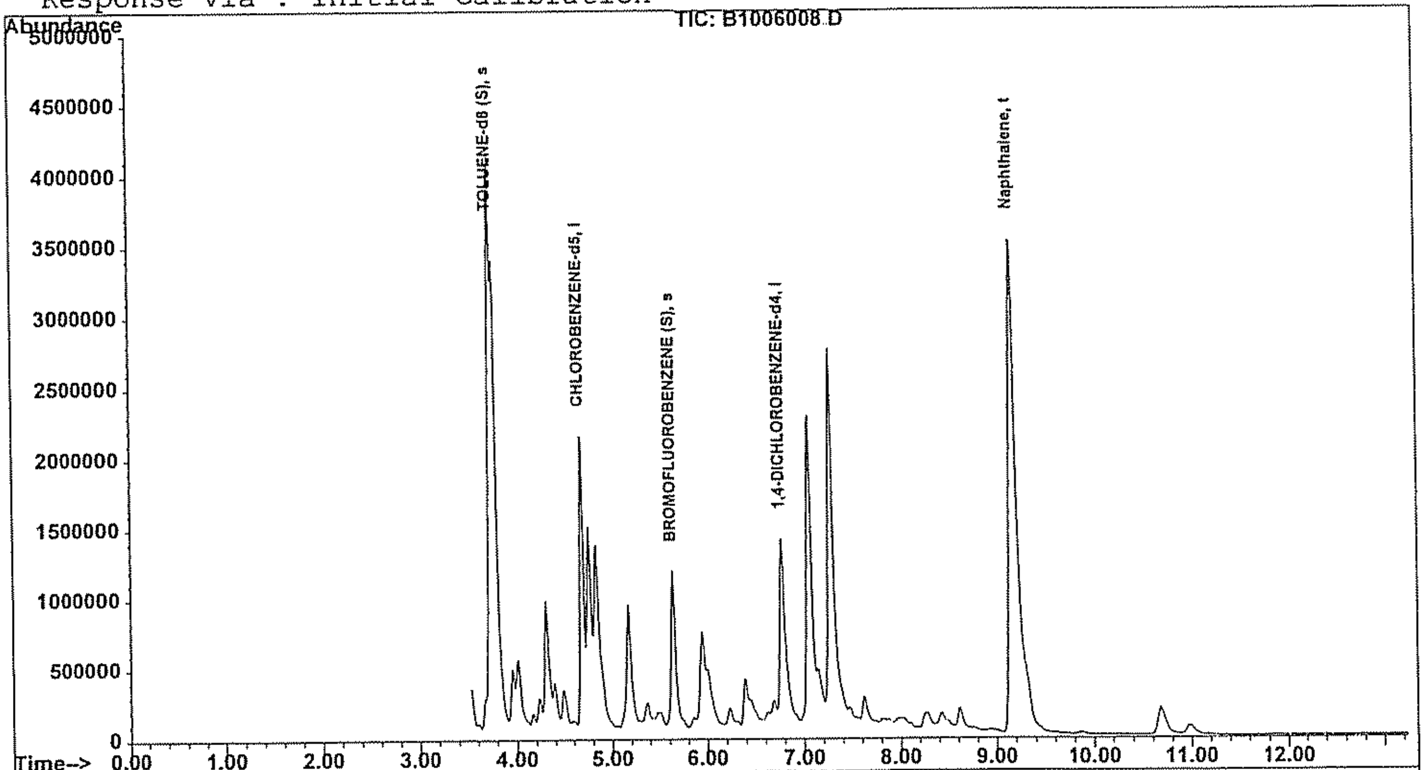


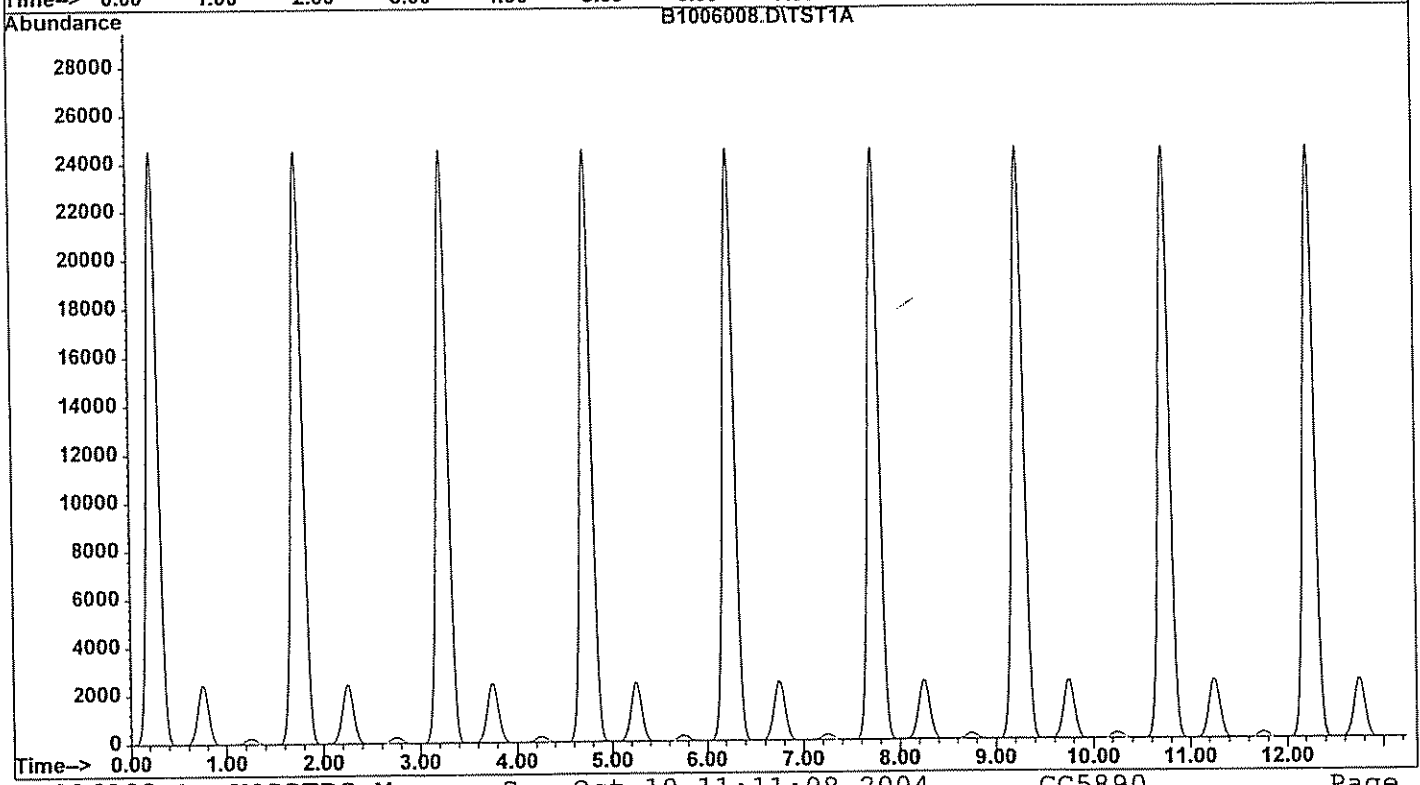


```
                         Quantitation Report    (QT Reviewed)

 Data File : C:\HPCHEM\1\DATA\B100604\B1006008.D          Vial: 1
 Acq On    :  6 Oct 2004  10:29 am                    Operator:
 Sample    : Retort door full tram 0-5min  AB105      Inst     : GC/MS Ins
 Misc      : 10ml/10L   Koppers,  Guthrie,KY          Multiplr: 1.00
 Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
 Quant Time: Oct  6 10:42 19104                Quant Results File: KOPPERS.RES

 Quant Method : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
 Title        : 8260 Volatiles
 Last Update  : Mon Oct 04 13:13:05 2004
 Response via : Initial Calibration
 DataAcq Meth : KOPPERS

Internal Standards                     R.T. QIon  Response  Conc Units Dev(Min)
-------------------------------------------------------------------------------
  1) CHLOROBENZENE-d5                  4.70  117 17782547    50.00 ppb    -0.05
  3) 1,4-DICHLOROBENZENE-d4            6.78  150 11563539    50.00 ppb    -0.05

System Monitoring Compounds
  2) TOLUENE-d8 (S)                    3.74   98 22292374    45.90 ppb    -0.05
  Spiked Amount      50.000   Range  75 - 125    Recovery   =    91.80%
  4) BROMOFLUOROBENZENE (S)            5.64   95  8336354    45.33 ppb    -0.07
  Spiked Amount      50.000   Range  75 - 125    Recovery   =    90.66%

Target Compounds                                                     Qvalue
  5) Naphthalene                       9.17  128 88371046   258.14 ppb      100
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006008.D          Vial: 1
Acq On    :  6 Oct 2004  10:29 am                       Operator:
Sample    : Retort door full tram 0-5min  AB105         Inst     : GC/MS Ins
Misc      : 10ml/10L   Koppers,  Guthrie,KY             Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  6 10:42 19104              Quant Results File: KOPPERS.RES

Method         : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
Title          : 8260 Volatiles
Last Update    : Fri Oct 08 18:37:49 2004
Response via   : Initial Calibration
```

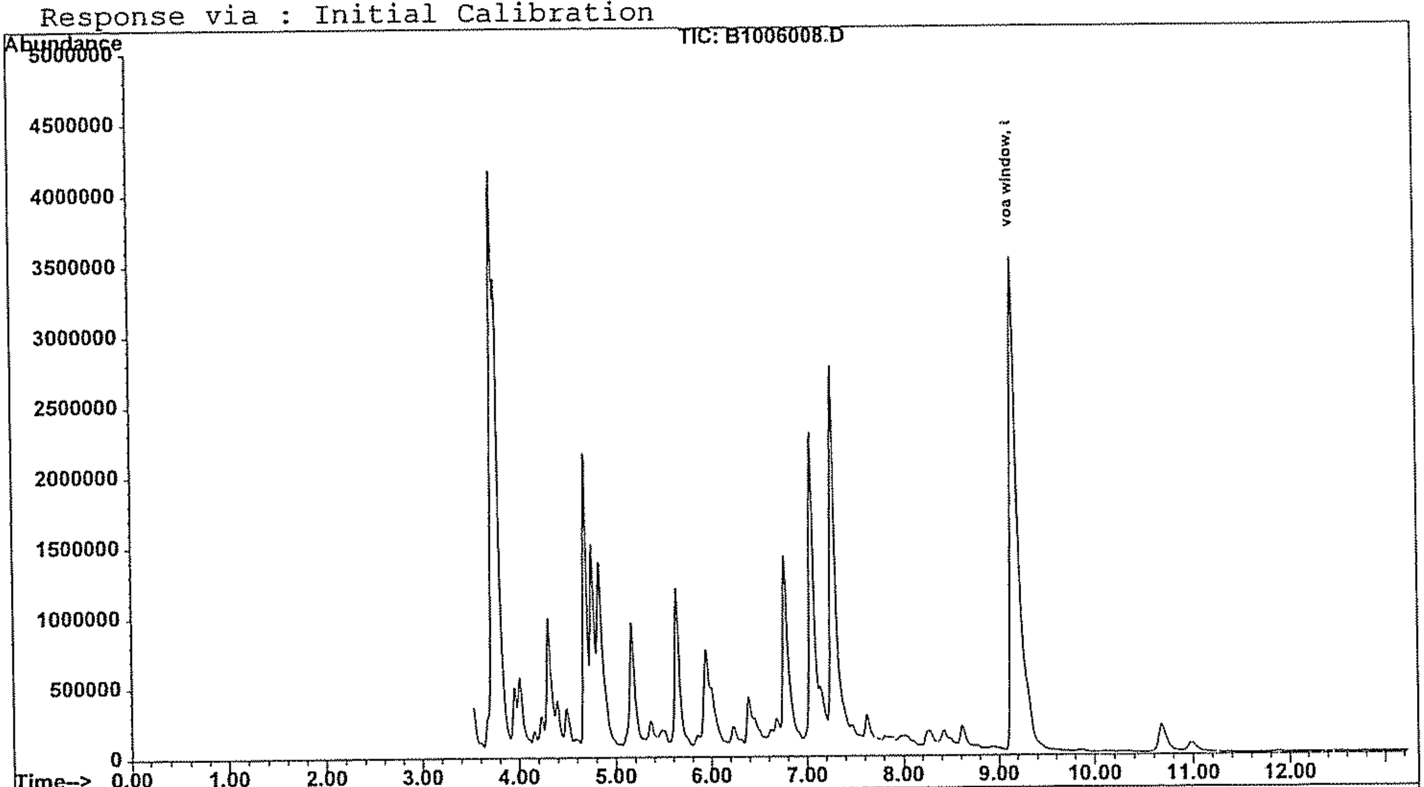


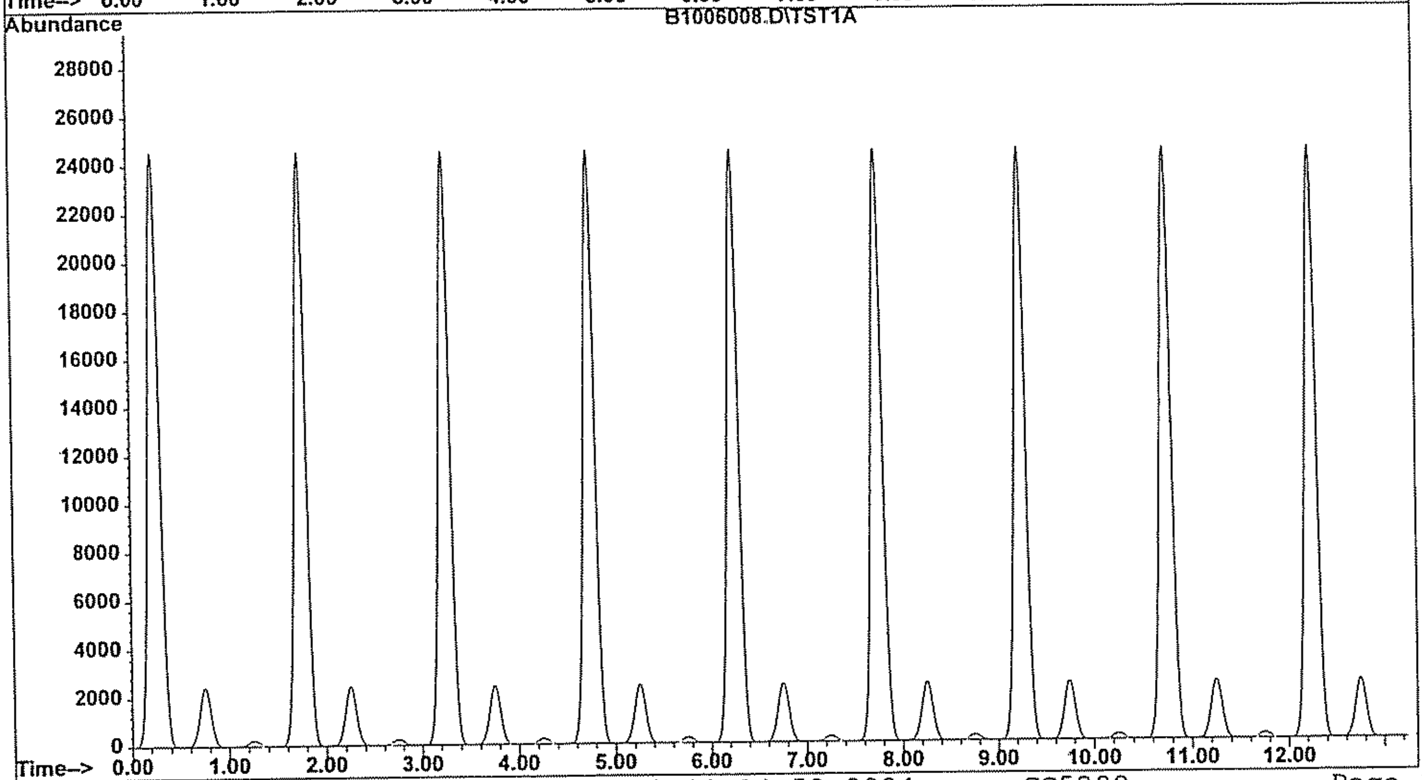


```
                         Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006008.D        Vial: 1
  Acq On    :  6 Oct 2004  10:29 am                   Operator:
  Sample    : Retort door full tram 0-5min  AB105     Inst     : GC/MS Ins
  Misc      : 10ml/10L   Koppers,  Guthrie,KY         Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7  7:50 19104               Quant Results File: WINDOW.RES

  Quant Method : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
  Title        : koppers volatile window
  Last Update  : Wed Oct 06 18:41:15 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS

Internal Standards                R.T. QIon  Response  Conc Units Dev(Min)
--------------------------------------------------------------------------

System Monitoring Compounds

                                                                 Qvalue
Target Compounds
  1) voa window                   9.17  TIC 751941577m   31.36 ng on

--------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006008.D        Vial: 1
Acq On    :  6 Oct 2004  10:29 am                   Operator:
Sample    : Retort door full tram 0-5min  AB105     Inst     : GC/MS Ins
Misc      : 10ml/10L   Koppers,  Guthrie,KY         Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7  7:50 19104               Quant Results File: WINDOW.RES

Method        : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
Title         : koppers volatile window
Last Update   : Fri Oct 08 18:40:27 2004
Response via  : Initial Calibration
```

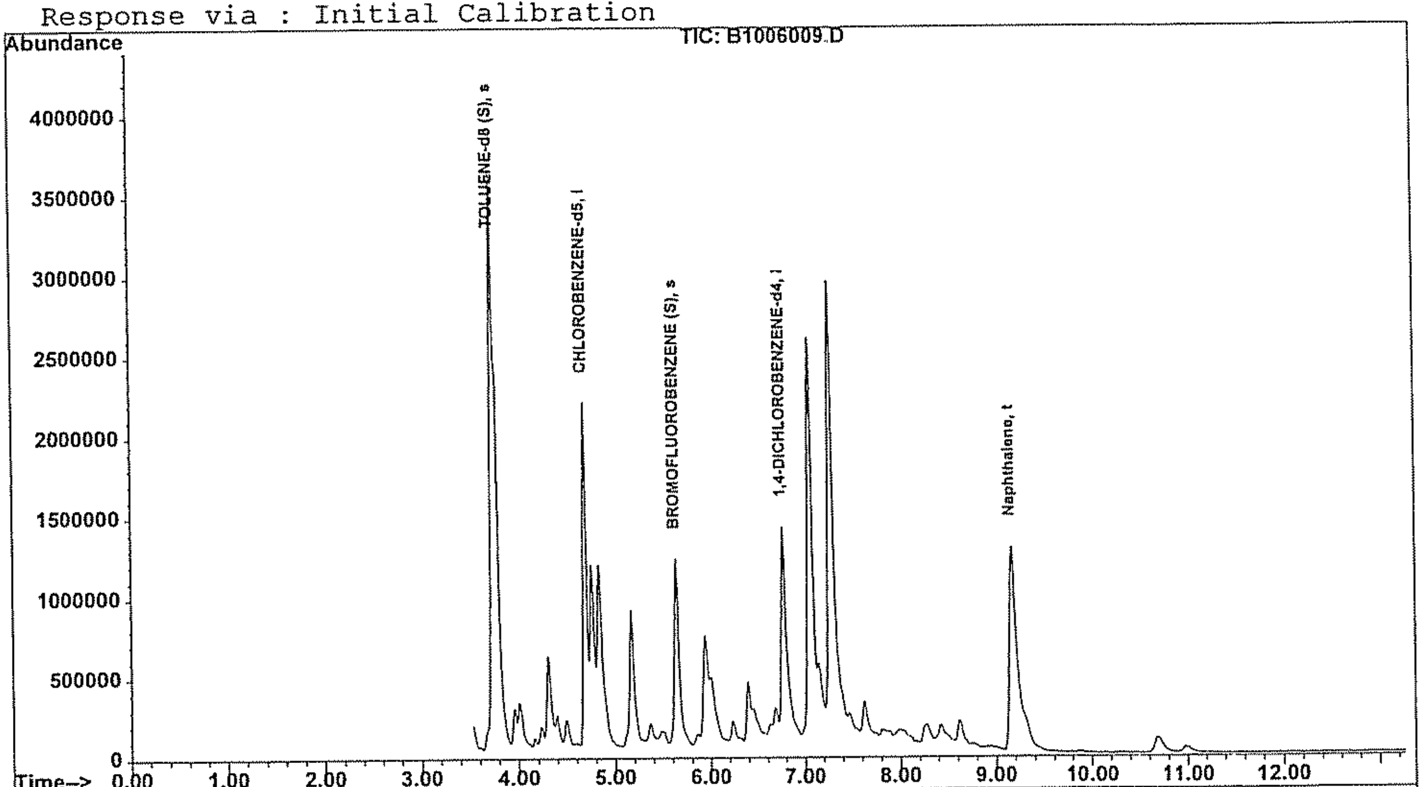


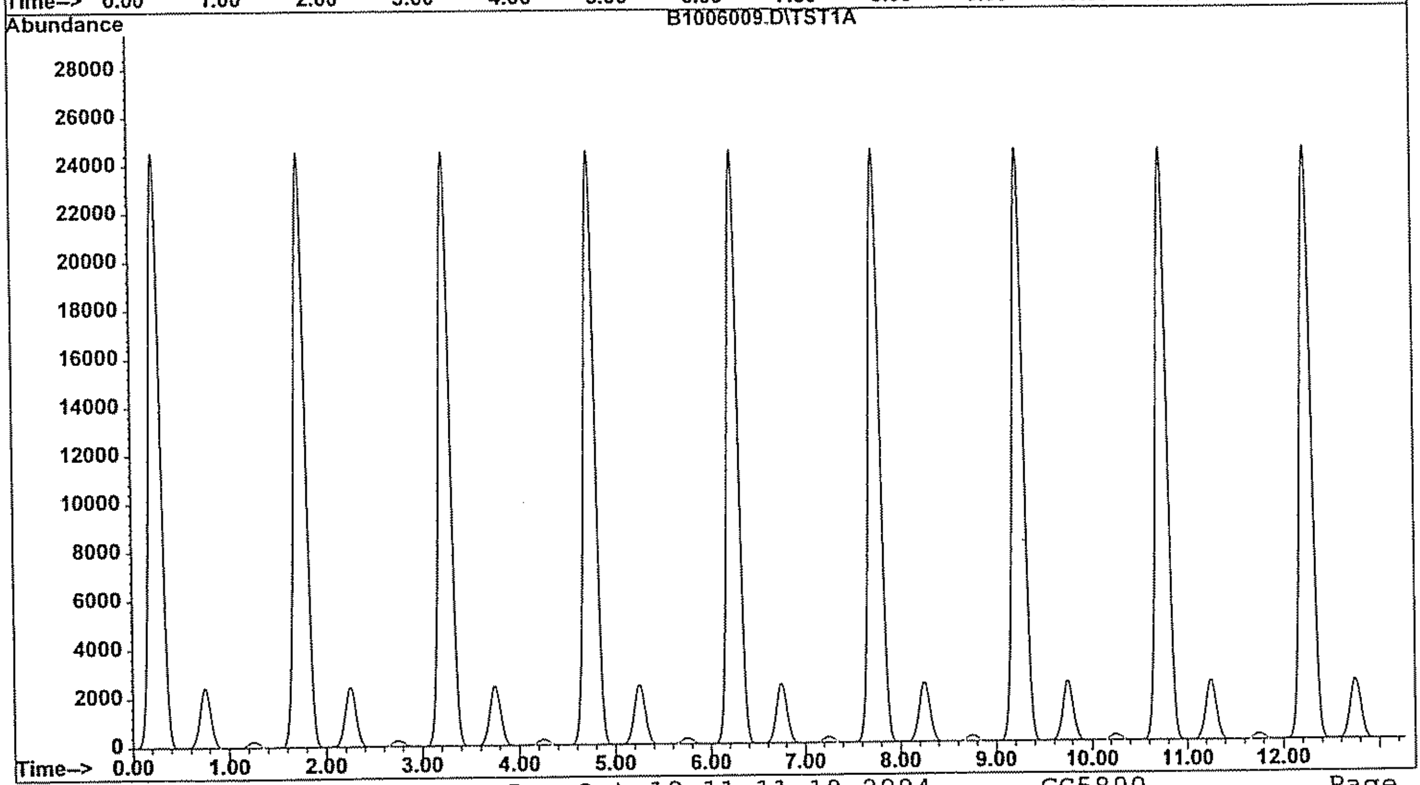


```
                           Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006009.D          Vial: 2
  Acq On    :  6 Oct 2004  10:58 am                     Operator:
  Sample    : Retort door full tram 5-15min  AB106      Inst    : GC/MS Ins
  Misc      : 10ml/10L   Koppers,  Guthrie,KY           Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  6 11:11 19104                 Quant Results File: KOPPERS.RES

  Quant Method : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
  Title        : 8260 Volatiles
  Last Update  : Mon Oct 04 13:13:05 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS

Internal Standards                    R.T. QIon  Response  Conc Units Dev(Min)
-----------------------------------------------------------------------------
  1) CHLOROBENZENE-d5                 4.70  117 17820007    50.00 ppb    -0.05
  3) 1,4-DICHLOROBENZENE-d4           6.78  150 11412148    50.00 ppb    -0.05

System Monitoring Compounds
  2) TOLUENE-d8 (S)                   3.74   98 23654844    48.60 ppb    -0.05
  Spiked Amount     50.000   Range  75 - 125    Recovery   =   97.20%
  4) BROMOFLUOROBENZENE (S)           5.65   95  8904070    49.06 ppb    -0.06
  Spiked Amount     50.000   Range  75 - 125    Recovery   =   98.12%

Target Compounds                                                       Qvalue
  5) Naphthalene                      9.18  128 32721268    96.85 ppb      100
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006009.D          Vial: 2
Acq On    :  6 Oct 2004  10:58 am                      Operator:
Sample    : Retort door full tram 5-15min  AB106       Inst     : GC/MS Ins
Misc      : 10ml/10L   Koppers,  Guthrie,KY            Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  6 11:11 19104               Quant Results File: KOPPERS.RES

Method         : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
Title          : 8260 Volatiles
Last Update    : Fri Oct 08 18:37:49 2004
Response via   : Initial Calibration
```

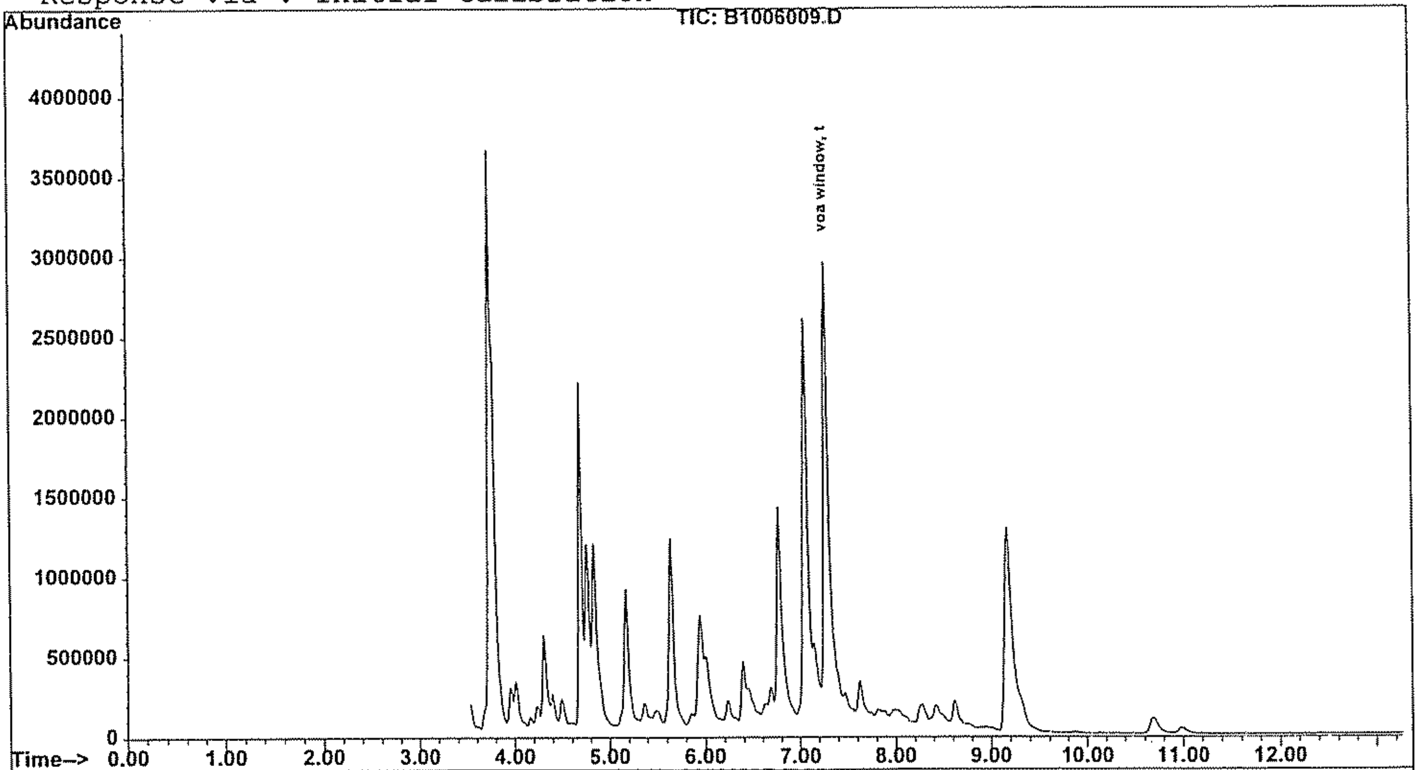


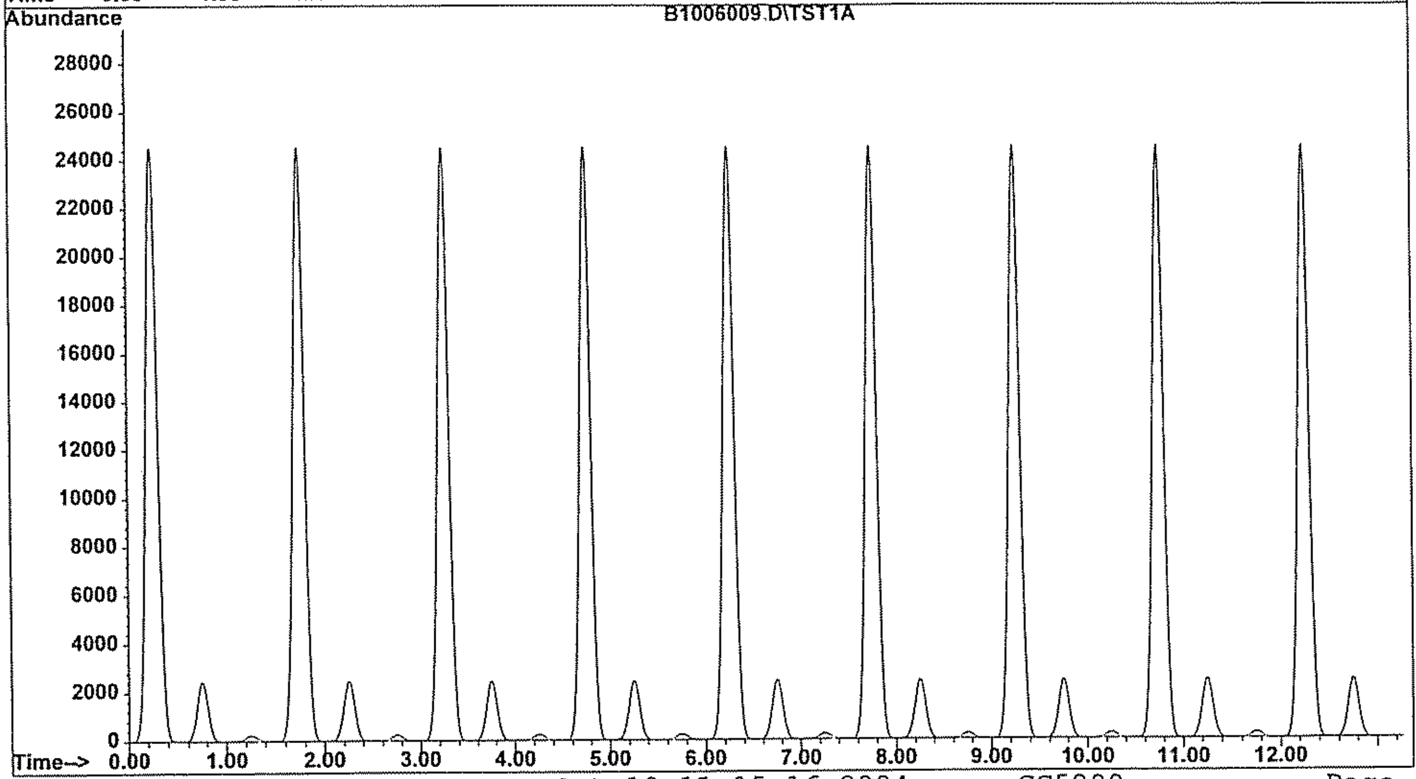


```
                         Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006009.D          Vial: 2
  Acq On    :  6 Oct 2004  10:58 am                     Operator:
  Sample    : Retort door full tram 5-15min  AB106      Inst     : GC/MS Ins
  Misc      : 10ml/10L   Koppers,  Guthrie,KY           Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7  7:51 19104               Quant Results File: WINDOW.RES

  Quant Method : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
  Title        : koppers volatile window
  Last Update  : Wed Oct 06 18:41:15 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS

Internal Standards                 R.T. QIon  Response  Conc Units Dev(Min)
---------------------------------------------------------------------------

System Monitoring Compounds

Target Compounds                                                  Qvalue
  1) voa window                     7.28  TIC 725023640m   29.95 ng on




 ---------------------------------------------------------------------------
 (#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006009.D        Vial: 2
Acq On    :  6 Oct 2004  10:58 am                     Operator:
Sample    : Retort door full tram 5-15min  AB106      Inst     : GC/MS Ins
Misc      : 10ml/10L   Koppers,  Guthrie,KY           Multiplr: 1.00
Integration Parameters - MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7  7:51 19104             Quant Results File: WINDOW.RES

Method          : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
Title           : koppers volatile window
Last Update     : Fri Oct 08 18:40:27 2004
Response via    : Initial Calibration
```



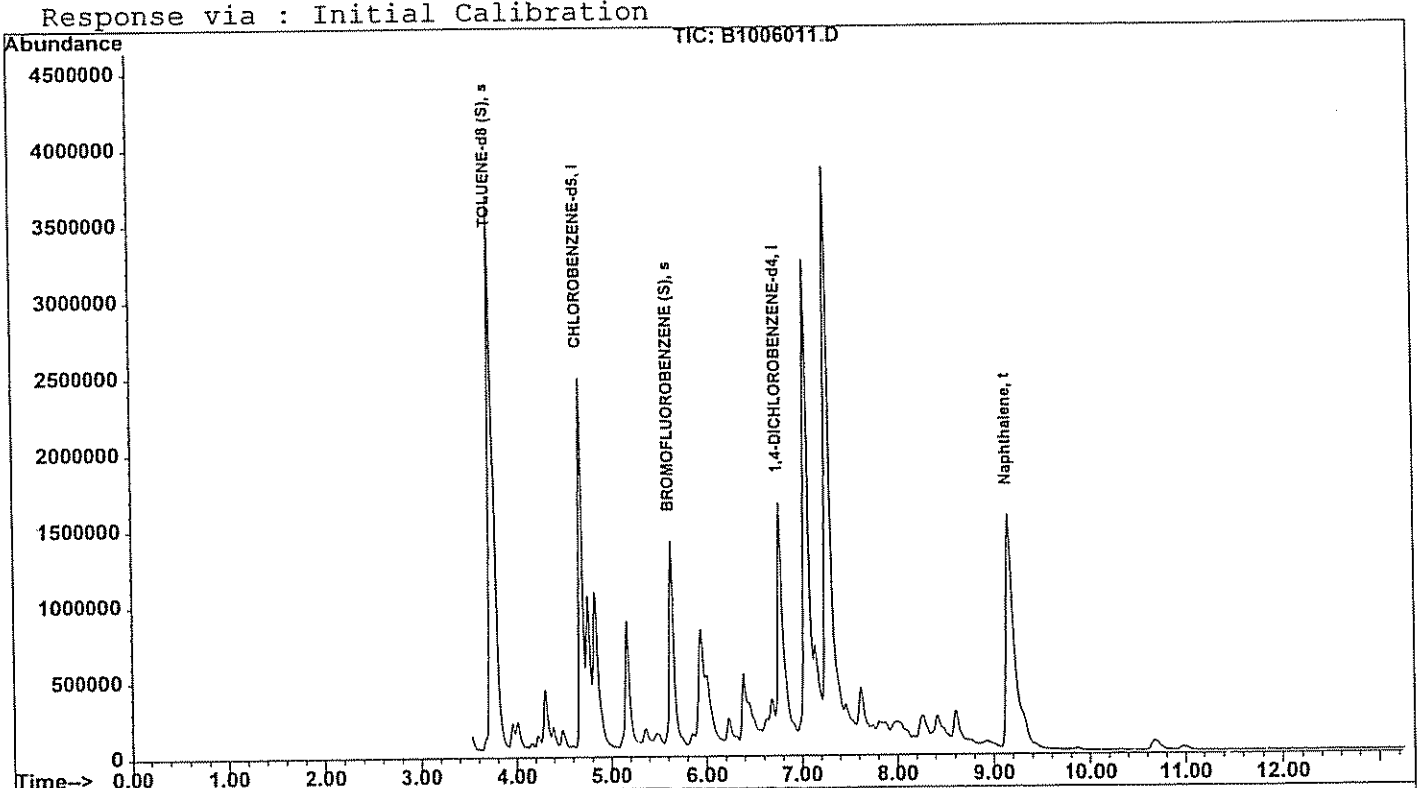


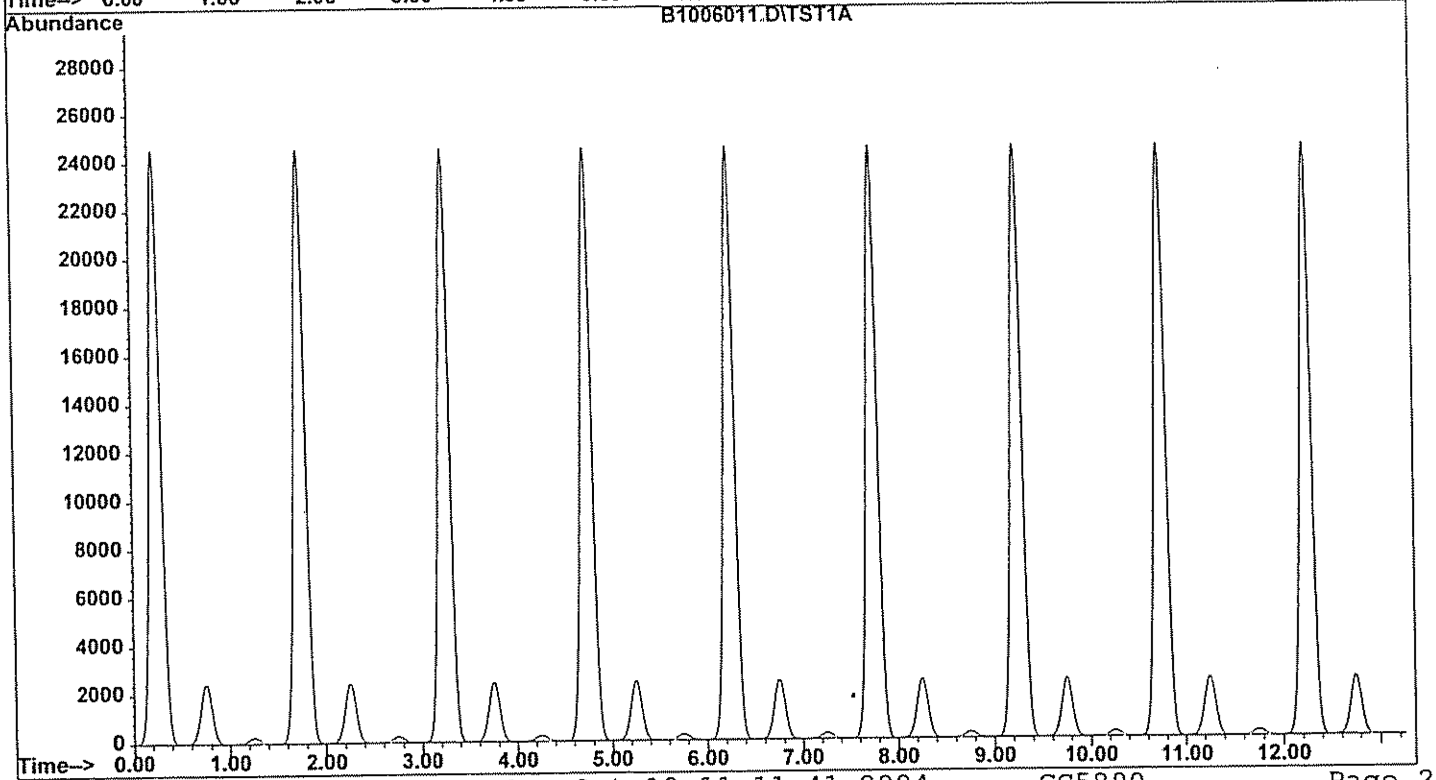
```
                          Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006011.D           Vial: 4
  Acq On    :  6 Oct 2004  11:56 am                      Operator:
  Sample    : Retort door full tram 15-25min  AB107      Inst     : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY             Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  6 12:10 19104                 Quant Results File: KOPPERS.RES

  Quant Method : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
  Title        : 8260 Volatiles
  Last Update  : Mon Oct 04 13:13:05 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS


Internal Standards                     R.T. QIon  Response  Conc Units Dev(Min)
-----------------------------------------------------------------------------
  1) CHLOROBENZENE-d5                  4.70  117 19842608    50.00 ppb    -0.05
  3) 1,4-DICHLOROBENZENE-d4            6.78  150 12575693    50.00 ppb    -0.05

System Monitoring Compounds
  2) TOLUENE-d8 (S)                    3.74   98 26035845    48.04 ppb    -0.05
  Spiked Amount     50.000   Range  75 - 125    Recovery   =    96.08%
  4) BROMOFLUOROBENZENE (S)            5.64   95  9998911    49.99 ppb    -0.07
  Spiked Amount     50.000   Range  75 - 125    Recovery   =    99.98%

Target Compounds                                                    Qvalue
  5) Naphthalene                       9.17  128 37981850   102.02 ppb       100
```

```
----------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006011.D          Vial: 4
Acq On    :  6 Oct 2004  11:56 am                     Operator:
Sample    : Retort door full tram 15-25min  AB107     Inst     : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY            Multiplr: 1.00
Integration Parameters -  MS: events.e    GC1: events2.e   GC2: events3.e
Quant Time: Oct  6 12:10 19104               Quant Results File: KOPPERS.RES

Method        : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
Title         : 8260 Volatiles
Last Update   : Fri Oct 08 18:37:49 2004
Response via  : Initial Calibration
```

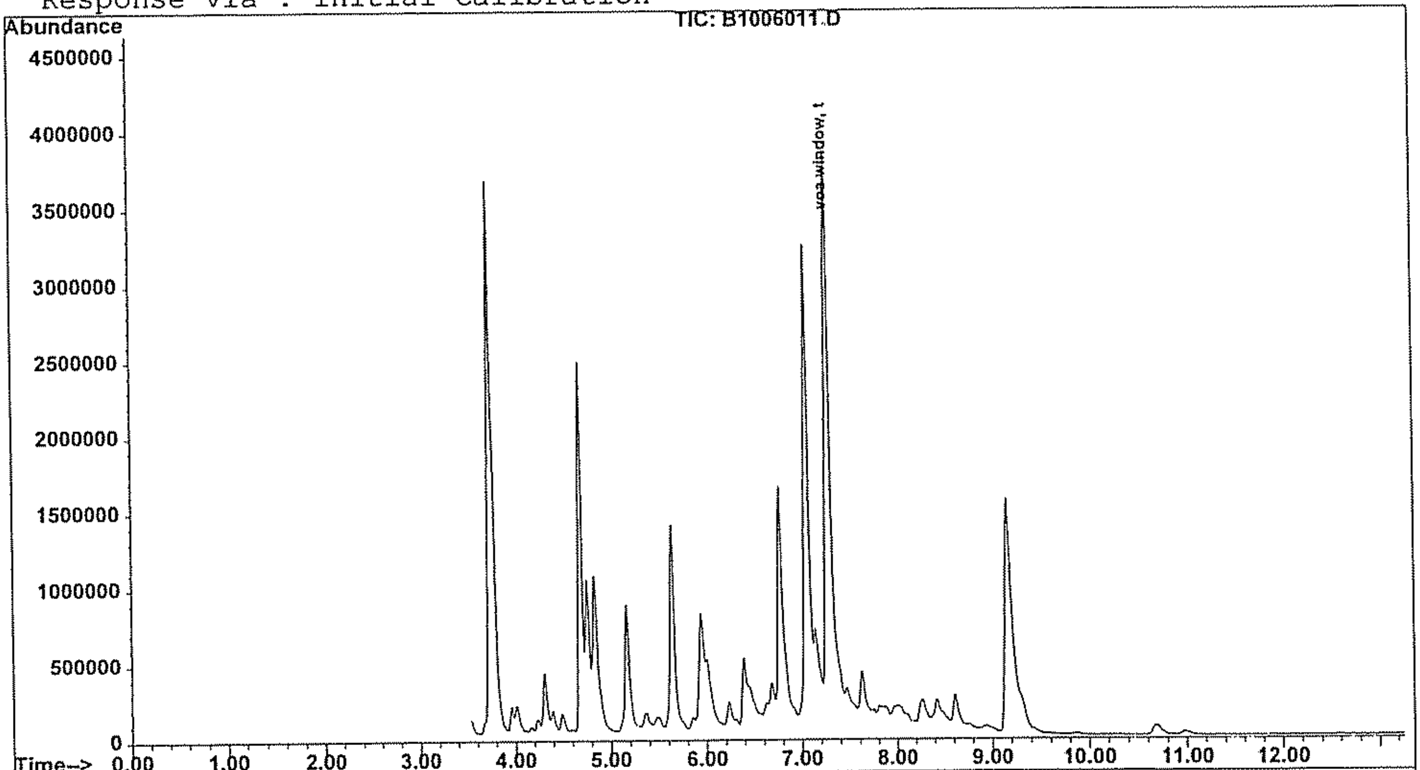


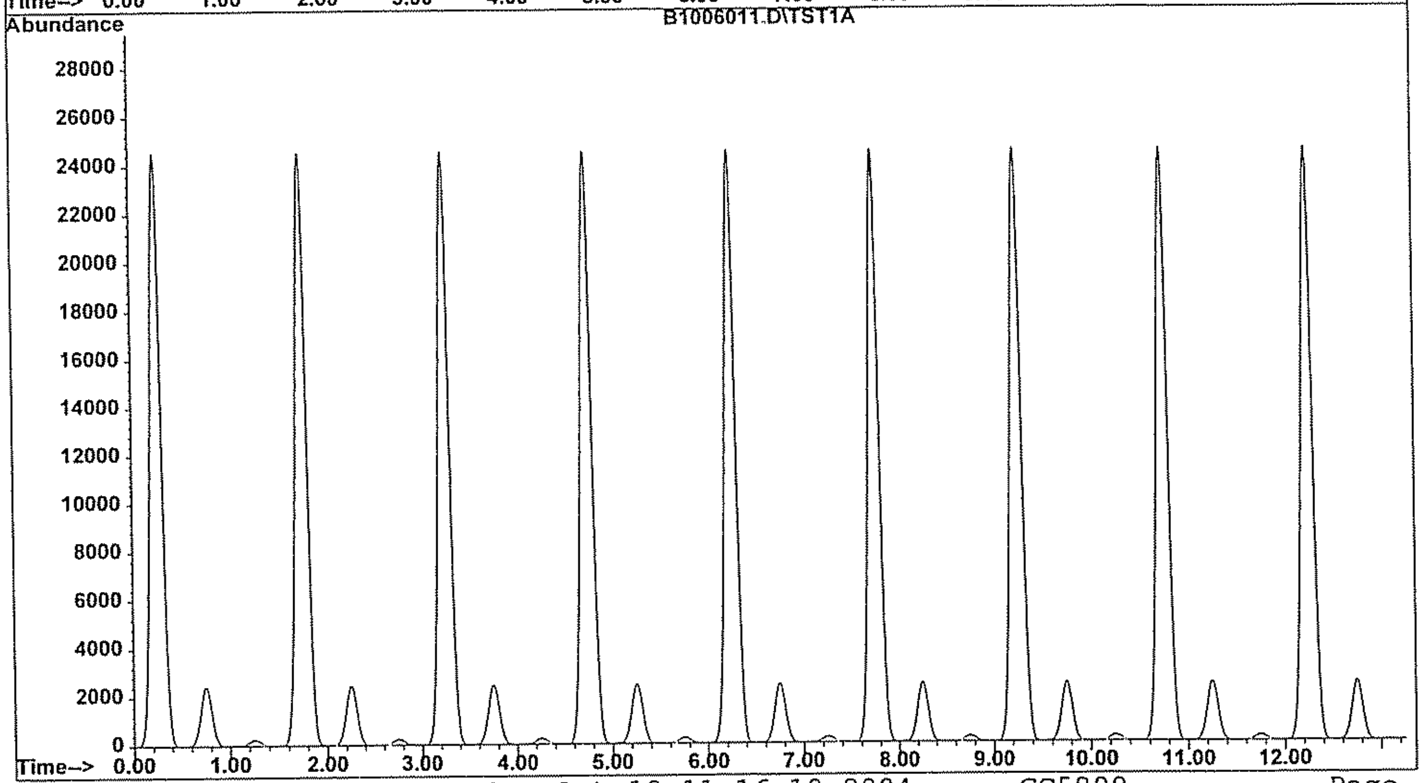


```
                          Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006011.D          Vial: 4
  Acq On    :  6 Oct 2004  11:56 am                     Operator:
  Sample    : Retort door full tram 15-25min  AB107     Inst     : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY            Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7  9:45 19104                 Quant Results File: WINDOW.RES

  Quant Method : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
  Title        : koppers volatile window
  Last Update  : Wed Oct 06 18:41:15 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS

Internal Standards                R.T. QIon  Response  Conc Units Dev(Min)
------------------------------------------------------------------------------

System Monitoring Compounds

Target Compounds                                                 Qvalue
  1) voa window                   7.27  TIC 867451703m   37.41 ng on




 -----------------------------------------------------------------------------
 (#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006011.D         Vial: 4
Acq On    :  6 Oct 2004  11:56 am                     Operator:
Sample    : Retort door full tram 15-25min  AB107     Inst     : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY            Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7  9:45 19104           Quant Results File: WINDOW.RES

Method        : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
Title         : koppers volatile window
Last Update   : Fri Oct 08 18:40:27 2004
Response via  : Initial Calibration
```

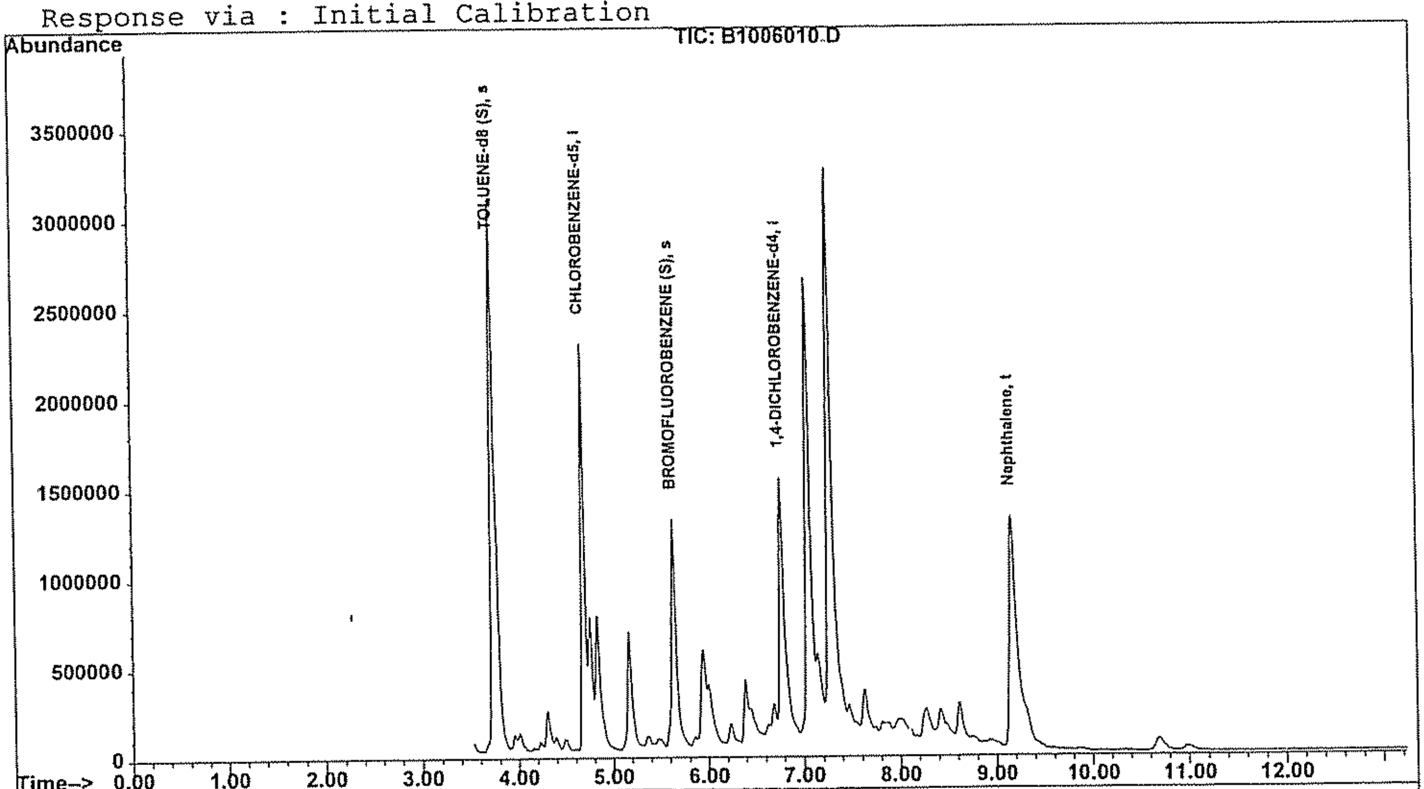


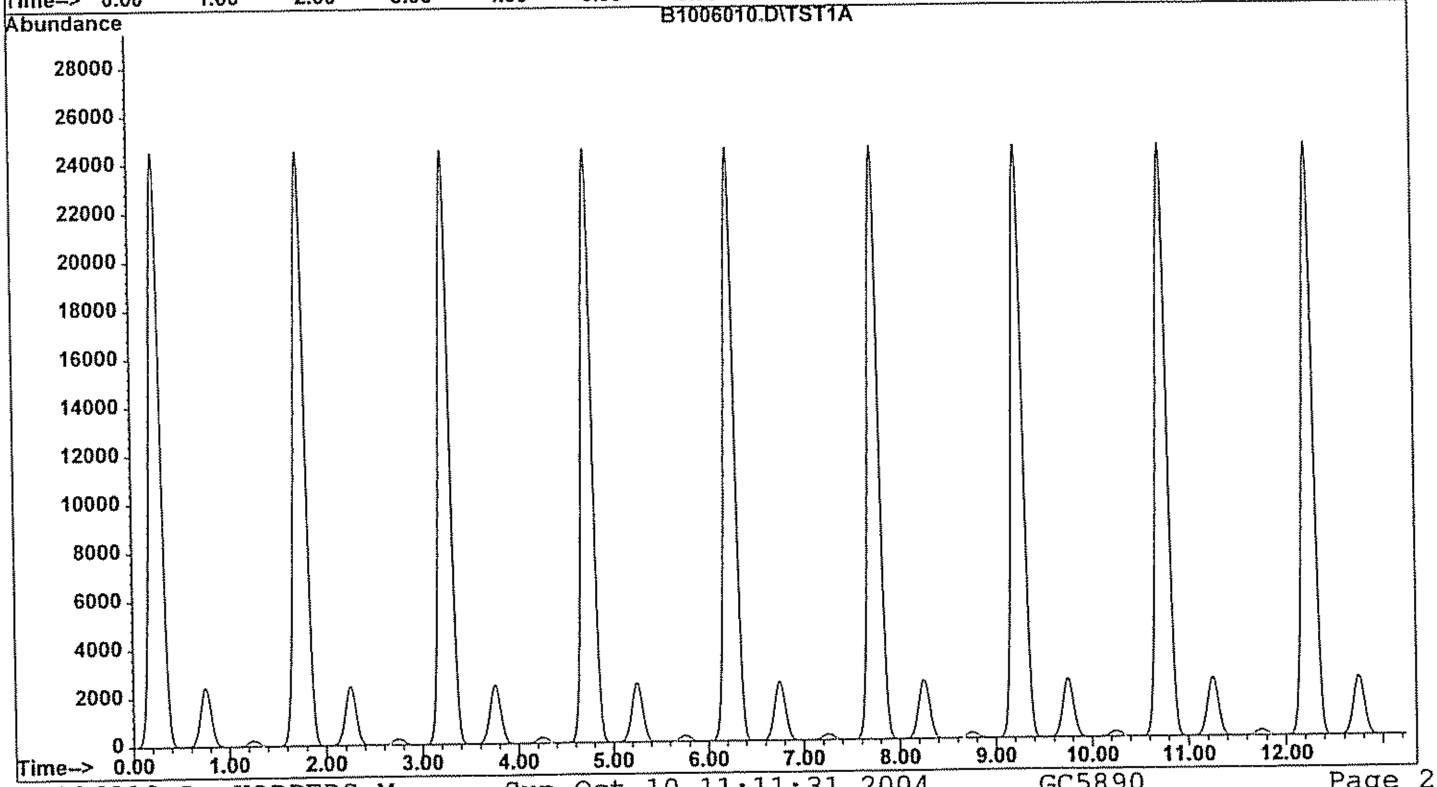


```
                        Quantitation Report    (QT Reviewed)

 Data File : C:\HPCHEM\1\DATA\B100604\B1006010.D        Vial: 3
 Acq On    :  6 Oct 2004  11:27 am                   Operator:
 Sample    : Retort door full tram 25/35min  AB108    Inst     : GC/MS Ins
 Misc      : 10ml/3L   Koppers,  Guthrie,KY          Multiplr: 1.00
 Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
 Quant Time: Oct  6 11:40 19104              Quant Results File: KOPPERS.RES

 Quant Method : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
 Title        : 8260 Volatiles
 Last Update  : Mon Oct 04 13:13:05 2004
 Response via : Initial Calibration
 DataAcq Meth : KOPPERS

Internal Standards                    R.T. QIon  Response  Conc Units Dev(Min)
-----------------------------------------------------------------------------
  1) CHLOROBENZENE-d5                 4.70  117 19011426    50.00 ppb    -0.05
  3) 1,4-DICHLOROBENZENE-d4           6.78  150 12197460    50.00 ppb    -0.05

System Monitoring Compounds
  2) TOLUENE-d8 (S)                   3.74   98 24663411    47.50 ppb    -0.05
  Spiked Amount     50.000   Range  75 - 125    Recovery   =    95.00%
  4) BROMOFLUOROBENZENE (S)           5.65   95  9155713    47.20 ppb    -0.06
  Spiked Amount     50.000   Range  75 - 125    Recovery   =    94.40%

Target Compounds                                                      Qvalue
  5) Naphthalene                      9.17  128 33475896    92.70 ppb      100

-----------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006010.D          Vial: 3
Acq On    :  6 Oct 2004  11:27 am                      Operator:
Sample    : Retort door full tram 25/35min  AB108      Inst    : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY             Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  6 11:40 19104                Quant Results File: KOPPERS.RES

Method         : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
Title          : 8260 Volatiles
Last Update    : Fri Oct 08 18:37:49 2004
Response via   : Initial Calibration
```

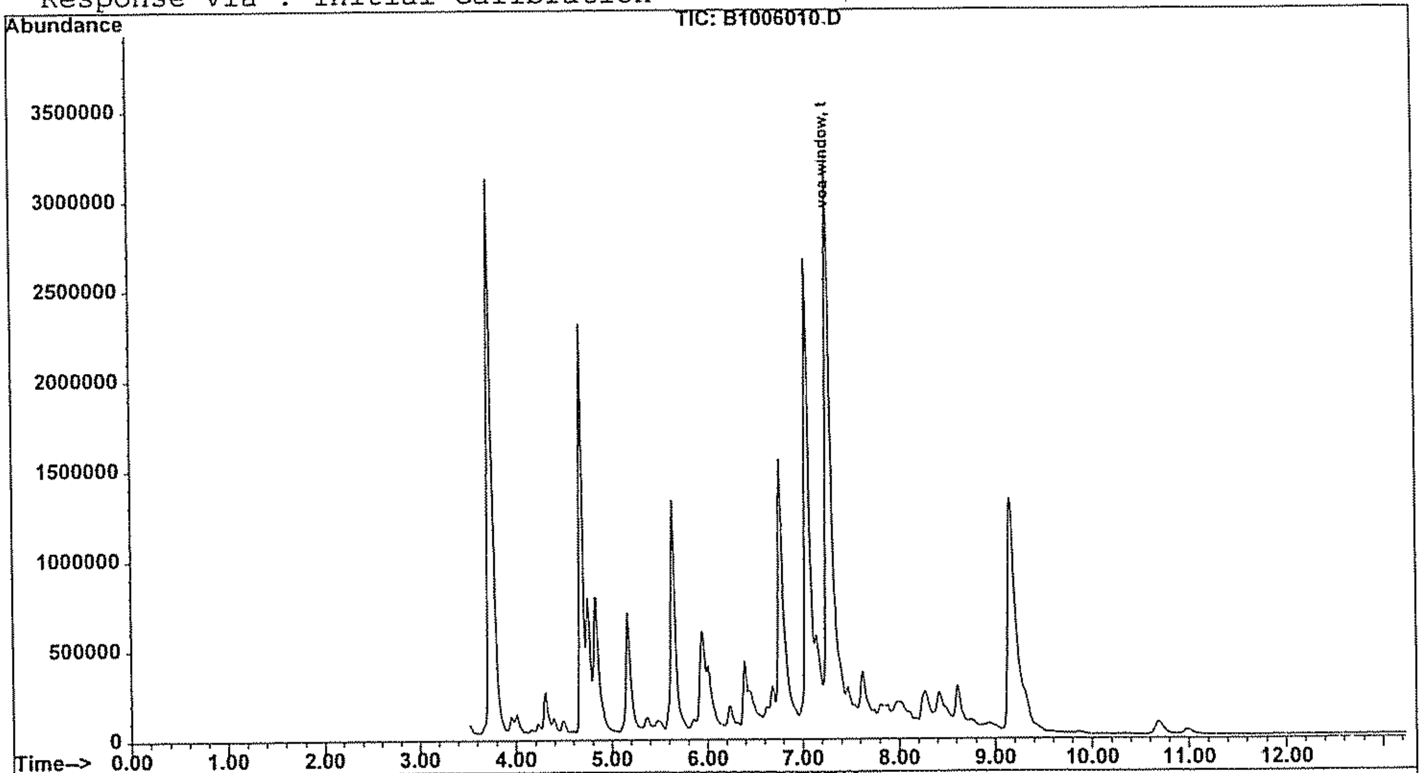


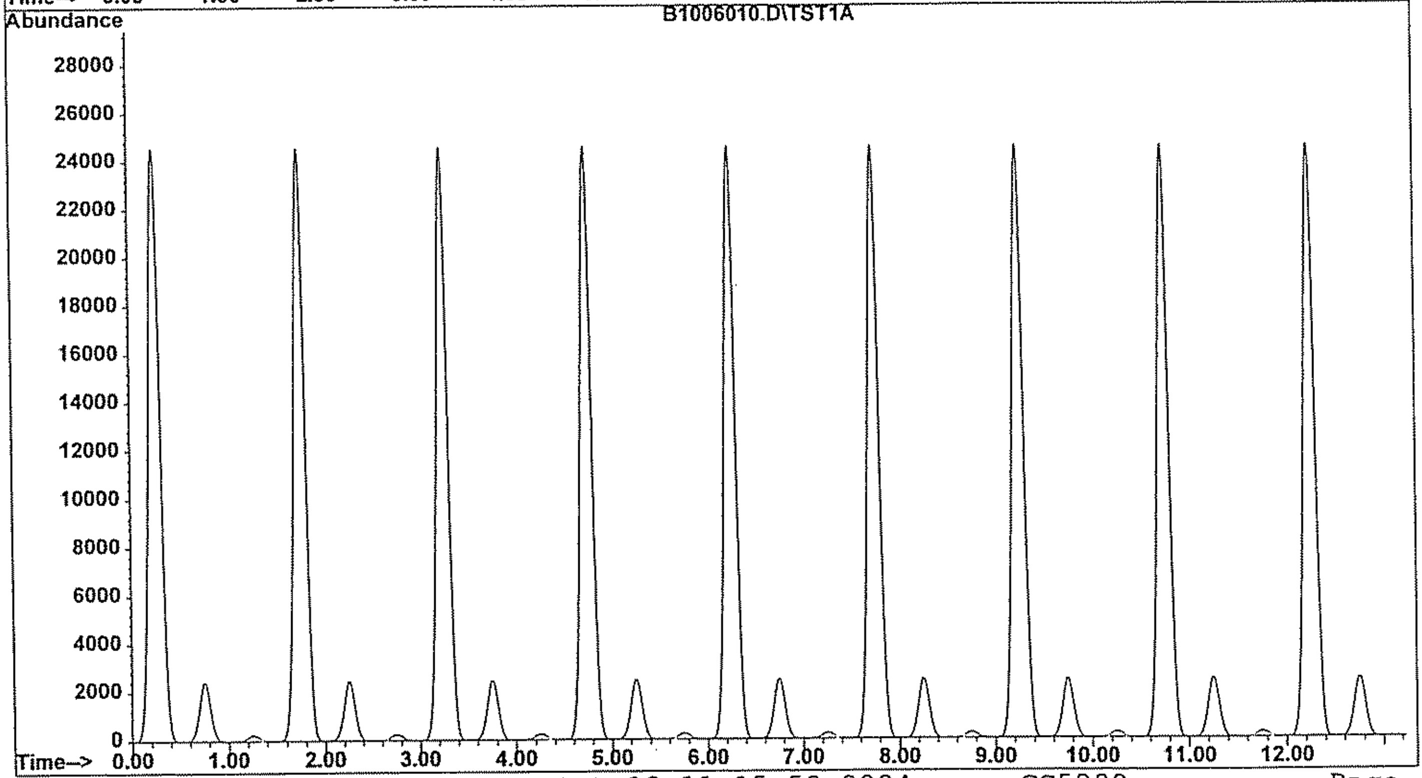


```
                              Quantitation Report    (QT Reviewed)

 Data File : C:\HPCHEM\1\DATA\B100604\B1006010.D          Vial: 3
 Acq On    :  6 Oct 2004  11:27 am                     Operator:
 Sample    : Retort door full tram 25/35min  AB108     Inst     : GC/MS Ins
 Misc      : 10ml/3L   Koppers,  Guthrie,KY            Multiplr: 1.00
 Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
 Quant Time: Oct  7  7:52 19104               Quant Results File: WINDOW.RES

 Quant Method : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
 Title        : koppers volatile window
 Last Update  : Wed Oct 06 18:41:15 2004
 Response via : Initial Calibration
 DataAcq Meth : KOPPERS

Internal Standards                  R.T. QIon  Response  Conc Units Dev(Min)
---------------------------------------------------------------------------

System Monitoring Compounds

                                                                   Qvalue
Target Compounds
  1) voa window                      7.28  TIC 729633372m   30.19 ng on

---------------------------------------------------------------------------
 (#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006010.D          Vial: 3
Acq On    :  6 Oct 2004  11:27 am                      Operator:
Sample    : Retort door full tram 25/35min  AB108      Inst     : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY             Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7  7:52 19104                   Quant Results File: WINDOW.RES

Method         : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
Title          : koppers volatile window
Last Update    : Fri Oct 08 18:40:27 2004
Response via   : Initial Calibration
```

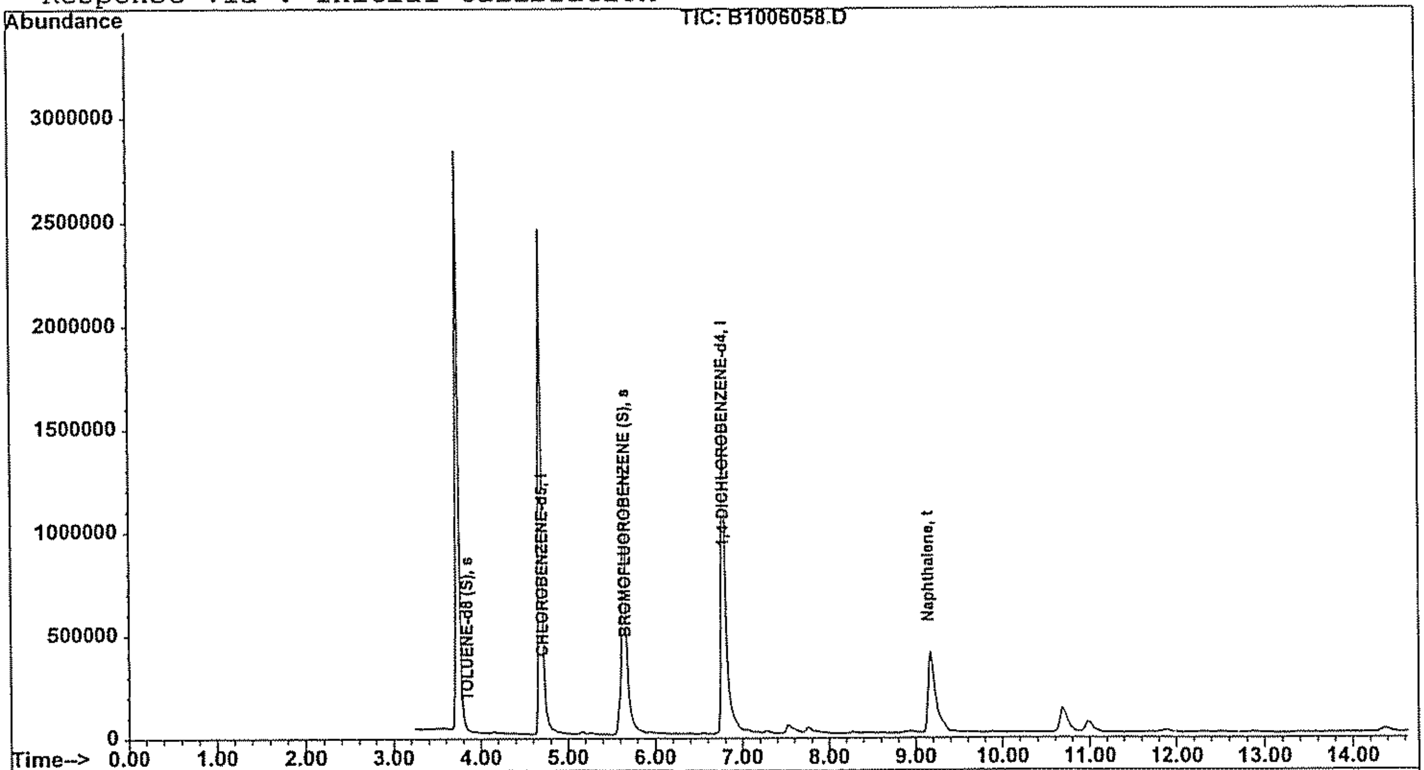


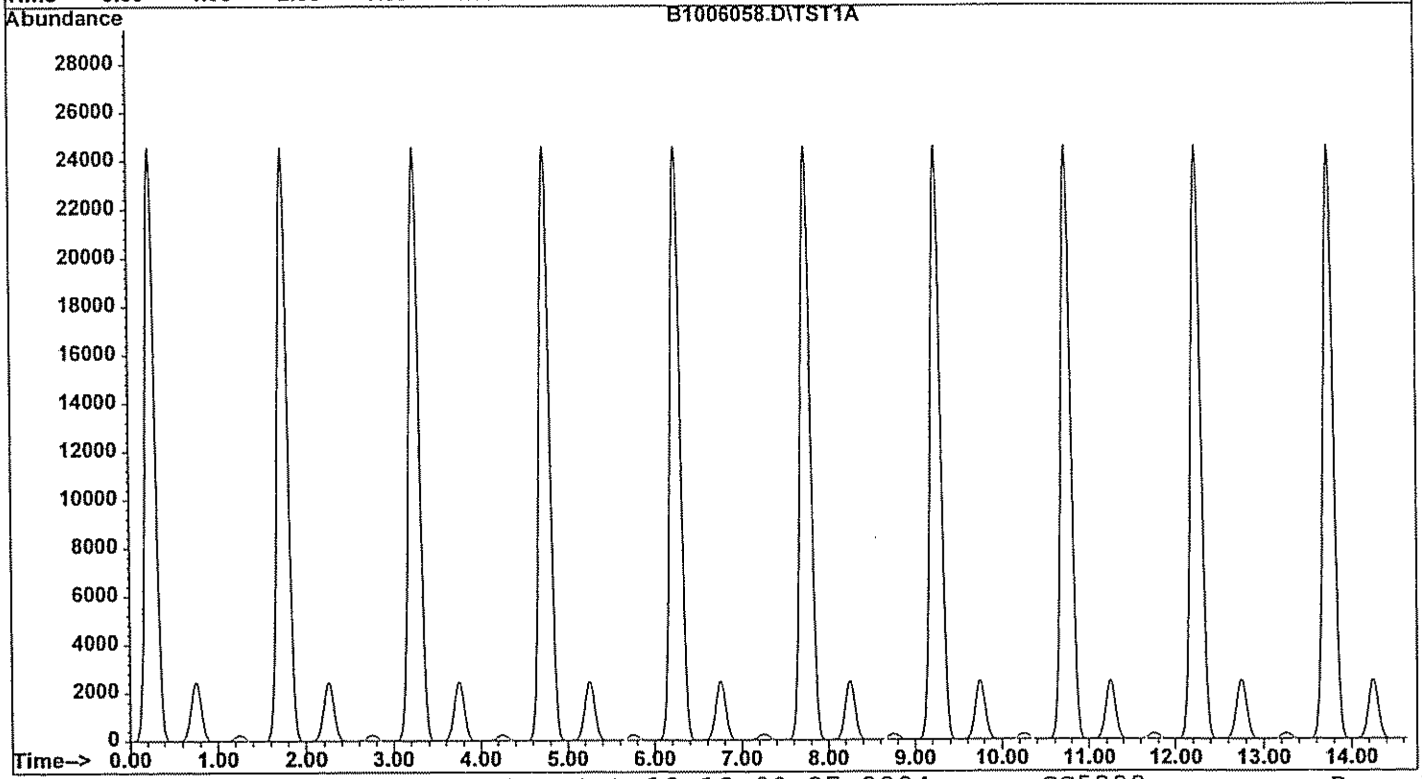


```
                    Quantitation Report    (QT Reviewed)

 Data File : C:\HPCHEM\1\DATA\B100604\B1006058.D        Vial: 9
 Acq On    :  7 Oct 2004   1:54 pm                    Operator:
 Sample    : Retort door empty Bkgd  AB123             Inst     : GC/MS Ins
 Misc      : 10ml/3L   Koppers,  Guthrie,KY            Multiplr: 1.00
 Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
 Quant Time: Oct  7 14:08 19104               Quant Results File: KOPPERS.RES

 Quant Method : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
 Title        : 8260 Volatiles
 Last Update  : Mon Oct 04 13:13:05 2004
 Response via : Initial Calibration
 DataAcq Meth : KOPPERS

Internal Standards                    R.T. QIon  Response  Conc Units Dev(Min)
-----------------------------------------------------------------------------
  1) CHLOROBENZENE-d5                 4.74  117 19506622    50.00 ppb     0.00
  3) 1,4-DICHLOROBENZENE-d4           6.81  150 12584256    50.00 ppb    -0.02

System Monitoring Compounds
  2) TOLUENE-d8 (S)                   3.88   98 24652867    46.27 ppb     0.09
  Spiked Amount      50.000   Range  75 - 125    Recovery   =   92.54%
  4) BROMOFLUOROBENZENE (S)           5.69   95 10198019    50.95 ppb    -0.02
  Spiked Amount      50.000   Range  75 - 125    Recovery   =  101.90%

Target Compounds                                                       Qvalue
  5) Naphthalene                      9.17  128   9210826    24.72 ppb      100

-----------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006058.D         Vial: 9
Acq On    :  7 Oct 2004   1:54 pm                     Operator:
Sample    : Retort door empty Bkgd  AB123             Inst     : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY            Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 14:08 19104               Quant Results File: KOPPERS.RES

Method         : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
Title          : 8260 Volatiles
Last Update    : Fri Oct 08 18:37:49 2004
Response via   : Initial Calibration
```

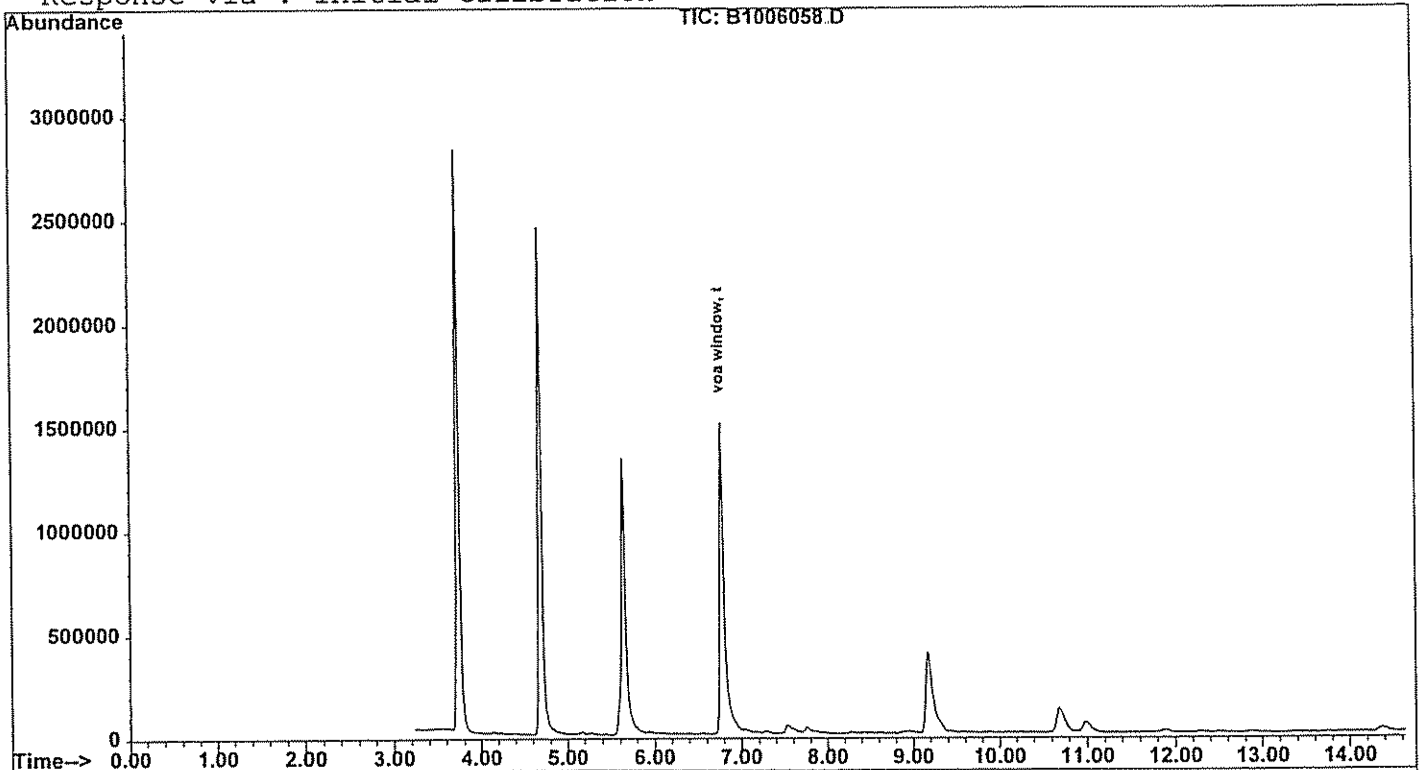


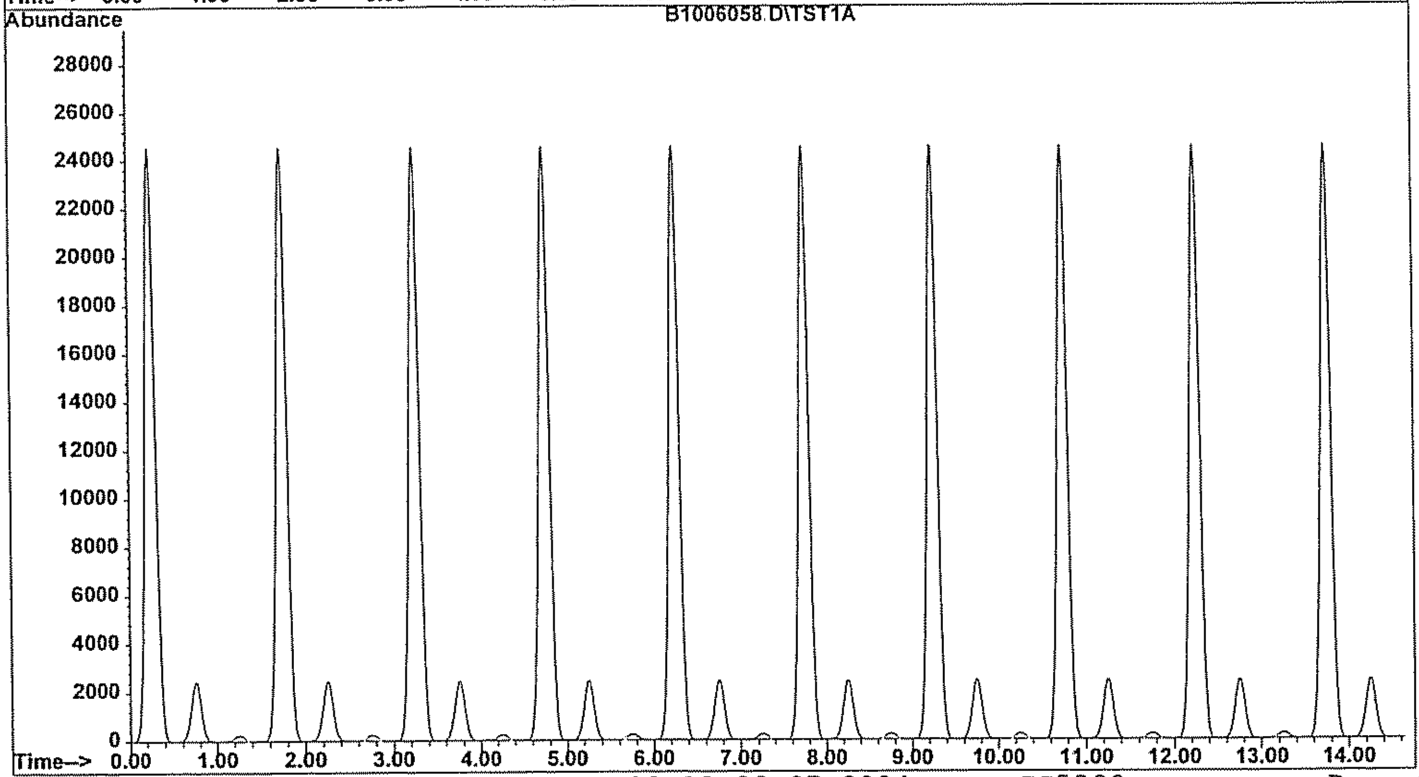


```
                          Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006058.D          Vial: 9
  Acq On    :  7 Oct 2004   1:54 pm                     Operator:
  Sample    : Retort door empty Bkgd  AB123             Inst     : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY            Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 14:10 19104              Quant Results File: WINDOW.RES

  Quant Method : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
  Title        : koppers volatile window
  Last Update  : Wed Oct 06 18:41:15 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS

Internal Standards                 R.T. QIon  Response  Conc Units Dev(Min)
------------------------------------------------------------------------------

System Monitoring Compounds

Target Compounds                                                   Qvalue
  1) voa window                     6.78  TIC 167581846m    5.77 ng on

------------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006058.D          Vial: 9
Acq On    :  7 Oct 2004   1:54 pm                    Operator:
Sample    : Retort door empty Bkgd  AB123            Inst     : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY           Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 14:10 19104              Quant Results File: WINDOW.RES

Method        : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
Title         : koppers volatile window
Last Update   : Fri Oct 08 18:40:27 2004
Response via  : Initial Calibration
```

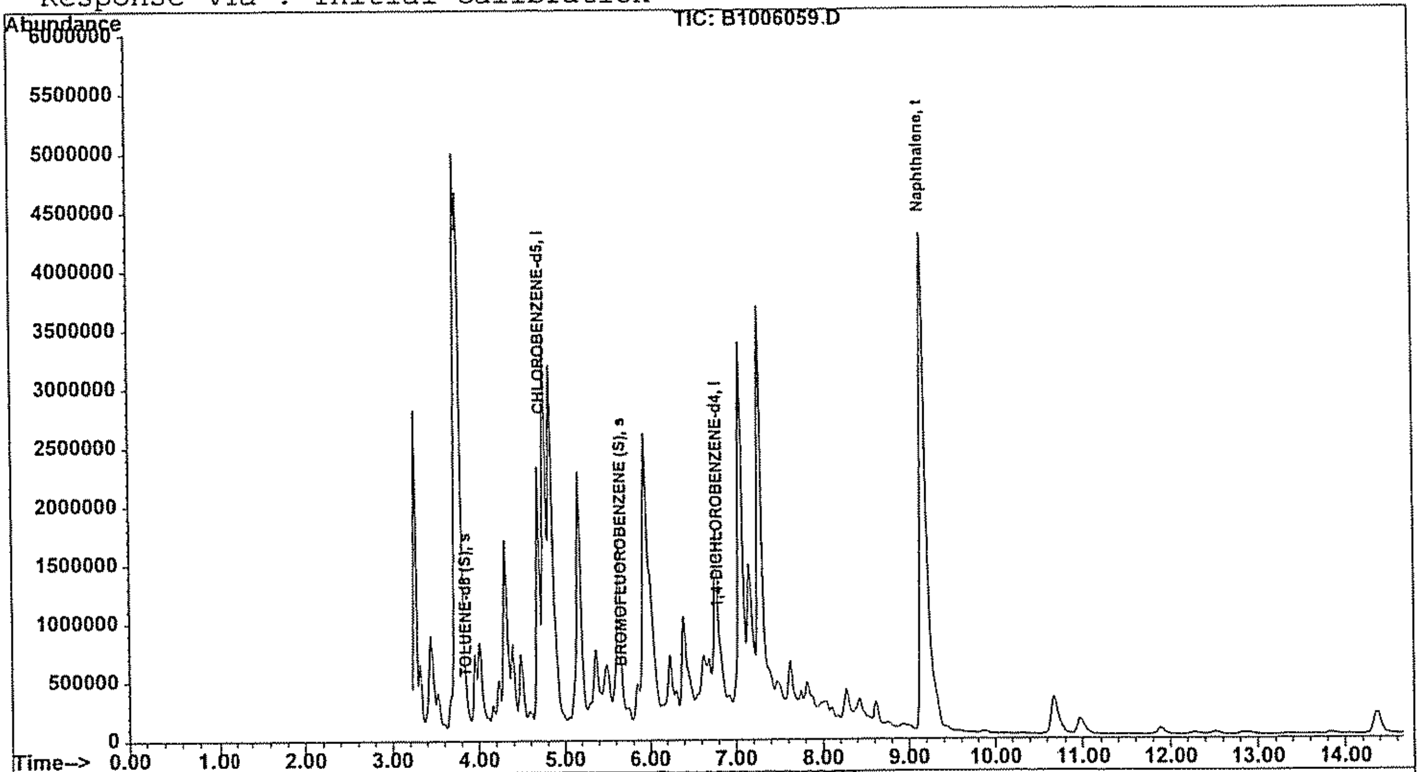


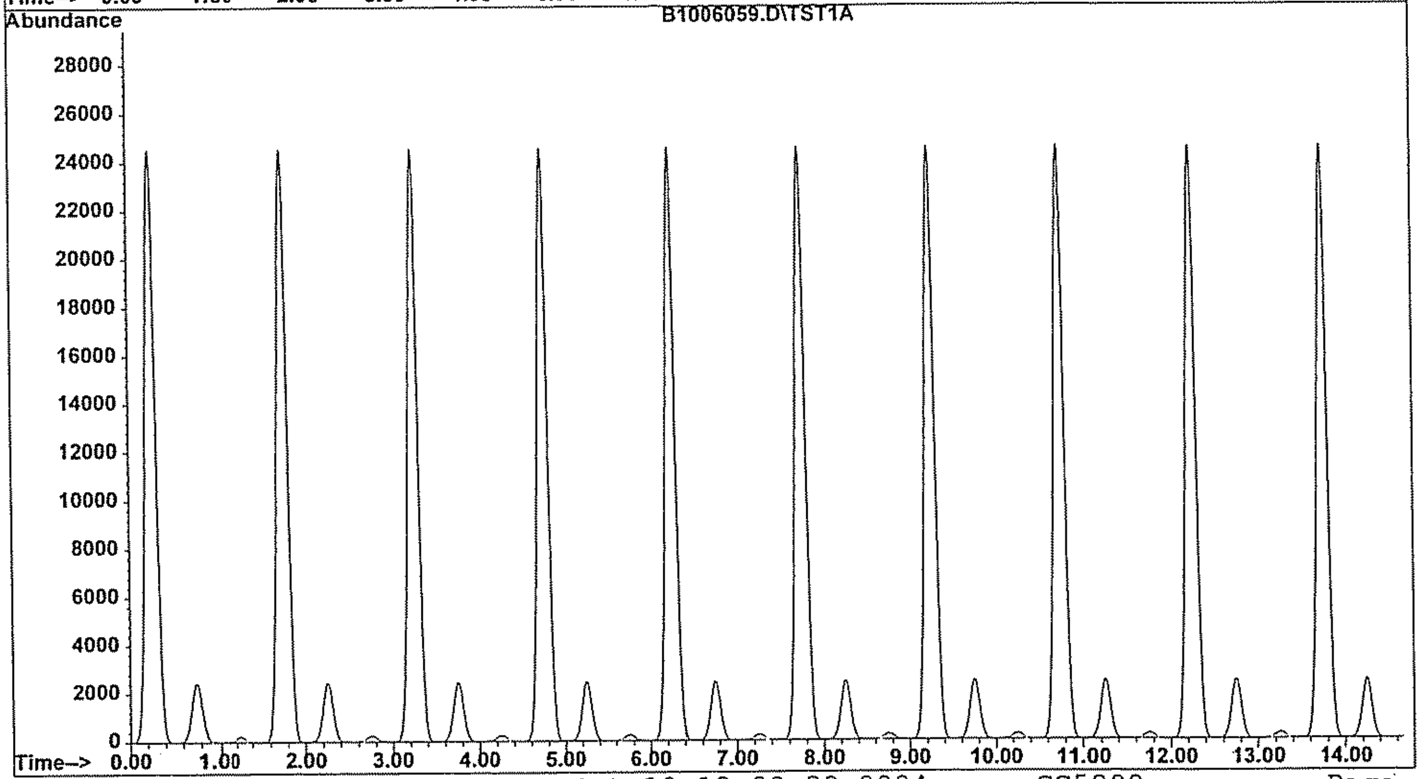


```
                          Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006059.D          Vial: 10
  Acq On    :  7 Oct 2004   2:22 pm                     Operator:
  Sample    : Retort door empty 0-5min AB124            Inst    : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY            Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 14:37 19104               Quant Results File: KOPPERS.RES

  Quant Method : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
  Title        : 8260 Volatiles
  Last Update  : Mon Oct 04 13:13:05 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS


Internal Standards                  R.T. QIon  Response  Conc Units Dev(Min)
-----------------------------------------------------------------------------

  1) CHLOROBENZENE-d5               4.75  117 16492928    50.00 ppb     0.00
  3) 1,4-DICHLOROBENZENE-d4         6.82  150 10736832    50.00 ppb    -0.01

System Monitoring Compounds
  2) TOLUENE-d8 (S)                 3.88   98 22913287    50.86 ppb     0.09
  Spiked Amount     50.000   Range  75 - 125    Recovery   =  101.72%
  4) BROMOFLUOROBENZENE (S)         5.69   95  8203288    48.04 ppb    -0.02
  Spiked Amount     50.000   Range  75 - 125    Recovery   =   96.08%

Target Compounds                                                      Qvalue
  5) Naphthalene                    9.18  128 90963916   286.17 ppb      100









-----------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006059.D          Vial: 10
Acq On    :  7 Oct 2004   2:22 pm                    Operator:
Sample    : Retort door empty 0-5min AB124           Inst     : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY           Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 14:37 19104              Quant Results File: KOPPERS.RES

Method        : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
Title         : 8260 Volatiles
Last Update   : Fri Oct 08 18:37:49 2004
Response via  : Initial Calibration
```

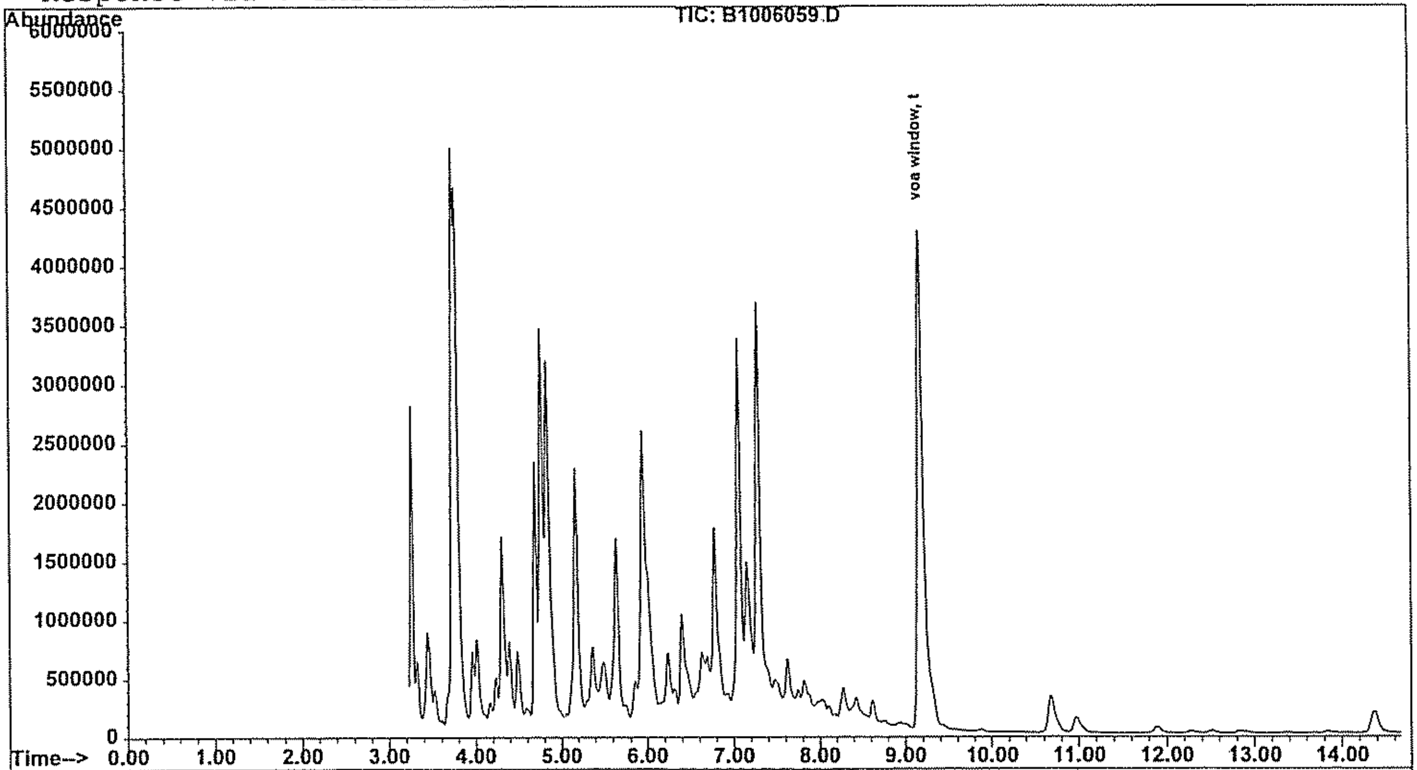


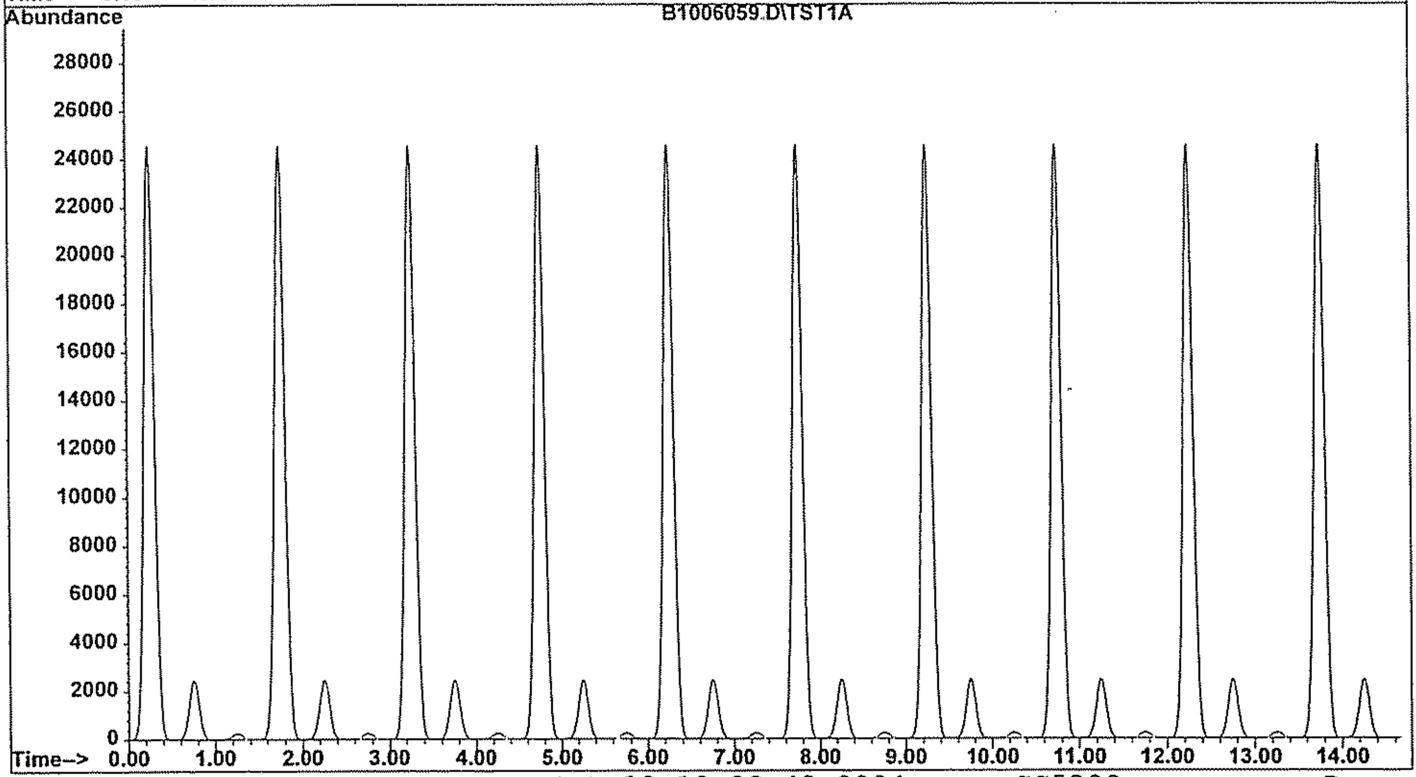


```
                            Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006059.D          Vial: 10
  Acq On    :  7 Oct 2004   2:22 pm                    Operator:
  Sample    : Retort door empty 0-5min AB124           Inst    : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY           Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 14:45 19104              Quant Results File: WINDOW.RES

  Quant Method : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
  Title        : koppers volatile window
  Last Update  : Wed Oct 06 18:41:15 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS

Internal Standards                R.T. QIon  Response  Conc Units Dev(Min)
-------------------------------------------------------------------------

System Monitoring Compounds

Target Compounds                                                   Qvalue
  1) voa window                   9.17  TIC 1330561437m   61.91 ng on

-------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006059.D          Vial: 10
Acq On    :  7 Oct 2004   2:22 pm                      Operator:
Sample    : Retort door empty 0-5min AB124             Inst    : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY             Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 14:45 19104                   Quant Results File: WINDOW.RES

Method         : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
Title          : koppers volatile window
Last Update    : Fri Oct 08 18:40:27 2004
Response via   : Initial Calibration
```

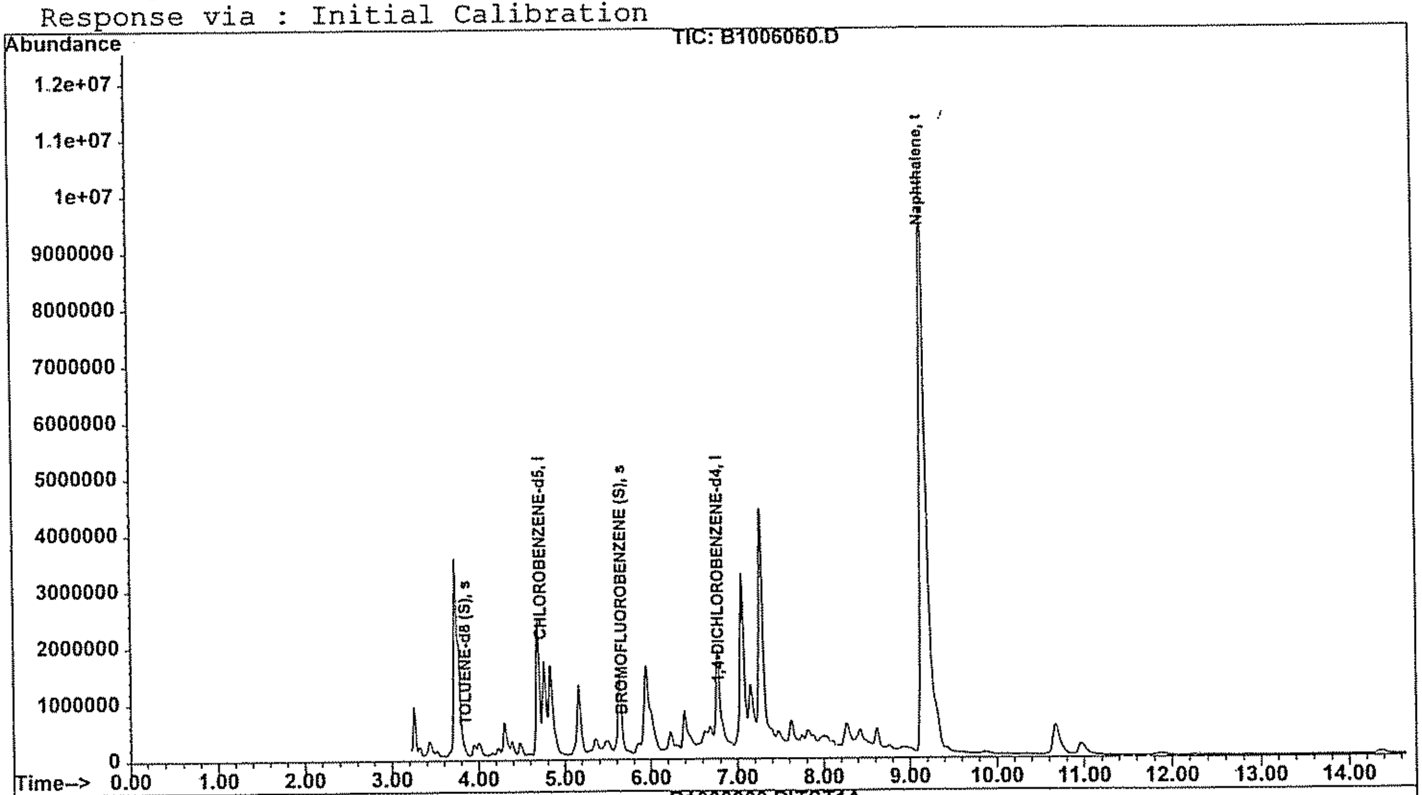


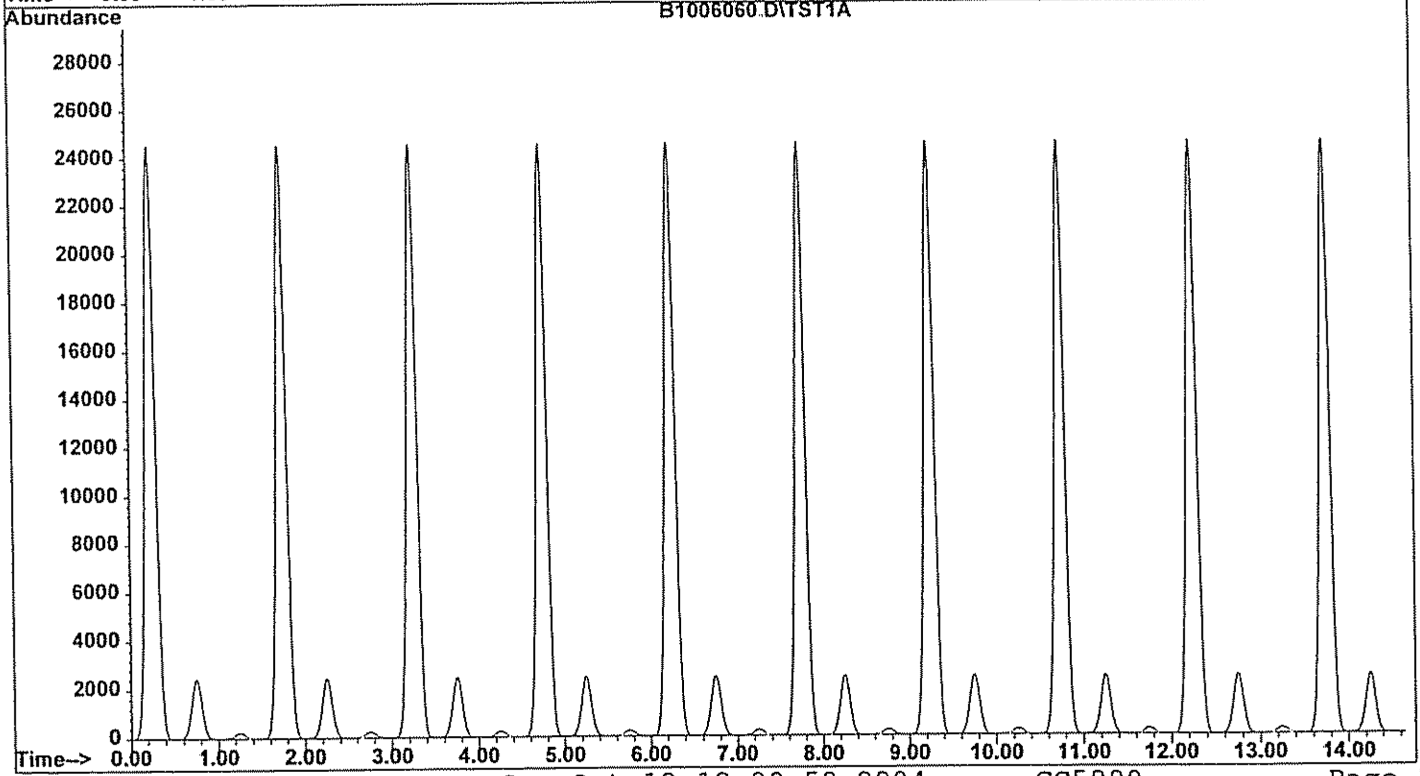


```
                          Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006060.D          Vial: 11
  Acq On    :  7 Oct 2004   2:52 pm                     Operator:
  Sample    : Retort door empty 5-10min AB125           Inst    : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY            Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 15:06 19104                  Quant Results File: KOPPERS.RES

  Quant Method : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
  Title        : 8260 Volatiles
  Last Update  : Mon Oct 04 13:13:05 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS


Internal Standards                      R.T. QIon  Response  Conc Units Dev(Min)
-------------------------------------------------------------------------------

  1) CHLOROBENZENE-d5                   4.75  117 18420338    50.00 ppb     0.00
  3) 1,4-DICHLOROBENZENE-d4             6.81  150 11936673    50.00 ppb    -0.02

System Monitoring Compounds
  2) TOLUENE-d8 (S)                     3.88   98 22287617    44.30 ppb     0.09
  Spiked Amount     50.000   Range  75 - 125    Recovery   =   88.60%
  4) BROMOFLUOROBENZENE (S)             5.69   95  8567343    45.13 ppb    -0.02
  Spiked Amount     50.000   Range  75 - 125    Recovery   =   90.26%

Target Compounds                                                     Qvalue
  5) Naphthalene                        9.17  128 215418989   609.58 ppb      100

 ------------------------------------------------------------------------------
 (#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006060.D          Vial: 11
Acq On    :  7 Oct 2004   2:52 pm                    Operator:
Sample    : Retort door empty 5-10min AB125          Inst     : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY           Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 15:06 19104                 Quant Results File: KOPPERS.RES

Method        : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
Title         : 8260 Volatiles
Last Update   : Fri Oct 08 18:37:49 2004
Response via  : Initial Calibration
```

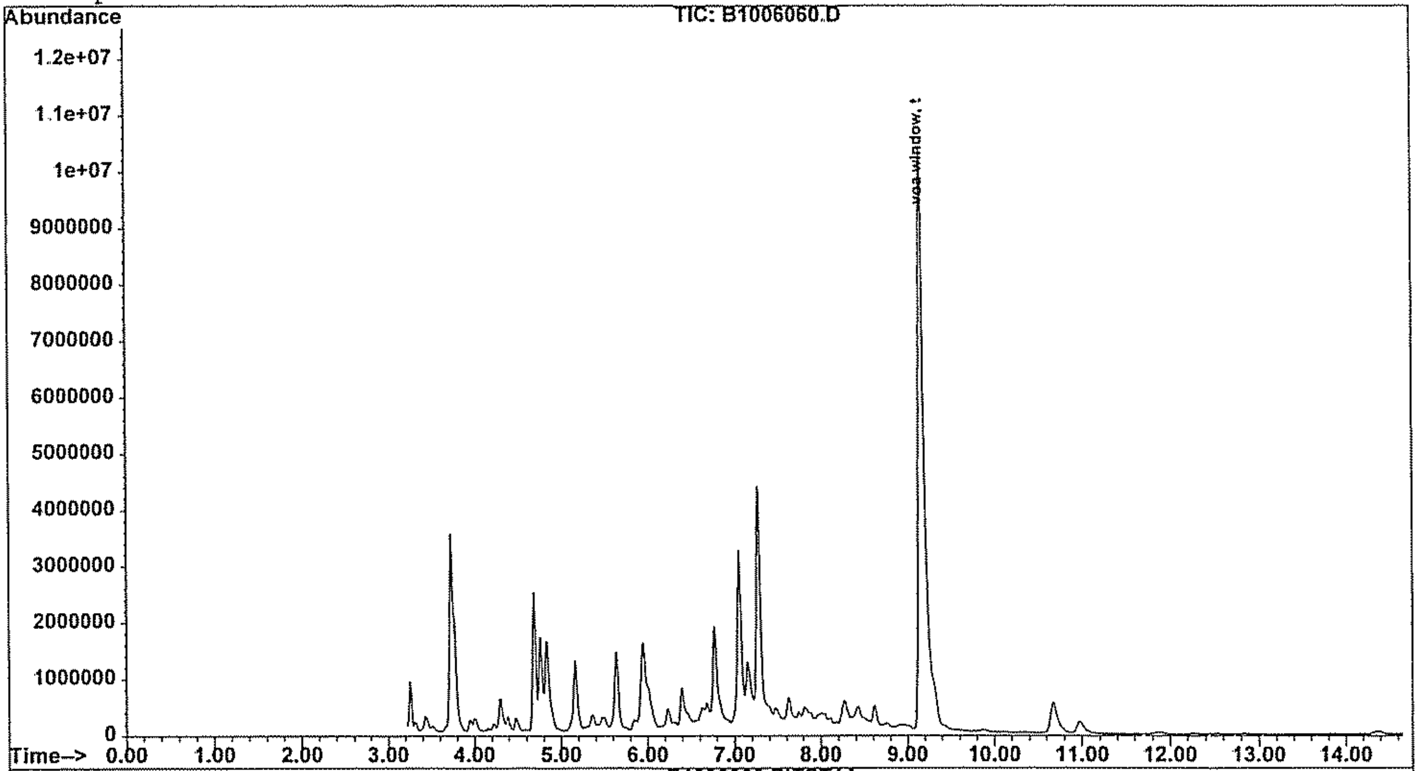


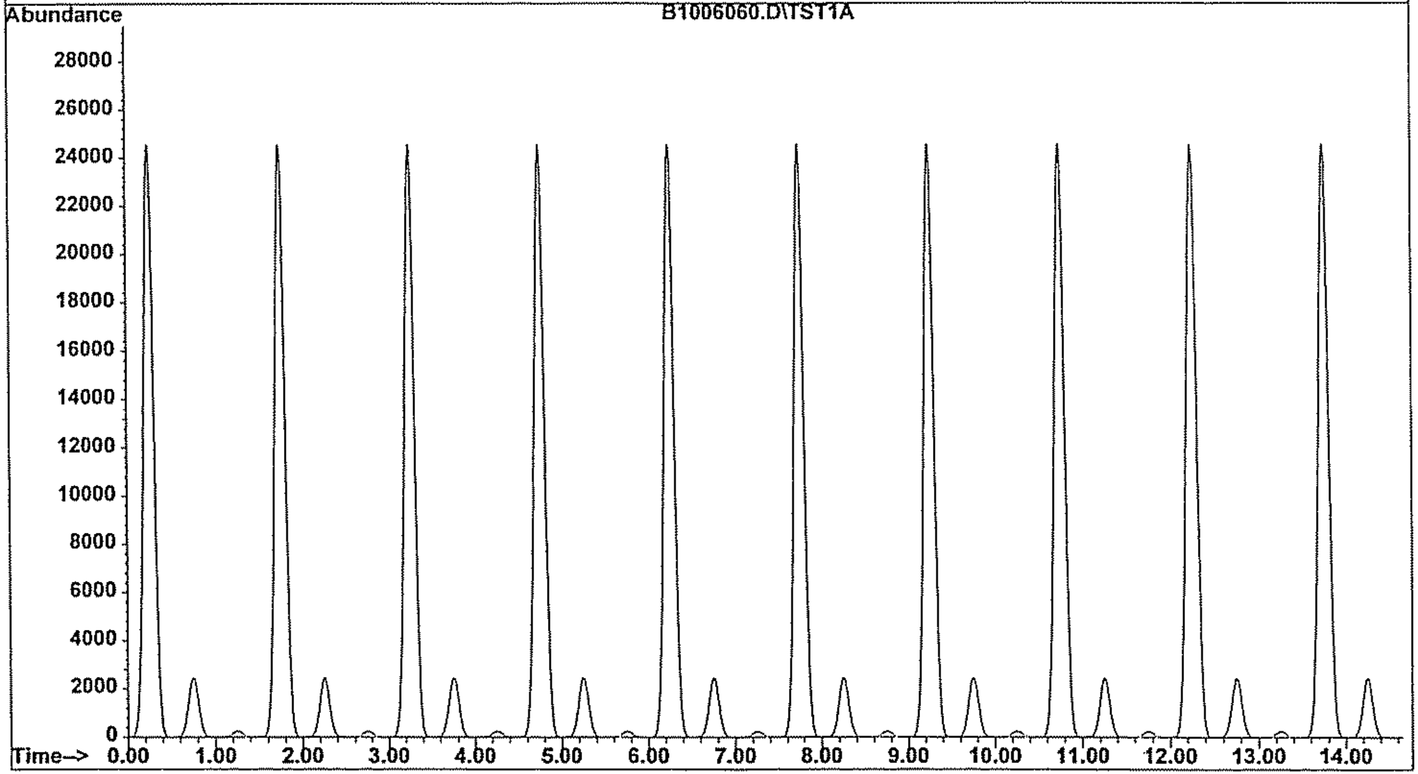


```
                          Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006060.D          Vial: 11
  Acq On    :  7 Oct 2004   2:52 pm                    Operator:
  Sample    : Retort door empty 5-10min AB125          Inst     : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY           Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 15:41 19104                Quant Results File: WINDOW.RES

  Quant Method : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
  Title        : koppers volatile window
  Last Update  : Wed Oct 06 18:41:15 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS

Internal Standards                 R.T. QIon  Response  Conc Units Dev(Min)
---------------------------------------------------------------------------

System Monitoring Compounds

Target Compounds                                                  Qvalue
  1) voa window                    9.16  TIC 1541635974m   72.10 ng on
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006060.D          Vial: 11
Acq On    :  7 Oct 2004   2:52 pm                     Operator:
Sample    : Retort door empty 5-10min AB125           Inst    : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY            Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 15:41 19104                 Quant Results File: WINDOW.RES

Method         : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
Title          : koppers volatile window
Last Update    : Fri Oct 08 18:40:27 2004
Response via   : Initial Calibration
```

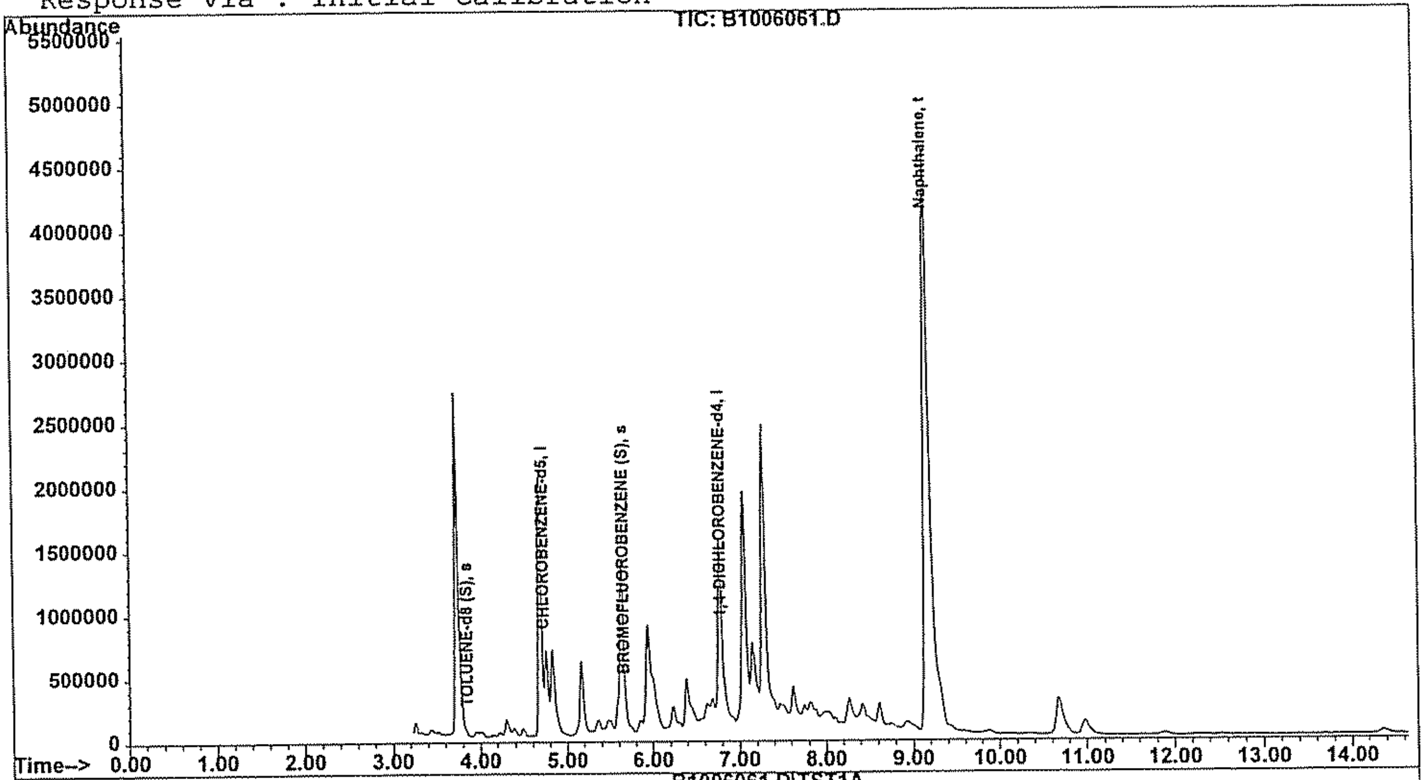


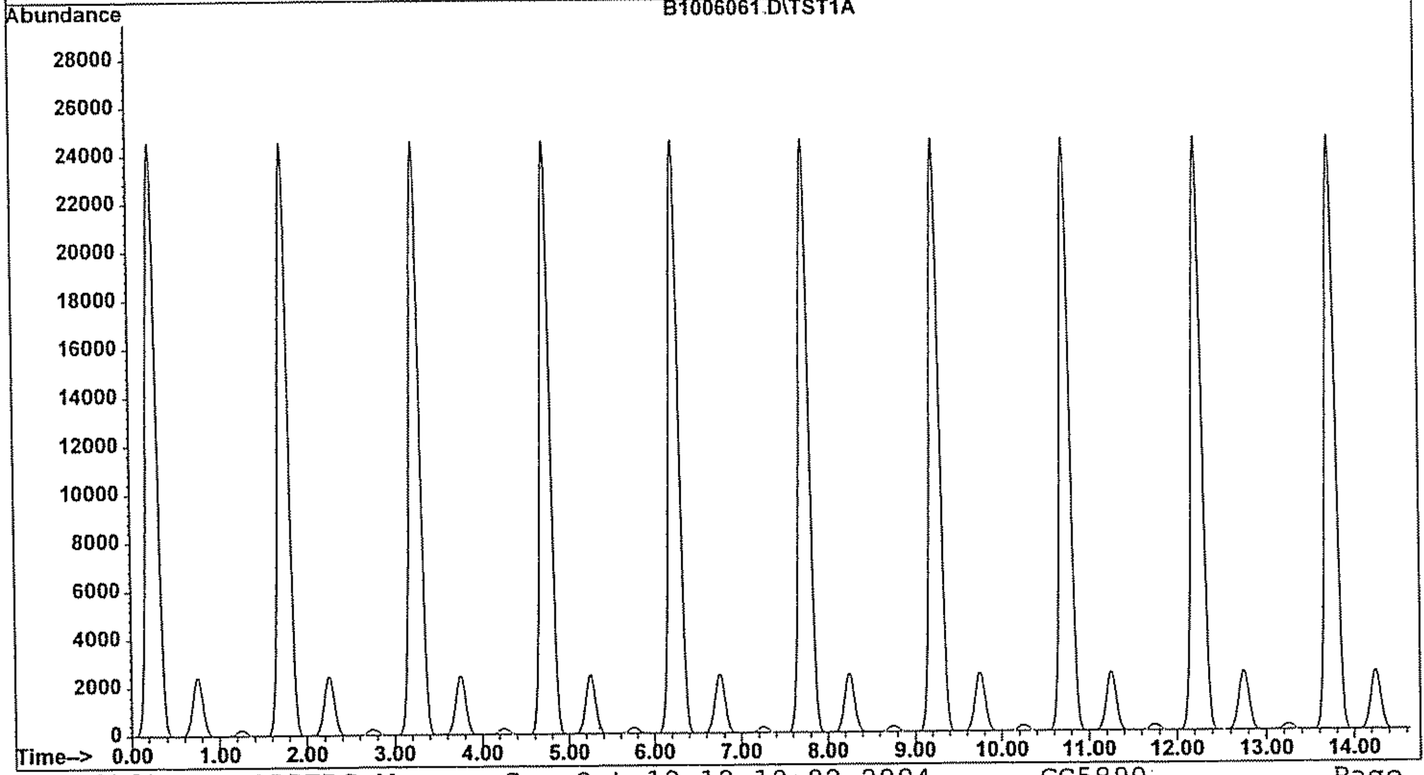


```
                         Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006061.D          Vial: 12
  Acq On    :  7 Oct 2004   3:21 pm                     Operator:
  Sample    : Retort door empty from cylinder at end A Inst     : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY  AB126     Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 15:36 19104                Quant Results File: KOPPERS.RES

  Quant Method : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
  Title        : 8260 Volatiles
  Last Update  : Mon Oct 04 13:13:05 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS


Internal Standards                        R.T. QIon  Response  Conc Units Dev(Min)
-----------------------------------------------------------------------------
  1) CHLOROBENZENE-d5                     4.74  117 16088038    50.00 ppb     0.00
  3) 1,4-DICHLOROBENZENE-d4               6.81  150 10503372    50.00 ppb    -0.02

System Monitoring Compounds
  2) TOLUENE-d8 (S)                       3.88   98 22571566    51.37 ppb     0.09
  Spiked Amount      50.000   Range  75 - 125    Recovery   =  102.74%
  4) BROMOFLUOROBENZENE (S)               5.69   95  9483969    56.77 ppb    -0.02
  Spiked Amount      50.000   Range  75 - 125    Recovery   =  113.54%

Target Compounds                                                           Qvalue
  5) Naphthalene                          9.17  128 96015864   308.78 ppb      100
```

```
-----------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

```
                              Quantitation Report

  Data File : C:\HPCHEM\1\DATA\B100604\B1006061.D          Vial: 12
  Acq On    :  7 Oct 2004   3:21 pm                    Operator:
  Sample    : Retort door empty from cylinder at end A Inst     : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY  AB126    Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 15:36 19104               Quant Results File: KOPPERS.RES

  Method          : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
  Title           : 8260 Volatiles
  Last Update     : Fri Oct 08 18:37:49 2004
  Response via : Initial Calibration
```

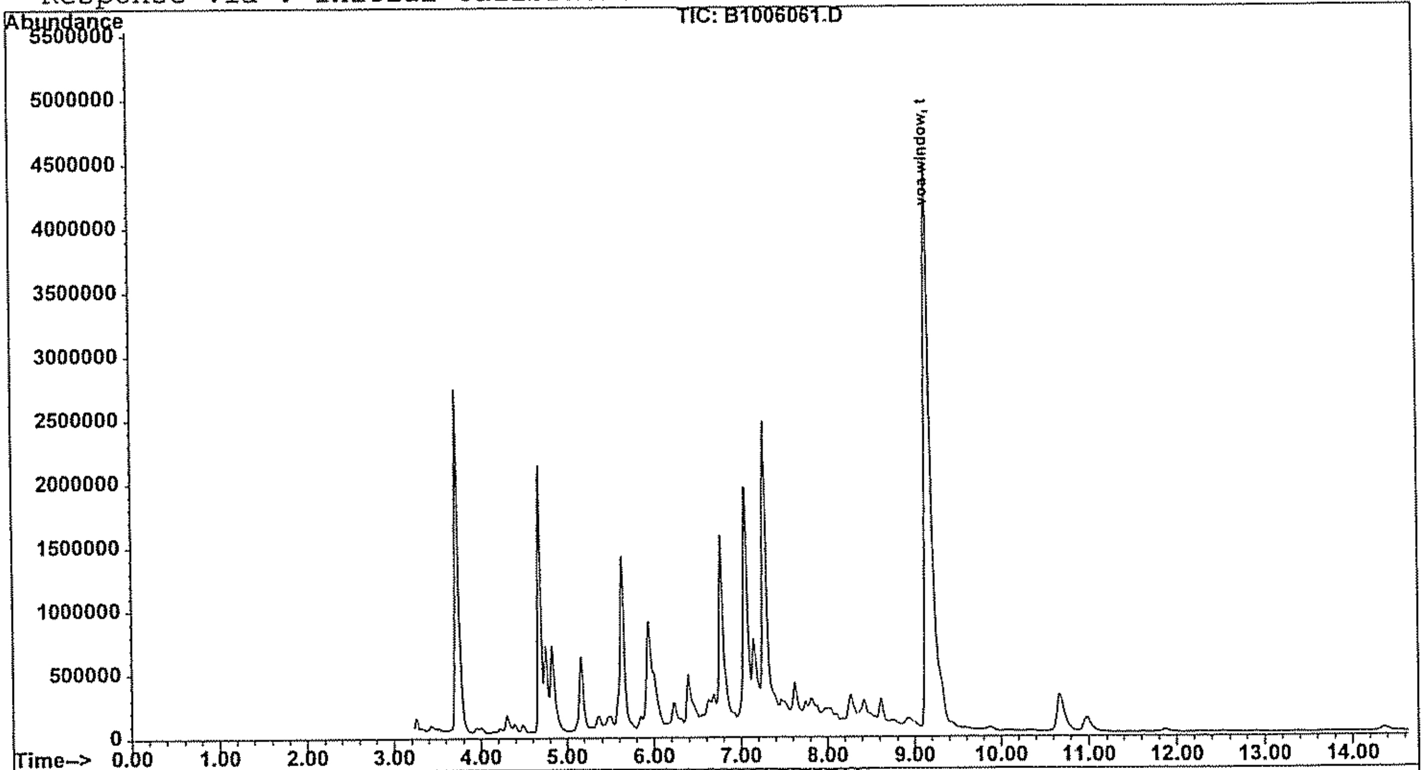


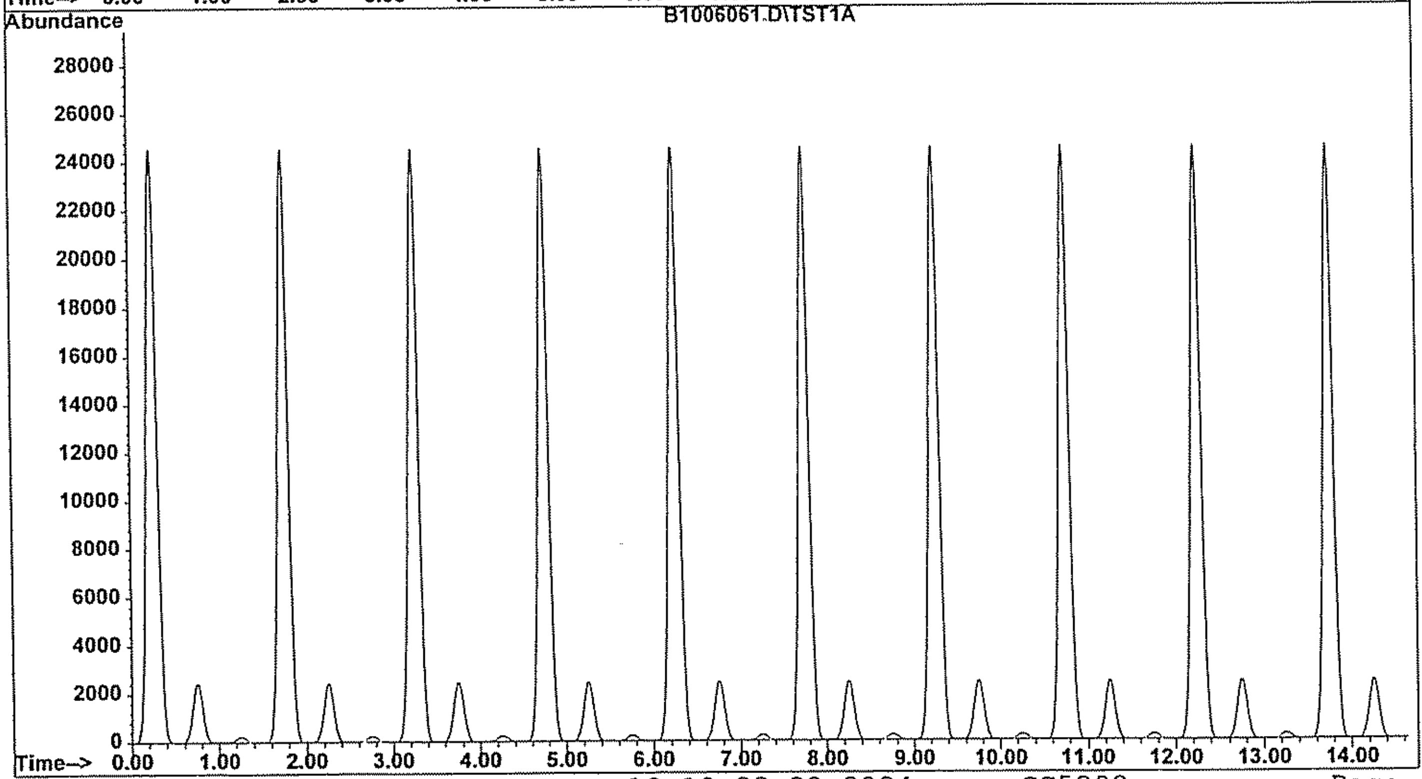


```
                              Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006061.D           Vial: 12
  Acq On    :  7 Oct 2004   3:21 pm                     Operator:`
  Sample    : Retort door empty from cylinder at end A Inst     : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY  AB126    Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 15:59 19104              Quant Results File: WINDOW.RES

  Quant Method : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
  Title        : koppers volatile window
  Last Update  : Wed Oct 06 18:41:15 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS


Internal Standards                R.T. QIon  Response  Conc Units Dev(Min)
--------------------------------------------------------------------------

System Monitoring Compounds

Target Compounds                                                   Qvalue
  1) voa window                  ,  9.17  TIC 946384451m   43.37 ng on




 --------------------------------------------------------------------------
 (#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006061.D          Vial: 12
Acq On    :  7 Oct 2004   3:21 pm                    Operator:
Sample    : Retort door empty from cylinder at end A Inst     : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY  AB126    Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 15:59 19104               Quant Results File: WINDOW.RES

Method        : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
Title         : koppers volatile window
Last Update   : Fri Oct 08 18:40:27 2004
Response via  : Initial Calibration
```



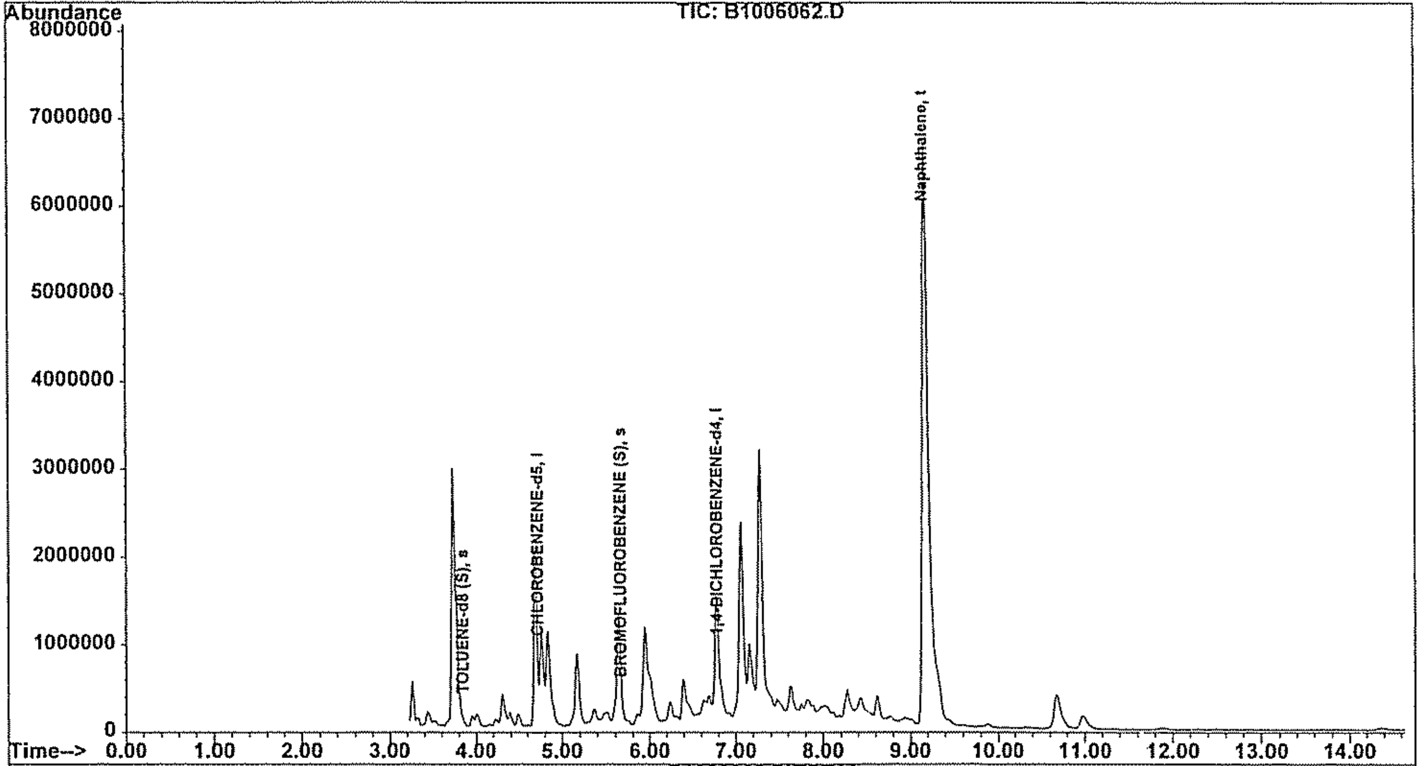


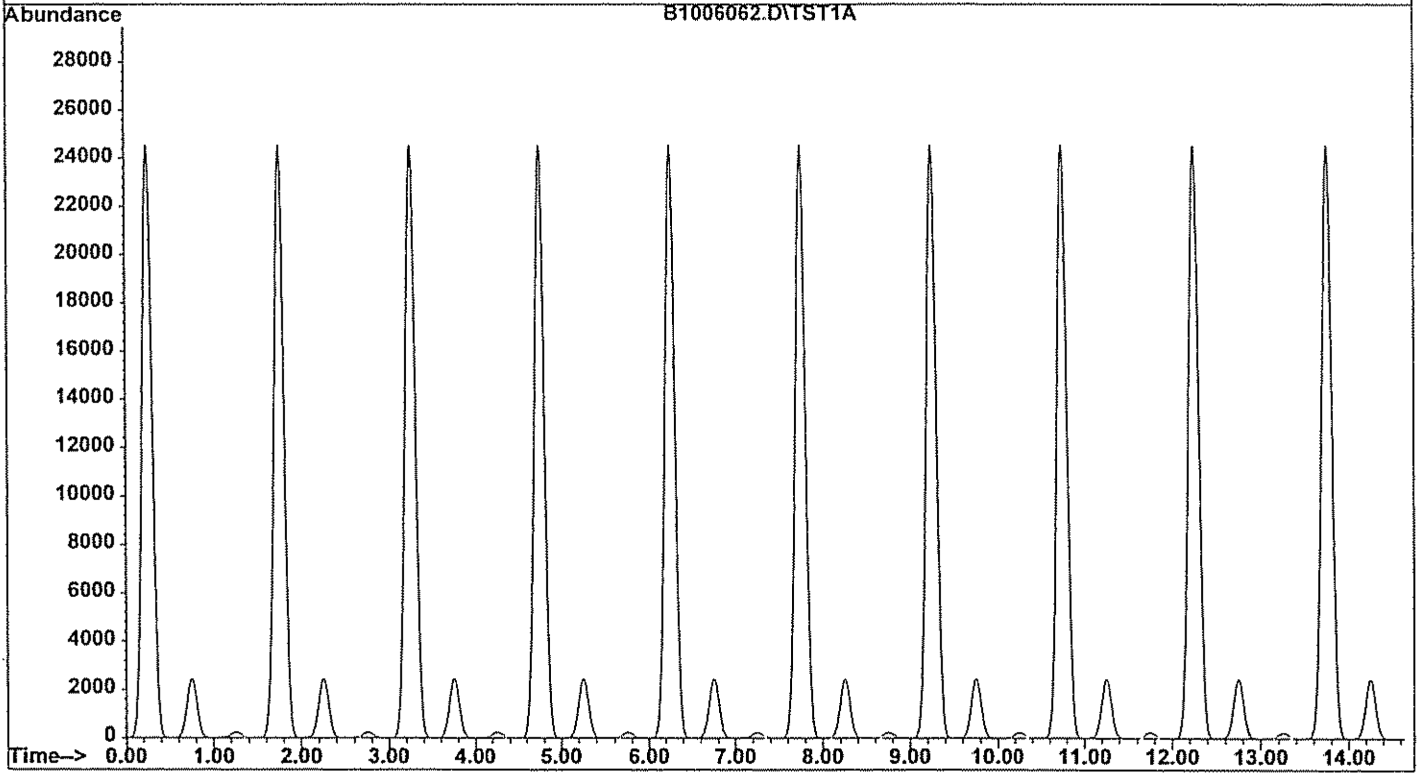
```
                              Quantitation Report    (QT Reviewed)

 Data File : C:\HPCHEM\1\DATA\B100604\B1006062.D          Vial: 13
 Acq On    :  7 Oct 2004   3:50 pm                     Operator:
 Sample    : Retort door empty 15-25min AB127          Inst     : GC/MS Ins
 Misc      : 10ml/3L   Koppers,  Guthrie,KY            Multiplr: 1.00
 Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
 Quant Time: Oct  7 16:05 19104                  Quant Results File: KOPPERS.RES

 Quant Method : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
 Title        : 8260 Volatiles
 Last Update  : Mon Oct 04 13:13:05 2004
 Response via : Initial Calibration
 DataAcq Meth : KOPPERS


Internal Standards                  R.T. QIon  Response  Conc Units Dev(Min)
-----------------------------------------------------------------------------

  1) CHLOROBENZENE-d5               4.74  117 15556052    50.00 ppb     0.00
  3) 1,4-DICHLOROBENZENE-d4         6.81  150 10185243    50.00 ppb    -0.02

System Monitoring Compounds
  2) TOLUENE-d8 (S)                 3.87   98 21121005    49.71 ppb     0.08
  Spiked Amount     50.000   Range  75 - 125    Recovery   =   99.42%
  4) BROMOFLUOROBENZENE (S)         5.69   95  8624885    53.24 ppb    -0.02
  Spiked Amount     50.000   Range  75 - 125    Recovery   =  106.48%

Target Compounds                                                   Qvalue
  5) Naphthalene                    9.17  128 143041329   474.37 ppb      100
```

```
-----------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006062.D         Vial: 13
Acq On    :  7 Oct 2004   3:50 pm                   Operator:
Sample    : Retort door empty 15-25min AB127        Inst    : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY          Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 16:05 19104               Quant Results File: KOPPERS.RES

Method        : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
Title         : 8260 Volatiles
Last Update   : Fri Oct 08 18:37:49 2004
Response via  : Initial Calibration
```



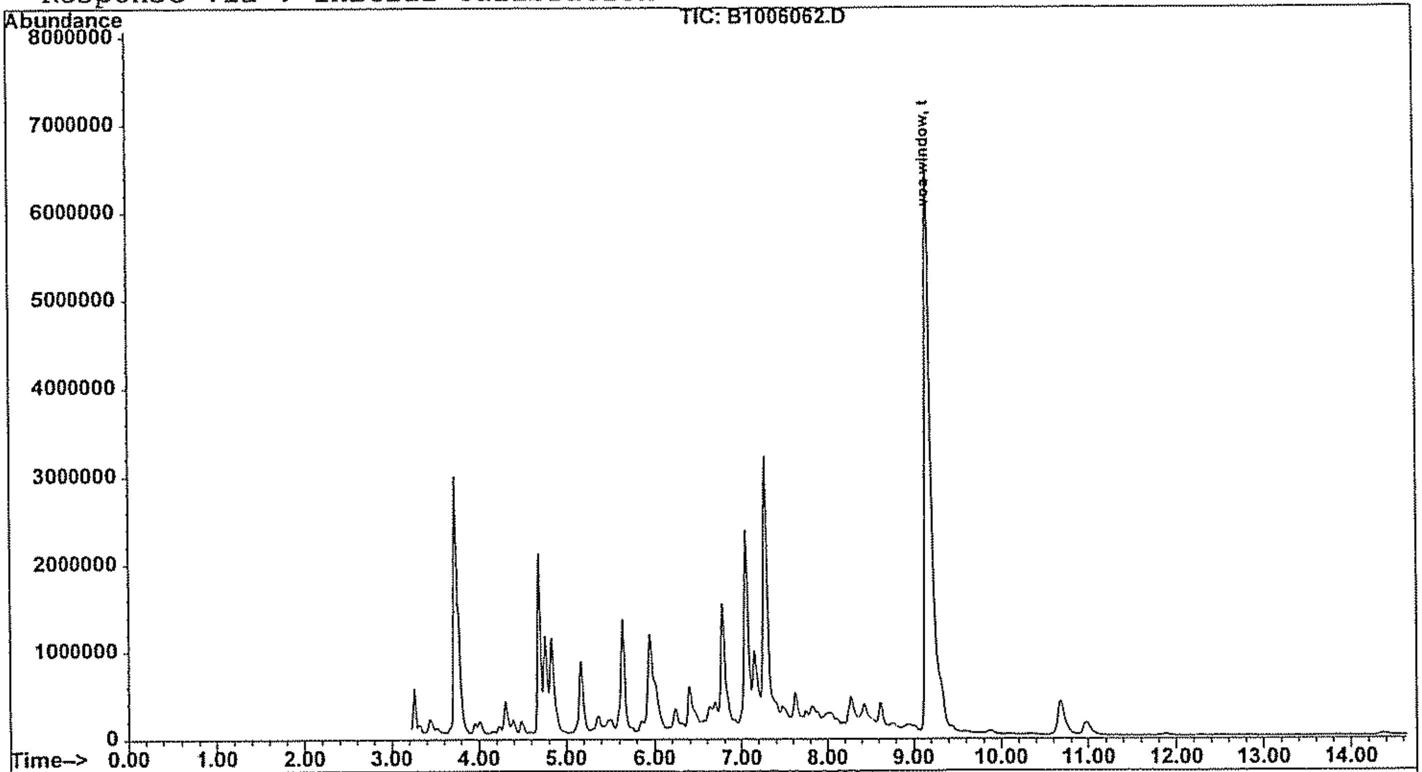


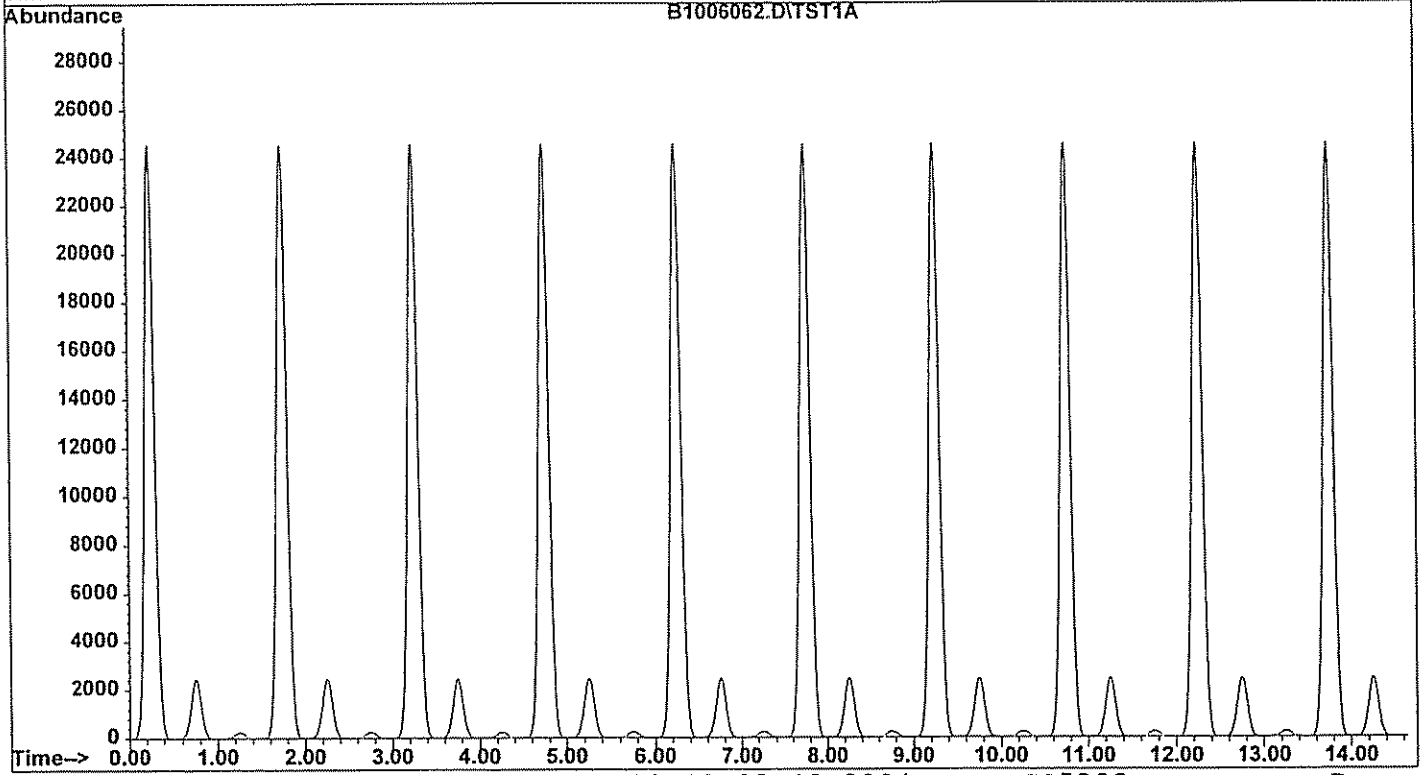
```
                         Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006062.D        Vial: 13
  Acq On    :  7 Oct 2004   3:50 pm                   Operator:
  Sample    : Retort door empty 15-25min AB127        Inst     : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY          Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 19:50 19104               Quant Results File: WINDOW.RES

  Quant Method : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
  Title        : koppers volatile window
  Last Update  : Wed Oct 06 18:41:15 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS


Internal Standards                R.T. QIon  Response  Conc Units Dev(Min)
---------------------------------------------------------------------------

System Monitoring Compounds

Target Compounds                                                     Qvalue
  1) voa window                   9.17  TIC 1175999089m   54.45 ng on
```

```
---------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

Quantitation Report

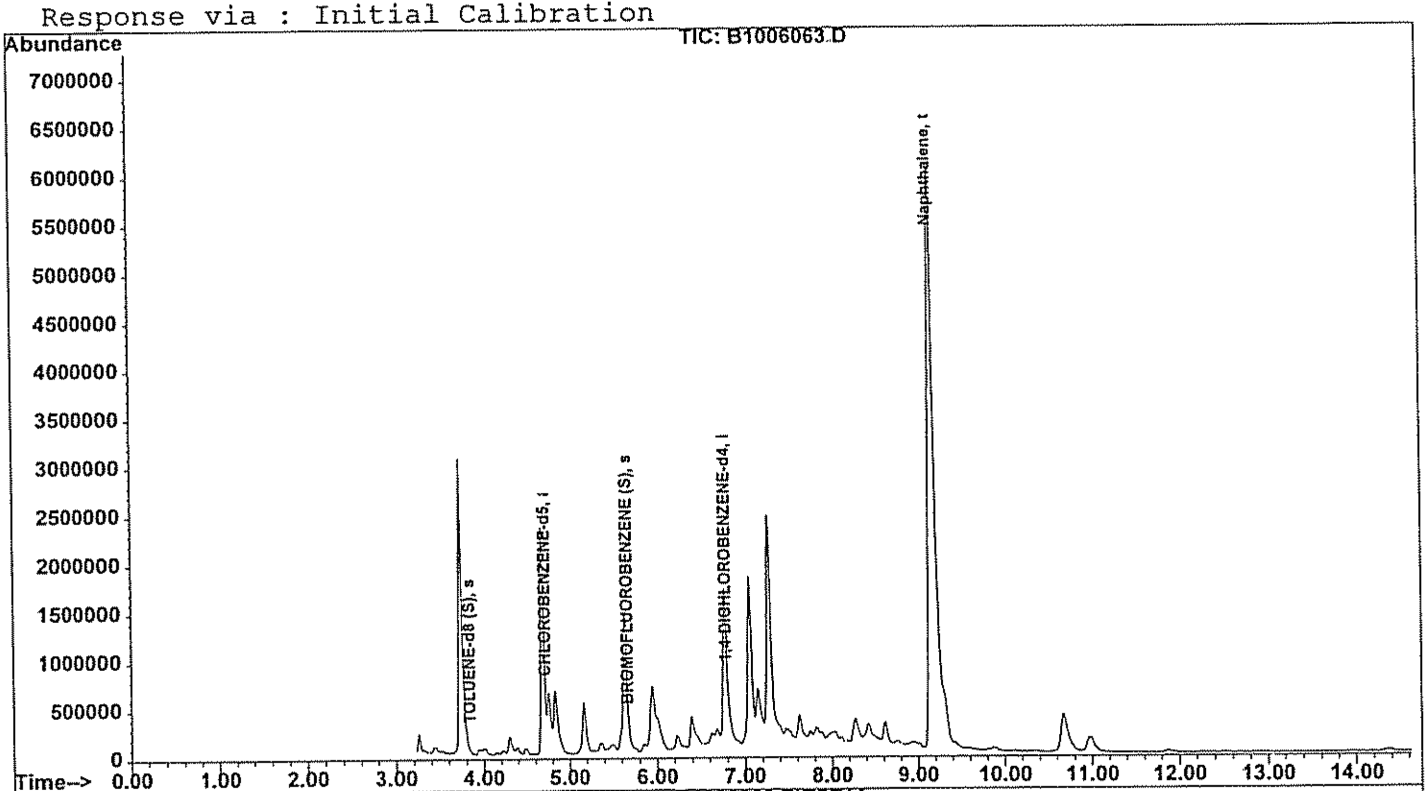
```
Data File : C:\HPCHEM\1\DATA\B100604\B1006062.D          Vial: 13
Acq On    :  7 Oct 2004   3:50 pm                   Operator:
Sample    : Retort door empty 15-25min AB127        Inst     : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY          Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 19:50 19104              Quant Results File: WINDOW.RES

Method         : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
Title          : koppers volatile window
Last Update    : Fri Oct 08 18:40:27 2004
Response via   : Initial Calibration
```

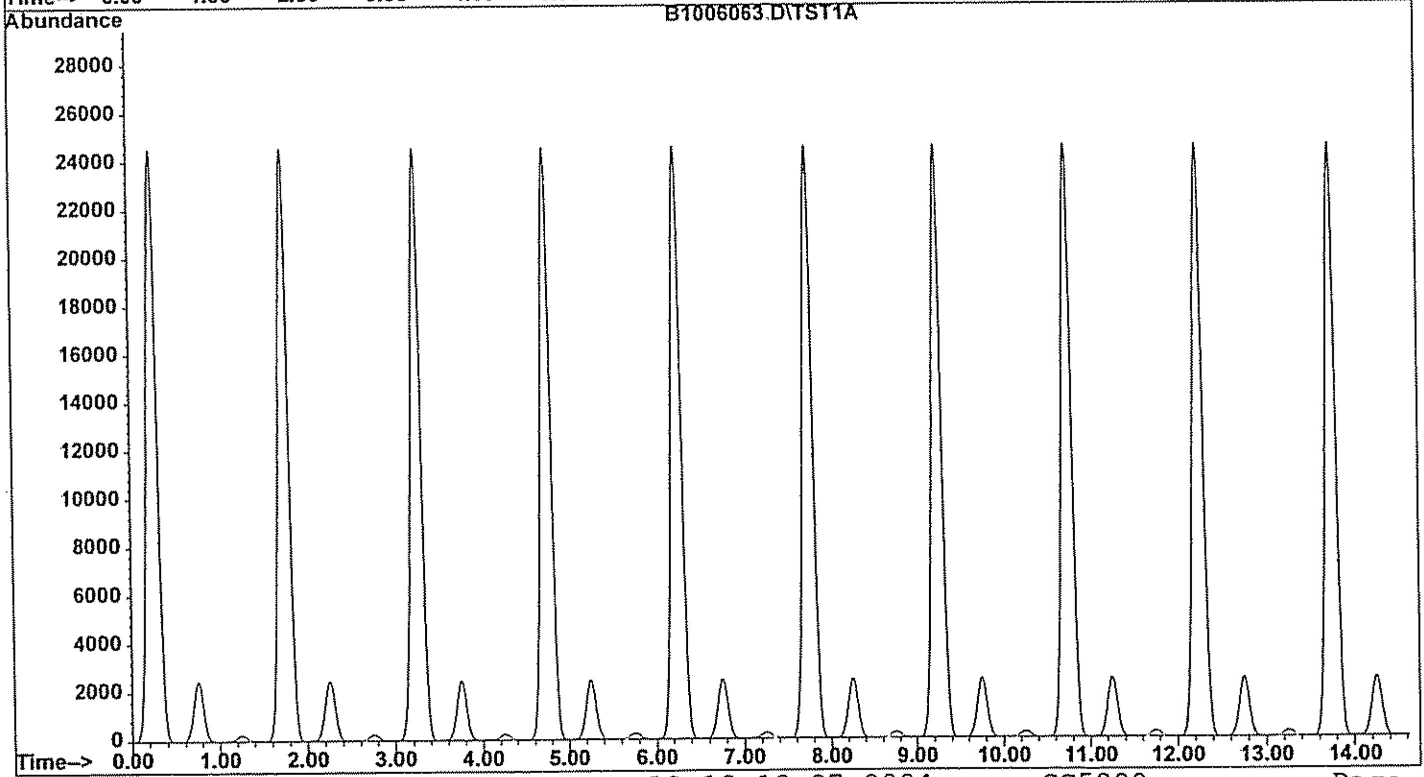




```
                              Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006063.D          Vial: 14
  Acq On    :  7 Oct 2004   4:20 pm                    Operator:
  Sample    : Retort door empty 20-30min AB128         Inst     : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY           Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 16:34 19104                   Quant Results File: KOPPERS.RES

  Quant Method : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
  Title        : 8260 Volatiles
  Last Update  : Mon Oct 04 13:13:05 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS


Internal Standards                      R.T. QIon  Response  Conc Units Dev(Min)
-----------------------------------------------------------------------------

  1) CHLOROBENZENE-d5                   4.74  117 17678790    50.00 ppb     0.00
  3) 1,4-DICHLOROBENZENE-d4             6.81  150 11534411    50.00 ppb    -0.02

System Monitoring Compounds
  2) TOLUENE-d8 (S)                     3.87   98 23631879    48.94 ppb     0.08
  Spiked Amount     50.000   Range  75 - 125    Recovery   =   97.88%
  4) BROMOFLUOROBENZENE (S)             5.69   95 10038659    54.72 ppb    -0.02
  Spiked Amount     50.000   Range  75 - 125    Recovery   =  109.44%

Target Compounds                                                      Qvalue
  5) Naphthalene                        9.17  128 129007977   377.79 ppb      100
```

```
                     Quantitation Report

Data File : C:\HPCHEM\1\DATA\B100604\B1006063.D        Vial: 14
Acq On    :  7 Oct 2004   4:20 pm                   Operator:
Sample    : Retort door empty 20-30min AB128        Inst    : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY          Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 16:34 19104               Quant Results File: KOPPERS.RES

Method       : C:\HPCHEM\1\METHODS\KOPPERS.M (Chemstation Integrator)
Title        : 8260 Volatiles
Last Update  : Fri Oct 08 18:37:49 2004
Response via : Initial Calibration
```



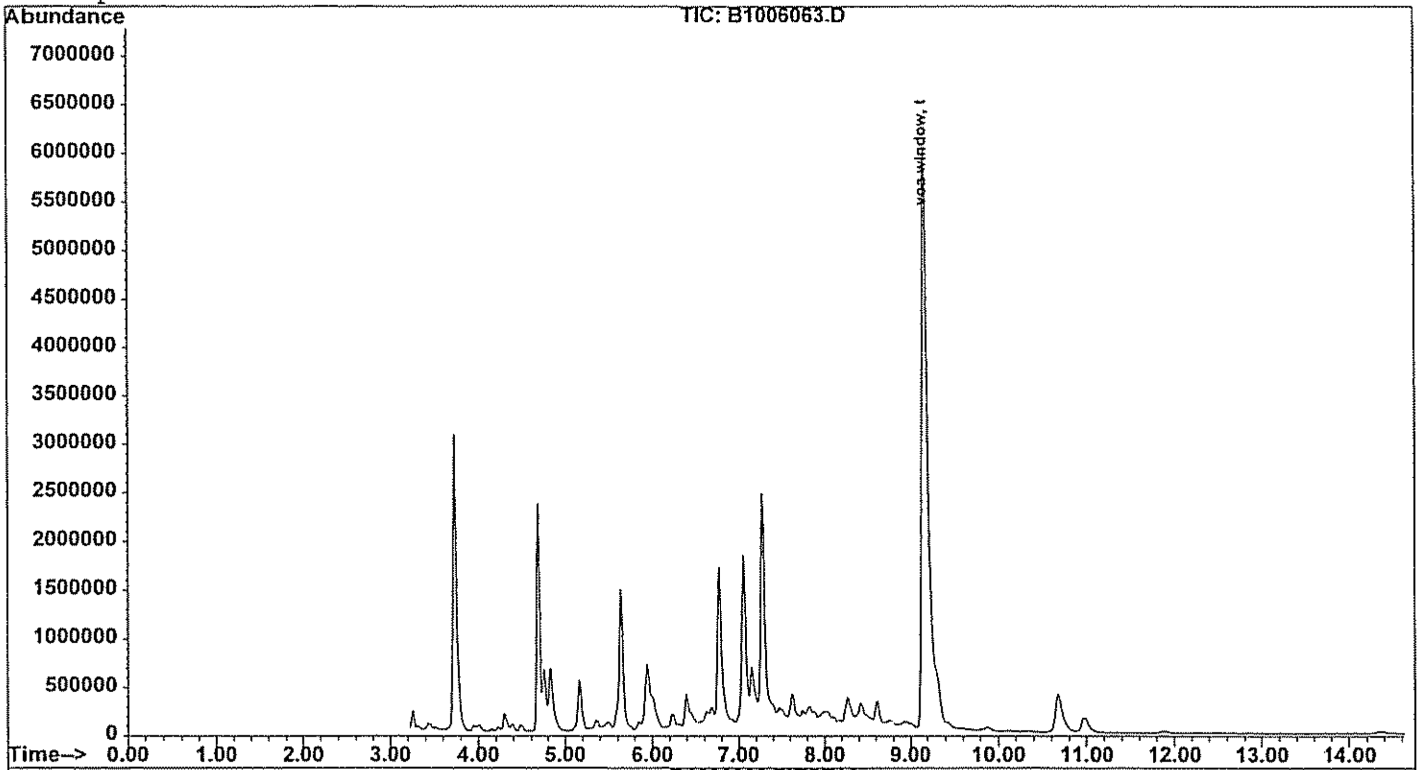


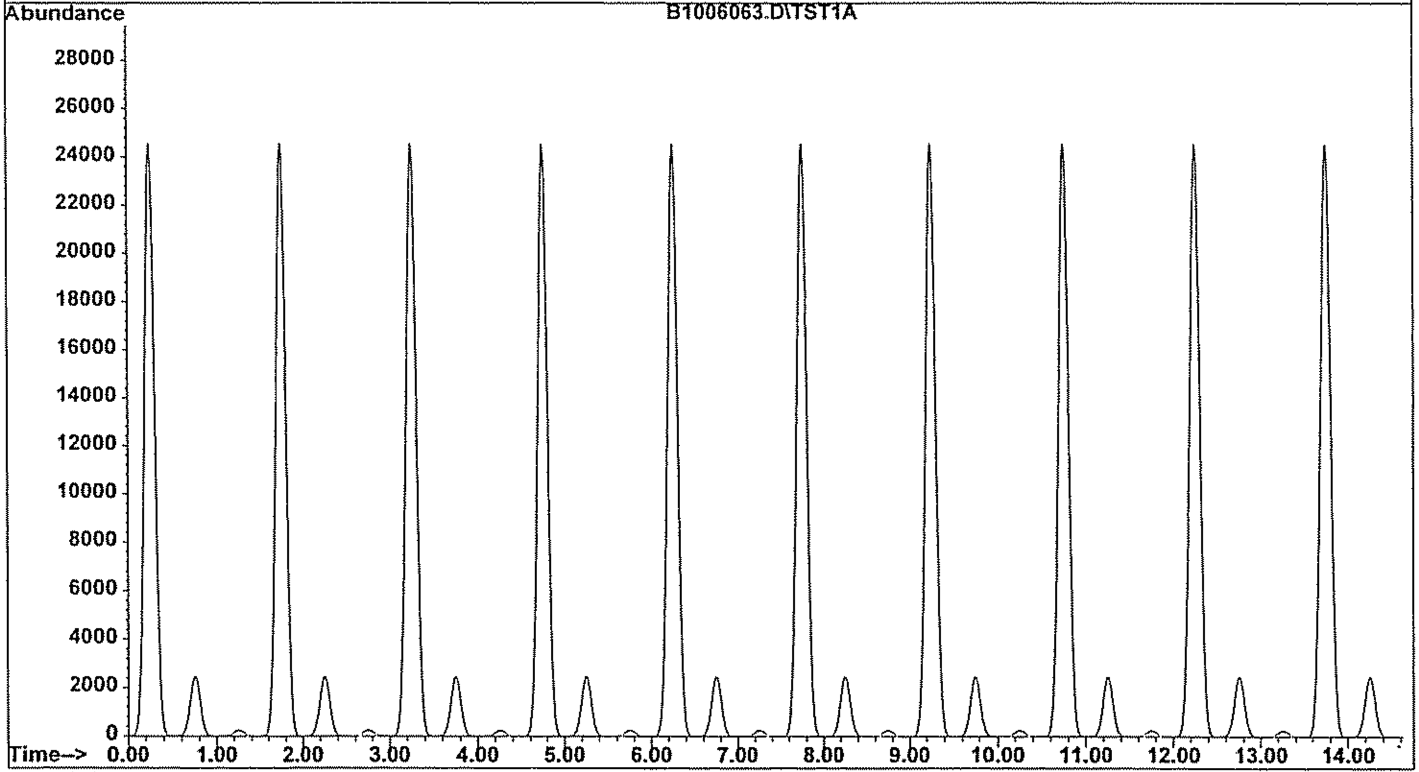
```
                            Quantitation Report    (QT Reviewed)

  Data File : C:\HPCHEM\1\DATA\B100604\B1006063.D          Vial: 14
  Acq On    :  7 Oct 2004   4:20 pm                    Operator:
  Sample    : Retort door empty 20-30min AB128         Inst     : GC/MS Ins
  Misc      : 10ml/3L   Koppers,  Guthrie,KY           Multiplr: 1.00
  Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
  Quant Time: Oct  7 19:50 19104              Quant Results File: WINDOW.RES

  Quant Method : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
  Title        : koppers volatile window
  Last Update  : Wed Oct 06 18:41:15 2004
  Response via : Initial Calibration
  DataAcq Meth : KOPPERS


Internal Standards                R.T. QIon  Response  Conc Units Dev(Min)
-------------------------------------------------------------------------

System Monitoring Compounds

Target Compounds                                                    Qvalue
  1) voa window                   9.17  TIC 942254275m   43.17 ng on
```

```
-------------------------------------------------------------------------
(#) = qualifier out of range (m) = manual integration
```

Quantitation Report

```
Data File : C:\HPCHEM\1\DATA\B100604\B1006063.D          Vial: 14
Acq On    :  7 Oct 2004   4:20 pm                      Operator:
Sample    : Retort door empty 20-30min AB128           Inst    : GC/MS Ins
Misc      : 10ml/3L   Koppers,  Guthrie,KY             Multiplr: 1.00
Integration Parameters -  MS: events.e   GC1: events2.e   GC2: events3.e
Quant Time: Oct  7 19:50 19104               Quant Results File: WINDOW.RES

Method        : C:\HPCHEM\1\METHODS\WINDOW.M (Chemstation Integrator)
Title         : koppers volatile window
Last Update   : Fri Oct 08 18:40:27 2004
Response via  : Initial Calibration
```





KOPPERS FIELD TEST
LABORATORY RESULTS - FULL RETORT

Sample ID	**Retort door background**	0554-0604
Lab ID	AB104	
Collection Date	10/5/04	
Analysis Date	10/5/04	5:57 PM
Run No.	B1005013	
sample matrix	A	

	Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
	Naphthalene	6.56	U	0.00	0
	VOA Window	1098	J	10.17	1017
ng/ml	**Surrogates**	**%**			
49.54	Toluene-d8	99.1%			
51.78	Bromofluorobenzene	103.6%			

Sample ID	**Retort door full tram 0-5 min**	0731-0736
Lab ID	AB105	
Collection Date	10/6/04	
Analysis Date	10/6/04	9:29 AM
Run No.	B1006008	
sample matrix	A	

	Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
	Naphthalene	6.56		258.14	129.07
	VOA Window	1098		31.36	3136
ng/ml	**Surrogates**	**%**			
45.90	Toluene-d8	91.8%			
45.33	Bromofluorobenzene	90.7%			

Sample ID	**Retort door full tram 5-15 min**	0736-0746
Lab ID	AB106	
Collection Date	10/6/04	
Analysis Date	10/6/04	9:58 AM
Run No.	B1006009	
sample matrix	A	

	Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
	Naphthalene	6.56		96.85	48.43
	VOA Window	1098		29.95	2995
ng/ml	**Surrogates**	**%**			
48.60	Toluene-d8	97.2%			
49.06	Bromofluorobenzene	98.1%			

KOPPERS FIELD TEST
LABORATORY RESULTS - FULL RETORT

Sample ID	**Retort door full tram 15-25 min**	0746-0756
Lab ID	AB107	
Collection Date	10/6/04	
Analysis Date	10/6/04	10:56 AM
Run No.	B1006011	
sample matrix	A	

	Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
	Naphthalene	6.56		102.02	51.01
	VOA Window	1098		37.41	3741
ng/ml	**Surrogates**	**%**			
48.04	Toluene-d8	96.1%			
49.99	Bromofluorobenzene	100.0%			

Sample ID	**Retort door full tram 25-30 min**	0756-0806
Lab ID	AB108	
Collection Date	10/6/04	
Analysis Date	10/6/04	10:27 AM
Run No.	B1006010	
sample matrix	A	

	Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
	Naphthalene	6.56		92.70	46.35
	VOA Window	1098		30.19	3019
ng/ml	**Surrogates**	**%**			
47.50	Toluene-d8	95.0%			
47.20	Bromofluorobenzene	94.4%			

KOPPERS FIELD TEST
LABORATORY RESULTS - EMPTY RETORT

	Sample ID	**Retort door empty Background**	1323-1333			
	Lab ID	AB123				
	Collection Date	10/6/04				
	Analysis Date	10/7/04	12:54 PM			
	Run No.	B1006058				
	sample matrix	A				
	Compound	**MDL**		**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
	Naphthalene	6.56			24.72	12.36
	VOA Window	1098		J	5.77	577
ng/ml	**Surrogates**	**%**				
46.27	Toluene-d8	92.5%				
50.95	Bromofluorobenzene	101.9%				

	Sample ID	**Retort door empty 0-5 min**	1339-1344			
	Lab ID	AB124				
	Collection Date	10/6/04				
	Analysis Date	10/7/04	1:22 PM			
	Run No.	B1006059				
	sample matrix	A				
	Compound	**MDL**		**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
	Naphthalene	6.56			286.17	143.09
	VOA Window	1098			61.91	6191
ng/ml	**Surrogates**	**%**				
50.86	Toluene-d8	101.7%				
48.04	Bromofluorobenzene	96.1%				

	Sample ID	**Retort door empty 5-10 min**	1344-1349			
	Lab ID	AB125				
	Collection Date	10/6/04				
	Analysis Date	10/7/04	1:52 PM			
	Run No.	B1006060				
	sample matrix	A				
	Compound	**MDL**		**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
	Naphthalene	6.56			609.58	304.79
	VOA Window	1098			72.1	7210
ng/ml	**Surrogates**	**%**				
44.3	Toluene-d8	88.6%				
45.13	Bromofluorobenzene	90.3%				

KOPPERS FIELD TEST
LABORATORY RESULTS - EMPTY RETORT

Sample ID	**Retort door empty from cylinder at end**	1418-1428
Lab ID	AB126	
Collection Date	10/6/04	
Analysis Date	10/7/04	2:21 PM
Run No.	B1006061	
sample matrix	A	

	Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
	Naphthalene	6.56		308.78	154.39
	VOA Window	1098		43.37	4337
ng/ml	**Surrogates**	**%**			
51.37	Toluene-d8	102.7%			
56.77	Bromofluorobenzene	113.5%			

Sample ID	**Retort door empty 10-20 min**	1349-1359
Lab ID	AB127	
Collection Date	10/6/04	
Analysis Date	10/7/04	2:50 PM
Run No.	B1006062	
sample matrix	A	

	Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
	Naphthalene	6.56		474.37	237.19
	VOA Window	1098		54.45	5445
ng/ml	**Surrogates**	**%**			
49.71	Toluene-d8	99.4%			
53.24	Bromofluorobenzene	106.5%			

Sample ID	**Retort door empty 20-30 min**	1359-1409
Lab ID	AB128	
Collection Date	10/6/04	
Analysis Date	10/7/04	3:20 PM
Run No.	B1006063	
sample matrix	A	

	Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
	Naphthalene	6.56		377.79	188.90
	VOA Window	1098		43.17	4317
ng/ml	**Surrogates**	**%**			
48.94	Toluene-d8	97.9%			
54.72	Bromofluorobenzene	109.4%			

APPENDIX 4

FIELD DATA

10/6/04 JGL

602 Arrive at Kopper's site to begin testing.
623 Outside Cylinder door 143°F
628 prepared cylinder for test
Stacks 72°, Air temperature 48°
enclosure is ready.
640 Shaw begins preparing Air testing equipment
7:22 cylinder opens, preparing enclosure for testing. 134°F
724 Enclosure goes on cylinder door
7:30 5:43 59 from time air is released until ko
731 begin testing (Shaw)
735 condens hot is leaking from testing pipe
736 pipe temp 107°
738 paul takes wet-dry temp
739 84° wet 88° dry.
743 Leah begins taking SVOC reading
744 pipe temp 106.5°F, temp has dropped .5°
745 ~~first~~ JGL second sample has been pulled and making it's way to lab in parking lot 300 yard away.

10/8/04 VGL

7:49 enclosure is checked by Gary (O.K.)

7:44 106.5° at 17.35 min into testing

754 temp of pipe is at 109°f, ~~[illegible]~~
slowest drop

755 ~~second~~ Third ss sample is pulled
32 min

8:04 Plywood 109°F

805 testing is complete 4 samples
have been pulled and are making thier
way to lab to be analyzed.

807 test went smoothly. Kopper is
preparing to remove timbers.

809 timbers are coming out.

810 final tram wood temp 147°

10/6/04 JGL

13:11 Moving to 2nd cylinder door for ~~duplicate~~ test. without timber

13:15 cylinder enclosure is being place on door

13:17 Cylinder door is being opened, test equipment is ready

1334 Door temperature 108.5°, air temp 75°

1336 inside cylinder 149°

1338 2:31 from time vapor was admitted until enclosure was on cylinder and testing started

1339 enclosure Adjusted to fit flush.

1341 test 87° pipe.

1344 first readings are taken,

1346 Wet bulb test started, wet bulb temp 86°, pipe temp 99.5, air temp 110;

1350 first sample is pulled. after five min

1352 pipe temp 104.5, temp. is increasing. to 142° inside cylinder, temp. is coming down.

1358 Third sample is taken, and is being brought to Lab.

1400 Take velocity reading, start wet bulb measurment

1405 Wet bulb temp [illegible] 78°

10/6/04 JGL

1408 Exhaust Air 119.5, pipe 104°; plywood 101.5°; inside cylind 109°

1410 Last sample is taken, ~~moving~~
~~back to timber & enclosure~~

1415 Take air sample from inside creosote processing area. Taking sample directly from vacuum pump.

1423 check sample bag, inflating fine

1428 Sample is collected, outside pump flang 74°.

APPENDIX 5

TEST PROCEDURES

Appendix 5a.
On-Site Laboratory Methods

Shaw™

Shaw Environmental & Infrastructure, Inc.

CHEMICAL QUALITY ASSESSMENT REPORT

FOR

ON-SITE LABORATORY OPERATIONS

AIR EMMISIONS STUDY

KOPPERS FACILITY GUTHRIE, KY

Guy Gallello, Jr- Project QA Chemist

November 10, 2004

INTRODUCTION

During the week of October 6, 2004 Shaw Environmental, Inc. (Shaw) a division of Shaw Group, Inc. performed an air emissions study at the Koppers Facility in Guthrie, KY. This study was supported by on-site laboratory analysis for Naphthalene and Total Volatile Creosote Envelope (TVC) provided by Direct Push Analytical, Inc.
The on-site analysis was performed in accordance with the protocols presented in a previously submitted Sampling and Analysis Plan for the Field Emissions Study, which is included elsewhere in this project report.

This Chemical Data Quality Assessment Report (CDQAR) is intended to provide an assessment of the overall data quality for the on-site laboratory analyses only. It will not address any of the field QC including duplicate performance as this has been discussed in other portions of the report. This assessment will include discussions of the analytical methods used, summaries of QC results, performance demonstration data, instrument calibrations, and comparisons to the previously established quality objectives.

ANALYSIS METHODS

The on-site laboratory utilized a modified purge and trap method with GC-MS detection for both the naphthalene and TVC analyses. The GC-MS system was operated in accordance with the requirements of method 8260B in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Update IV.* The air samples were analyzed by drawing a known volume from the Tedlar™ bag and injecting it into a measured volume of water through the purge and trap instrument port and then analyzing the resulting solution via SW-8260B.

Naphthalene by GC-MS

The GC-MS system was calibrated for naphthalene along with two of the Method 8260B surrogate compounds-toluene-d8 and Bromoflourobenzene. The GC parameters were modified from those in method 8260B to provide for a more rapid and targeted analysis. The modification to the program included a higher starting temperature (80 degrees C) and faster temperature ramp. This provided naphthalene analysis in a GC-MS run-time of approximately 27 minutes with a sample cycle time of approximately 45 minutes.

Sample analysis consisted of heating each Tedlar™ bag sample in a heated water bath, held at 60 degrees Celsius, for a minimum of 10 minutes. This heating served to force the less volatile components into the vapor phase and allowed for analysis of air bags while at an equilibrium state. Following the requisite 10minutes in the heated bath each sample bag was removed and 10ml of the headspace withdrawn and injected into 5ml of water containing the surrogate and internal standard compounds. The resulting sample air solution was then analyzed and the total mass of naphthalene determined. The result was then mathematically expressed in ng/ml of air for reporting purposes.

Total Volatile Creosote Envelope Analysis

Originally TVC analysis was to be performed using direct injection of air samples onto a GC-FID system calibrated with standards made from a Koppers supplied creosote liquid material. This method proved difficult due mainly to the large amount of low-volatility compounds present in the creosote material and apparent solvation of volatiles in heavier non-volatile components of the mixture. These affects were evident when it became impossible to produce an acceptable calibration curve using the spiked bag technique.

A review of the sample chromatograms from the naphthalene analyses indicated the presence of other non-naphthalene components that encompassed a TVC envelope of purgeable and volatile components of the creosote mixture, several of which were identified from their mass spectral information. Following discussions with Koppers representatives it was decided to determine TVC by quantitation of the Total Ion Chromatogram (TIC) response of each sample.

A five point calibration curve was developed using known amounts of the Koppers supplied creosote mix in the same manner as for naphthalene. Each sample was "analyzed" only once- to determine naphthalene and surrogate spike performance. The TVC envelope was determined by performing data analysis only of the files against the quantitation file established for the TVC analysis. Thus, each sample analysis on the instrument provided data for both the naphthalene and TVC results. Calibration checks were performed with separate analytical runs- one check standard containing naphthalene and surrogates only, the second containing a known amount of the Koppers creosote material.

METHOD PERFORMANCE DEMONSTRATION

During the initial set-up and prior to analyzing any actual samples the ability of the analysis methods to accurately determine known amounts of naphthalene and creosote TVC was demonstrated in accordance with the procedure in SW-846. This procedure entails spiking and analyzing at least 7 bags at a concentration in air assumed to be close to the detection limit. The precision of this data is then used to estimate a method detection limit and the ability of the assay to adequately determine the target analytes in actual air matrices.

It should be noted that the Koppers supplied creosote material is composed primarily of non-volatile compounds as demonstrated by a mass loss analysis performed at 60 degrees C. This data, attached to this report resulted in an approximate five-percent volatile content determination. This "actual" TVC content was factored into the performance demonstration and detection-limit study by adjusting the known creosote spike values to reflect only the volatile mass component.

The data, attached to this report, is summarized below.

Performance Demonstration Results						
Analyte	**Spike in Air**	**Average**	**Std Deviation**	**% Recovery**	**MDL**	**PQL**
Naphthalene	2.5 ng/ml	2.4ng/ml	2.08	96.2	6.56ng/ml	19.7ng/ml
TVC envelope-adjusted for percent volatile content	510 ug/ml	570ug/ml	349	112	1100ug/ml	3300ug/ml

Based upon these results data was reported with J-flagging to the calculated MDLs.

INSTRUMENT CALIBRATION

The GC-MS instrument was mass-spectral tuned to 50ng Bromofluorobenzene (BFB) at the beginning of analyses and each 12 hours as required in method 8260B. Both the naphthalene and TVC calibration curves were 5-point multi-point calibrations. In addition, the two surrogate compounds were also 5-point calibrated. Calibration curves met method and SAP requirements for minimum response ratios and linearity.

Each 12-hours of operation the GC-MS BFB tune was checked and verified to be within compliance. A method blank, to demonstrate laboratory environment artifacts and possible bias on results was also analyzed within each 12-hour window. Calibration check standards for both the Naphthalene and TVC analyses were also analyzed. Criteria for these calibration checks were +/- 20% of known value for naphthalene and +/-35% for TVC. All calibration checks met requirements.

SURROGATE COMPOUND PERFORMANCE

Known concentrations of two surrogate compounds (Toluene-d8 and BFB) were added to the each sample prior to analysis. The surrogate performance serves as an indicator of purge efficiency and the ability of the analytical system to quantitate compounds with similar behavior to the target analytes. The surrogate responses were determined and reported in the quantitation process used to determine naphthalene.

All surrogates were recovered in accordance with the SAP criteria for all samples, calibration checks, and QC runs. The surrogate recoveries are included in the summary data for each sample located elsewhere in the project report.

LABORATORY DUPLICATES

Three site samples were analyzed in duplicate by withdrawing and analyzing a second 10ml aliquot of air from the Tedlar™ bag to ascertain and verify precision of the analytical system and methods. The results are summarized here.

Naphthalene- Relative Percent Difference (RPD) values ranged from 5.2 to 26 percent, well within the goals established in the SAP

TVC Envelope- RPD values in the two samples with detectable levels were less than 10 percent; also well within the criteria established.

MATRIX QUALITY CONTROL

Three air aliquots were re-analyzed along in water spiked with known concentrations of naphthalene and TVC in order to determine if matrix effects were present that could adversely affect the ability of the analytical system to properly determine the target analytes. These spiked sample aliquots were also analyzed in duplicate (MS/MSD) to ascertain the precision of the assay in the sample matrix. The results are summarized here.

Naphthalene- Recoveries ranged from 90 to 110 percent with precision estimates (RPD) values for each pair ranging from 11 to 27 percent. This performance is within the criteria established for acceptable data.

TVC- Recoveries ranged from 56 to 91 percent with an average of 73.5 percent. Precision (RPD) values ranged from 22.5 to 26.7, within the SAP established criteria.

OVERALL DATA QUALITY

The on-site laboratory data is supported by calibration and QC results that meet SAP established criteria and data quality goals. The data demonstrates that the analytical system was performing as expected and that results accurately reflect the concentrations of the target analytes in each air sample analyzed.

Appendix 5b.
Off-Site Laboratory Methods

DIRECT PUSH ANALYTICAL CORP. 18482 Sycamore Woods Dr.
Lawrenceburg, IN 47025
Sampling & Analysis 812-537-9140

Shaw Environmental and Infrastructure, Inc
2790 Mosside Blvd.
Monroeville, PA 15146

Koppers Field Test
Guthrie, KY

October 5 - 8, 2004

Case Narrative

All samples collected by Shaw E&I personnel for analysis by the mobile laboratory for this project were analyzed for target volatile compounds (naphthalene) and the total volatile window by SW-846 Method 8260b using Purge and Trap techniques to introduce the target compounds to the GC/MS system.

Project specific MDL studies for both naphthalene and the “total volatile window” were performed on-site to demonstrate the effectiveness of the procedures to be used for the project.

All samples that were collected by site personnel were stored in the dark prior to analysis to minimize the potential of any photo-degradation of the samples. Just prior to analysis, the samples in the Tedlar bags were placed in a temperature controlled water bath at $60\pm2^{o}C$ for 5-8 minutes to bring the samples to a constant temperature and increase the volatilization of target compounds. Once thermal equilibrium had been reached, an aliquot of the air in the bags (10 ml) was injected into the purge and trap system during the purge cycle. At the completion of the Tekmar cycle, the samples were desorbed onto the GC/MS system and analyzed by Method 8260b for the presence of naphthalene. A separate method was used to determine the area associated with the predominant volatile window associated with the compounds present in the “volatile window” that contained the primary peaks present from the first surrogate (Toluene-d8) to near the end of the analytical run.

Although results are presented in the report that are less than the statistically derived MDL, the analytical system is sensitive enough to see below this level. All results below the statistically derived MDL listed in the report should be considered as ESTIMATED values even though they are not flagged with an “E”.

NOTE:

All Naphthalene results are in ng/ml of sample purged
All “Volatile window” results are in ug/ml of sample purged

Data Qualifiers

B	Compound was detected in the blank
U	Compound was analyzed for but not detected above the lower detection ability of the instrument
J	The compound results were between the MDL and the RL
E	The concentration found in the sample exceeds the calibration range of the instrument; RESULTS ARE ESTIMATED
NOTE:	Reporting Limits do not reflect any sample dilutions that may have been performed

This report is for the exclusive use of the client. Any reproduction or dissemination without the express permission of the client is prohibited.

DIRECT PUSH ANALYTICAL CORP.

18482 Sycamore Woods Dr.
Lawrenceburg, IN 47025
812-537-9140

Sampling & Analysis

8260 Volatile Results

Sample ID	**Retort door background**	0554-0604
Lab ID	AB104	
Collection Date	10/5/04	
Analysis Date	10/5/04	5:57 PM
Run No.	B1005013	
sample matrix	A	

Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	U	0.00	
VOA Window	1.1	B	10.17	1.02ug/ml
Surrogates	**%**			
Toluene-d8	99.1			
Bromofluorobenzene	104			

Sample ID	**Retort door full tram 0-5 min**	0731-0736
Lab ID	AB105	
Collection Date	10/6/04	
Analysis Date	10/6/04	9:29 AM
Run No.	B1006008	
sample matrix	A	

Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	B	258.14	129.07
VOA Window	1.1	B	31.36	3.14ug/ml
Surrogates	**%**			
Toluene-d8	91.8			
Bromofluorobenzene	90.7			

Sample ID	**Retort door full tram 5-15 min**	0736-0746
Lab ID	AB106	
Collection Date	10/6/04	
Analysis Date	10/6/04	9:58 AM
Run No.	B1006009	
sample matrix	A	

Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	B	96.85	48.43
VOA Window	1.1	B	29.95	3.00ug/ml
Surrogates	**%**			
Toluene-d8	97.2			
Bromofluorobenzene	98.1			

Sample ID	**Retort door full tram 15-25 min**	0746-0756
Lab ID	AB107	
Collection Date	10/6/04	
Analysis Date	10/6/04	10:56 AM
Run No.	B1006011	
sample matrix	A	

Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	B	102.02	51.01
VOA Window	1.1	B	37.41	3.74ug/ml
Surrogates	**%**			
Toluene-d8	96.1			
Bromofluorobenzene	100			

DIRECT PUSH ANALYTICAL CORP.

18482 Sycamore Woods Dr.
Lawrenceburg, IN 47025
812-537-9140

Sampling & Analysis

Sample ID	**Retort door full tram 25-30 min**	0756-0806
Lab ID	AB108	
Collection Date	10/6/04	
Analysis Date	10/6/04	10:27 AM
Run No.	B1006010	
sample matrix	A	

Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	B	92.70	46.35
VOA Window	1.1	B	30.19	3.02ug/ml
Surrogates	**%**			
Toluene-d8	95			
Bromofluorobenzene	94.4			

Sample ID	**Retort door empty Background**	1323-1333
Lab ID	AB123	
Collection Date	10/6/04	
Analysis Date	10/7/04	12:54 PM
Run No.	B1006058	
sample matrix	A	

Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	B	24.72	12.36
VOA Window	1.1	B	5.77	0.577ug/ml
Surrogates	**%**			
Toluene-d8	92.5			
Bromofluorobenzene	102			

Sample ID	**Retort door empty 0-5 min**	1339-1344
Lab ID	AB124	
Collection Date	10/6/04	
Analysis Date	10/7/04	1:22 PM
Run No.	B1006059	
sample matrix	A	

Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	B	286.17	143.09
VOA Window	1.1	B	61.91	6.19ug/ml
Surrogates	**%**			
Toluene-d8	102			
Bromofluorobenzene	96.1			

Sample ID	**Retort door empty 5-10 min**	1344-1349
Lab ID	AB125	
Collection Date	10/6/04	
Analysis Date	10/7/04	1:52 PM
Run No.	B1006060	
sample matrix	A	

Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	BE	609.58	304.79
VOA Window	1.1	B	72.1	7.21ug/ml
Surrogates	**%**			
Toluene-d8	88.6			
Bromofluorobenzene	90.3			

Sample ID	**Retort door empty from cylinder at end**	1418-1428
Lab ID	AB126	
Collection Date	10/6/04	
Analysis Date	10/7/04	2:21 PM
Run No.	B1006061	
sample matrix	A	

Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	B	308.78	154.39
VOA Window	1.1	B	43.37	4.34ug/ml
Surrogates	**%**			
Toluene-d8	103			
Bromofluorobenzene	114			

Sample ID	**Retort door empty 15-25 min**	1349-1359
Lab ID	AB127	
Collection Date	10/6/04	
Analysis Date	10/7/04	2:50 PM
Run No.	B1006062	
sample matrix	A	

Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	BE	474.37	237.19
VOA Window	1.1	B	54.45	5.44ug/ml
Surrogates	**%**			
Toluene-d8	99.4			
Bromofluorobenzene	107			

Sample ID	**Retort door empty 20-30 min**	1359-1409
Lab ID	AB128	
Collection Date	10/6/04	
Analysis Date	10/7/04	3:20 PM
Run No.	B1006063	
sample matrix	A	

Compound	**MDL**	**Qualifier**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	B	377.79	188.90
VOA Window	1.1	B	43.17	4.32ug/ml
Surrogates	**%**			
Toluene-d8	97.9			
Bromofluorobenzene	110			

QUALITY CONTROL

INSTRUMENT / METHOD BLANKS

Sample ID		
Lab ID		
Collection Date		
Analysis Date	10/5/04	10:21 AM
Run No.	B1005003	
sample matrix	A	

Compound	**MDL**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	2.73	1.37
VOA Window	1.1	ND	U
Surrogates	**%**		
Toluene-d8	97.8		
Bromofluorobenzene	98.3		

Sample ID		
Lab ID		
Collection Date		
Analysis Date	10/6/04	9:00 AM
Run No.	B1006007	
sample matrix	A	

Compound	**MDL**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	1.95	0.98
VOA Window	1.1	ND	U
Surrogates	**%**		
Toluene-d8	100		
Bromofluorobenzene	96.9		

DIRECT PUSH ANALYTICAL CORP.

Sampling & Analysis

18482 Sycamore Woods Dr.
Lawrenceburg, IN 47025
812-537-9140

Sample ID		
Lab ID		
Collection Date		
Analysis Date	10/6/04	9:00 PM
Run No.	B1006030	
sample matrix	A	

Compound	**MDL**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	8.11	4.06
VOA Window	1.1	2.91	0.291ug/ml
Surrogates	**%**		
Toluene-d8	92.5		
Bromofluorobenzene	91.6		

Sample ID		
Lab ID		
Collection Date		
Analysis Date	10/7/04	10:01 AM
Run No.	B1006052	
sample matrix	A	

Compound	**MDL**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	15.23	7.62
VOA Window	1.1	0.49	0.049ug/ml
Surrogates	**%**		
Toluene-d8	101		
Bromofluorobenzene	106		

DIRECT PUSH ANALYTICAL CORP.
Sampling & Analysis

18482 Sycamore Woods Dr.
Lawrenceburg, IN 47025
812-537-9140

Sample ID		
Lab ID		
Collection Date		
Analysis Date	10/7/04	9:10 PM
Run No.	B1006073	
sample matrix	A	

Compound	**MDL**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	9.66	4.83
VOA Window	1.1	4.82	0.482ug/ml
Surrogates	**%**		
Toluene-d8	112		
Bromofluorobenzene	119		

Sample ID		
Lab ID		
Collection Date		
Analysis Date	10/8/04	7:56 AM
Run No.	B1006094	
sample matrix	A	

Compound	**MDL**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	11.75	5.88
VOA Window	1.1	7.72	0.772ug/ml
Surrogates	**%**		
Toluene-d8	103		
Bromofluorobenzene	108		

DIRECT PUSH ANALYTICAL CORP.

Sampling & Analysis

18482 Sycamore Woods Dr.
Lawrenceburg, IN 47025
812-537-9140

Sample ID		
Lab ID		
Collection Date		
Analysis Date	10/8/04	7:18 PM
Run No.	B1006118	
sample matrix	A	

Compound	**MDL**	Instrument result **reading**	Final Result **ng/mL**
Naphthalene	1.77	7.47	3.74
VOA Window	1.1	6.59	0.659ug/ml
Surrogates	**%**		
Toluene-d8	89.5		
Bromofluorobenzene	97.9		

INSTRUMENT CALIBRATION CHECK STANDARDS

Run #	Analysis Date	Time	Surrogates		**Naphthalene**	
			Toluene-d8	Bromofluorobenzene	Result ug/mL	%REC
B1005002	10/5/04	9:52 AM	103.9%	99.5%	43.21	86.4%
B1005006	10/6/04	8:31 AM	104.7%	99.3%	42.12	84.2%
B1006029	10/6/04	8:31 PM	96.1%	98.4%	54.9	109.8%
B1006050	10/7/04	8:37 AM	98.6%	98.0%	47.25	94.5%
B1006071	10/7/04	7:51 PM	95.3%	106.0%	53.64	107.3%
B1006092	10/8/04	6:59 AM	103.8%	111.3%	56.77	113.5%
B1006116	10/8/04	6:21 PM	100.8%	111.3%	56.76	113.5%

Run #	Analysis Date	Time	Surrogates		**VOA Window(49.25ug/mL)**	
			Toluene-d8	Bromofluorobenzene	Result ug/mL	%REC
B1006051	10/7/04	9:30 AM			49.05	99.6%
B1006072	10/7/04	8:40 PM			36.94	75.0%
B1006093	10/8/04	7:27 AM			50.31	102.2%
B1006117	10/8/04	6:48 PM			32.46	65.9%

APPENDIX 6

CREOSOTE SEMI-VOLATILE ORGANIC COMPONENTS

Sample ID: Creosote Solution

Sample Lot: # 2 Cyl. Door Emission Test Date Collected: October 06, 2004

RTI ID No.: 11218-29 Plant Source: # 2 Work Tank

MS Data 020205-Creosote-10.D

Ret. Time (min)	Component Identification	% w/w
11.94	1,2,3,4-Tetrahydronaphthalene (Int. Std.)	IS
12.54	Naphthalene	5.4
12.71	Benzo[c]thiohene	0.1
13.81	Quinoline	0.3
15.14	2-Methylnaphthalene	4.0
15.47	1-Methylnaphthalene	1.5
17.01	1,1'-Biphenyl	1.0
17.31	1- Ethylnaphthalene (isomer)	0.4
17.57	Dimethylnaphthalene (isomer)	0.6
17.83	Dimethylnaphthalene (isomer)	0.8
18.26	Dimethylnaphthalene (isomer)	0.2
18.44	Acenaphthylene	0.3
19.15	Acenaphthene	5.1
19.44	4-Methylbiphenyl	0.1
19.62	$C_{13}H_{12}$ (isomer)	0.1
19.69	Methylbipheyl (isomer)	0.2
19.83	Dibenzofran	2.1
20.77	Trimethylnaphthalene (isomer)	0.2
21.15	9H-Fluorene	3.1
21.35	Methylbipheyl (isomer)	0.2
21.38	Dimethylbihenyl (isomer)	0.1
21.40	Methylbiphel (isomer)	0.2
21.47	Diphenylmethane	0.2

(Continued)

Ret. Time (min)	Component Identification	% w/w
21.53	Methylacenahthylene (isomer)	0.2
21.64	2-Methylbiphenyl	0.3
21.84	Methyldibenzofuran (isomer)	0.1
22.02	Dimethylbiphenyl (isomer)	0.4
22.14	Methyldibenzofuran (isomer)	0.1
22.54	Dimethylbiphenyl (isomer)	0.1
22.87	9,10-Dihydroanthracene	0.2
23.32	Methylfluorene (isomer)	0.2
23.59	Methylfluorene (isomer)	0.2
24.00	$C_{15}H_{16}$ (isomer)	0.2
24.24	Dibenzothiophene	1.1
24.80	Phenanthrene	11.5
24.97	Anthracene	2.6
25.15	Acridine	0.1
25.35	Dimethyfluorene (isomer)	0.1
25.55	5,6-benzoquinoline or pheanthridine	0.1
25.79	9H-Carbazole	1.2
26.00	Methyldibenzothiophene (isomer)	0.1
26.07	1-Phenylnaphthalene	0.3
26.34	Methyldibenzthiophene (isomer)	0.1
26.70	Methylphenanthrene (isomer)	0.8
26.79	2-Methylphenanthrene	1.0
27.00	4H-Cyclopenta[def]phenanthrene	0.9
27.06	1-Methylphenanthrene	0.1
27.16	Methylphenanthrene (isomer) or methylindene (isomer)	0.3
27.30	Tetramethylacenaphthylene (isomer)	0.1
27.69	Methylcarbazole (isomer)	0.1
27.97	2-Phenylnaphthalene	0.5
28.62	Dimethylphenanthrene (isomer)	0.1

(Continued)

Ret. Time (min)	Component Identification	% w/w
28.68	Ethylanthracene (isomer)	0.2
28.90	Dimethylphenanthrene (isomer)	0.2
29.35	Fluoranthene	5.3
29.73	Benzylnaphthalene (isomer)	0.1
29.80	$C_{16}H_{12}$ (isomer)	0.1
29.96	9-Anthracenecarbonitrile	0.1
30.13	Pyrene	3.4
30.20	$C_{16}H_{12}$ (isomer)	0.8
30.30	Benzonaphthofuran (isomer)	0.1
30.75	Benzonaphthofuran (isomer)	0.2
31.15	Methylpyrene (isomer)	0.1
31.27	pyrrolocarbazole or 9H-fluorenecarbonitrile	0.1
31.55	Benzofluorene (isomer)	0.4
31.82	Benzo[a]fluorene	0.3
31.88	Phenylmethylnaphthalene + $C_{18}H_{12}$(isomers)	0.1
32.02	Methylpyrene or benzofluorene (isomer)	0.2
32.20	Methylpyrene or benzofluorene (isomer)	0.1
32.32	$C_{18}H_{16}$ (isomer)	0.1
33.29	Terphenyl (isomer)	0.1
33.88	Benzonaphthothiophene (isomer)	0.2
34.00	Unknown	0.1
34.84	2,3-Benzanthracene	0.8
34.96	Chrysene	0.8
35.02	Unknown	0.1
35.19	Benz[a]anthracene	0.2
38.71	Benzo[b]fluoranthene	0.5
38.80	Benzo[k]fluoranthene	0.2
39.55	Benzo[a]pyrene	0.2

(Continued)

Ret. Time (min)	Component Identification	% w/w
39.72	Benzofluoranthene (isomer)	0.3
40.28	Unknown	0.1

APPENDIX 7

EMISSION FACTOR CALCULATION

AquAeTer
optimizing environmental resources
water, air, earth

Project Number: 061504 Sheet No. ____ of ____
Project Name: Guthrie
Prepared by: DMS Date: 4/16/2007
Checked by: PJm Date: 4/19/2007
Title: Extrapolated NAPH Mass Flow Rates

Scenario A: Tram Inside of Retort

TIME ⓪

t	m
8.5	0.74
16	0.28

$m = \frac{0.74-0.28}{8.5-16} = -0.0613$ ✓

$0.74 = -0.0613(8.5) + b$

$\underline{\underline{b = 1.261}}$ ✓

Scenario B: Empty Retort

TIME ⓪

t	m
8.5	1.96
16	1.57

$m = \frac{1.96-1.57}{8.5-16} = -0.052$ ✓

$1.96 = -0.052(8.5) + b$

$\underline{\underline{b = 2.402}}$ ✓

TIME 41

t	m
16	1.57
26	1.25

$m = \frac{1.57-1.25}{16-26} = -0.032$ ✓

$1.57 = -0.032(16) + b$

$b = 2.082$ ✓

$X = (-0.032)(36) + 2.082$

$\underline{\underline{X = 0.93}}$ ✓

AquAeTer
optimizing environmental resources
water, air, earth

Project Number: 061504 Sheet No. ____ of ____
Project Name: Guthrie
Prepared by: WMO Date: 4/16/2007
Checked by: JMC Date: 4/17/07
Title: Ave Emiss Rate from Open Cylinder Door

Full Cylinder
(g/min)

1.27
0.74
0.28
0.30
0.27

Empty Cylinder
(g/m)

2.40
1.96
1.57
1.25
0.93

Average = $\frac{\overset{\checkmark}{10.97}\ g/m}{10}$ = $\underline{\underline{1.10\ g/m}}$ ✓

AquAeTer

optimizing environmental resources
water, air, earth

Project Number: 04030 Sheet No. 1 of 1
Project Name: Guthrie
Prepared by: PJm Date: 10/13/2004
Checked by: DMS Date: 3/18/2005
Title: Tram Volume Calculations

Tram Volume Calculation

(from Paper - Intro to Mechanics of Solids)

$\rho_{steel} = 0.283 \frac{lb}{in^3}$ $\rho = M/V \Rightarrow V = \frac{M}{\rho}$ ✓

$\frac{V}{Tram} = \frac{2500 lb}{0.283 lb/in^3} * \left(\frac{ft}{12 in}\right)^3 = \frac{2500 lb}{0.283 lb/in^3} * \frac{ft^3}{1728 in^3} = 5.11 ft^3/Tram$ ✓

Cylinder Volume Calculation

ID = 7 ft
L = 130 ft

$V_{cyl} = \frac{\pi}{4} D^2 L = \frac{\pi (7)^2}{4} * 130 ft^3 = 5003 ft^3$ ✓

Total Tram Volume Calculation

$V_{\substack{Tram\\Total}} = V_{wood} + V_{Tram} = \overset{\#ties/tram}{49}\Big[\overbrace{\left(\frac{7}{12}\right)\left(\frac{9}{12}\right)8.5}^{tie\ dimensions}\Big] ft^3 + 5.11 ft^3$

$= 182.2 ft^3 + 5.11 ft^3 = \underline{187.3} ft^3$ ✓

Cylinder Charge Displacement Volume

$V_{Displaced} = 15 \times V_{\substack{Tram\\Total}} = 15*(187.3 ft^3) = \underline{2810 ft^3}$ ✓

$\% Retort = 2810 ft^3 / 5003 ft^3 * 100\% = 56\%$ ✓

Project Number: 061504 Sheet No. 2 of

Project Name: Guthrie

Prepared by: PJm Date: 3/5/2007

Checked by: DMB Date: 3/6/2007

Title:

Emission Factor For
Empty Cylinder - Vent Sample

Naphthalene Concentration = $154.39 \frac{ng}{mL}$

$$154.39 \frac{ng}{mL} \times \frac{10^{-9} g}{1 ng} * \frac{1000 mL}{L} * \frac{28.32 L}{ft^3} = \underline{0.0044 \frac{g}{ft^3}}$$ ✓

Retort Length = 130 ft
Retort Diameter = 7 ft
Retort Volume = $\frac{\pi (7 ft)^2}{4} 130 ft = 5003.0 ft^3$ ✓

Volume Displaced = $2810 ft^3$ = Full Trams = Wood + Trams
(calculated previously)

– In order to calculate an emission factor that is a function of cylinder size, normalize as follows:

$$0.0044 \frac{g}{ft^3} * 2810 ft^3 * \frac{1}{5003 ft^3} = 0.0025 \frac{g \text{ Naphthalene}}{ft^3 \text{ cylinder Volume} * \text{charge}}$$ ✓

– For this Test, the emission Factor for the re-load part of the cycle is:

$$0.0025 \frac{g}{ft^3} * 5003 ft^3 = 12.51 \frac{g}{\text{charge}}$$ ✓

AquAeTer
optimizing environmental resources
water, air, earth

Project Number: 061504 Sheet No. ____ of ____
Project Name: Guthrie
Prepared by: WMO Date: 4/16/2007
Checked by: JME Date: 4/17/07
Title: Door Opening Cycle Emission Factor

Inputs: Door Opening (minutes) = T
Cylinder Volume (ft^3) = V
Number of Charges /year = N

$$\text{Naphthalene Emissions} = \left[\underbrace{\frac{\overset{\checkmark}{1.10}\,g}{min} * \overset{\checkmark}{T}}_{\substack{\text{average door}\\ \text{emission rate}\\ \text{multiplied by}\\ \text{the minutes the}\\ \text{cylinder door}\\ \text{is open}}} + \underbrace{\left[\frac{\overset{\checkmark}{0.0025}\,g * V}{ft^3\ \text{cyl. vol.} * \text{charge}} \right]}_{\substack{\text{emissons from}\\ \text{the displacement}\\ \text{volume}}} \right] * \overset{\checkmark}{N} = \text{Naphthalene} \left[\frac{g}{year} \right]$$

AquAeTer
optimizing environmental resources
water, air, earth

Project Number: 061504 Sheet No. ____ of ____

Project Name: Guthrie

Prepared by: Wmo Date: 4/16/2007

Checked by: JMc Date: 4/17/07

Title: Example Door Opening Cycle Emiss. Factor

Assume : 130ft long × 7ft diameter cylinder
730 charges per year (two per day)
30 minute door opening

$$V = \frac{130\,ft}{4}(\pi)(7ft)^2 = 5003\,ft^3$$ ✓

$$\text{Door Emissions} = \left[\left(\frac{1.10\,g}{min}\right)\left(\frac{30\,min}{charge}\right) + \left(\frac{0.0025\,g}{ft^3}\right)\left(\frac{5003\,ft^3}{charge}\right)\right] * \frac{730\ charges}{year}$$

$$= \left[\frac{33\,g}{charge} + \frac{12.508\,g}{charge}\right] * \frac{730\ chrge}{yr} = 33{,}221\,\frac{g}{yr}$$ ✓

$$33{,}221\,\frac{g}{yr} \times \frac{lb}{454\,g} = 73.2\,\frac{lb}{year}\ \left(0.04\,\frac{tons}{yr}\right)\ \text{Naphthalene}$$

NOTE: 730 $\frac{charges}{yr}$ corresponds to approximately

$$\left(\frac{730\ charge}{yr}\right)\left(\frac{5003\,ft^3}{charge}\right)\underset{\substack{\uparrow\\ \text{approximate}\\ \text{wood}\\ \text{volume}}}{(0.56)} = 2{,}045{,}226\,\frac{ft^3}{yr}\ \text{treated wood}$$ ✓

AquAeTer optimizing resources | water, air, earth

Project Number:	*091887*	*Sheet No.*	*1 of 3*
Project Name:	*Water Vapor Report*		
Prepared by:	*JMC*	*Date:*	*5/3/2010*
Checked by:	*PJM*	*Date:*	*5/3/2010*
Title:	*Mass of Napthalene from Cylinder Door Opening*		

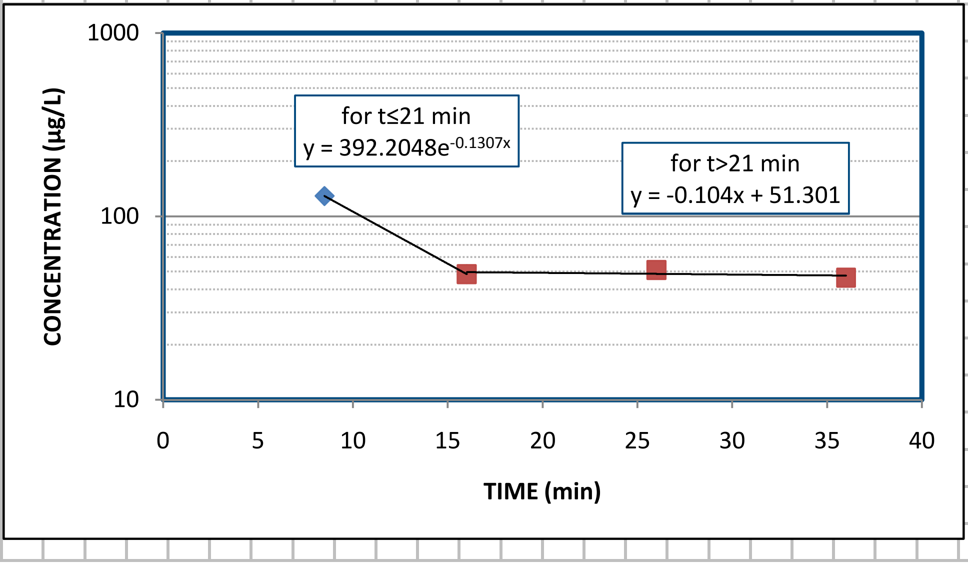
Tests were conducted on emissions from the door opening after a treatment cycle. These test results are for the test with wood in the cylinder after a treatment cycle.

The sampling was as follows:

Sample	Collection Time	Sampling Mid-point	Measured Concentration
First	6 - 11 minutes	8.5	129.1 ng/mL
Second	11 - 21 minutes	16	48.43 ng/mL
Third	21 - 31 minutes	26	51.01 ng/mL
Fourth	31 - 41 minutes	36	46.35 ng/mL

For the purposes of graphing, the midpoint of the sample time period will be used.

The initial two samples show an exponential decline. After 21 minutes, the emission rate follows more of a linear decline.



This equation assumes that the initial concentrations were greater than the sample collected between six and eleven minutes.

In order to determine an average concentration over the time of the door opening the equation is integrated:

$$Average\ Concentration = \frac{1}{t}\int_0^t 392.06 * e^{-0.1307*t}\, dt$$

$$Average\ Concentration = -\frac{392.2}{t * 0.1307} * e^{-0.1307*t}\Big]_0^t$$

AquAeTer optimizing resources | water, air, earth

Project Number:	*091887*	*Sheet No.*	*2 of 3*
Project Name:	*Water Vapor Report*		
Prepared by:	*JMC*	*Date:*	*5/3/2010*
Checked by:	*PJM*	*Date:*	*5/3/2010*
Title:	*Mass of Napthalene from Cylinder Door Opening*		

$$Average\ Concentration = -\frac{392.2}{t * 0.1307} * \left(e^{-0.1307*t} + e^{-0.1307*0}\right)$$

$$Average\ Concentration = \frac{392.2}{t * 0.1307} * \left(1 - e^{-0.1307*t}\right)$$

In order to convert the concentration to a mass, the volumetric flow during the sampling is used.

The air flow rate is given for each sample

Sample	Flow rate (standard cubic feet per minute)
First	210
Second	210
Third	211
Fourth	211

To account for only the first third of the door opening, t is divided by three. The equation is converted from concentration to mass by:

$$\frac{grams\ of\ naphthalene}{\min\ of\ door\ opening} = \frac{392.2\ \mu g \cdot L^{-1}}{\left(\frac{t}{3}\right) * 0.1307\ min^{-1}} * 210\frac{scf}{min} * \frac{1{,}000\ L}{\left(\frac{1}{0.3048^3}\right) ft^3} * \frac{1\ g}{1{,}000{,}000\ \mu g} * \left(1 - e^{-0.1307*\left(\frac{t}{3}\right)}\right)$$

This equation simplifies to:

$$\frac{grams\ of\ naphthalene}{\min\ of\ door\ opening} = \frac{53.53}{t} * \left(1 - e^{-0.1307*\left(\frac{t}{3}\right)}\right)$$

This equation is multiplied through by the time of door opening for each charge for the total mass per charge.
This accounts for the air flow leaving the cylinder during the door opening, based on measurements.

Assume that this air flow is the emission source from the time of the door opening until the beginning of the tram removal process.

Assume that this is one-third of the door opening time.

During the removal of the tram, air from outside of the cylinder is brought in to replace the volume in the cylinder. This effectively dilutes the concentration present inside the cylinder by the volume of air coming in.

If we assume that there is no air flow leaving while the trams are removed, then there are no emissions for this period. Assume this period is the second third of the door opening time.

For the last third of the door opening period, the new tram is pushed in. This displaces a volume of air equal to the

AquAeTer optimizing resources | water, air, earth

Project Number:	091887	Sheet No.	3 of 3
Project Name:	Water Vapor Report		
Prepared by:	JMC	Date:	5/3/2010
Checked by:	PJM	Date:	5/3/2010
Title:	Mass of Napthalene from Cylinder Door Opening		

volume of wood on the tram. The concentration of the constituents in the cylinder at the time of new tram insertion is calculated as follows:

$$Concentration\ after\ Tram\ Removal = \frac{Concentration_{Void\ Volume} * Volume_{void} + Concentration_{outside} * Volume_{wood}}{Cylinder\ Volume}$$

Assuming that the concentration of naphthalene outside the cylinder is negligible compared to the concentration inside the cylinder, the equation can be simplified as:

$$Concentration\ after\ Tram\ Removal = \frac{Concentration_{Void\ Volume} * Volume_{void}}{Cylinder\ Volume}$$

The concentration in the cylinder at the beginning of the tram removal is:

$$Concentration_{void\ volume} = \frac{392.2}{\frac{t}{3} * 0.1307} * \left(1 - e^{-0.1307 * \left(\frac{t}{3}\right)}\right)$$

The mass of naphthalene emitted due to the air displacement is:

$$\frac{Mass\ of\ naphthalene}{charge} = Concentration\ after\ tram\ removal * Wood\ Volume$$

Plugging these values in:

$$\frac{grams\ of\ naphthalene}{charge} = \frac{392.2}{\frac{t}{3} * 0.1307} * \left(1 - e^{-0.1307 * \frac{t}{3}}\right) * \frac{Volume_{void}}{Volume_{Cylinder}} * Wood\ Volume$$

The mass of emissions emitted during the displacement of air is thus:

$$\frac{grams\ of\ naphthalene}{charge} = \left(53.53 + \frac{0.255}{t} * \frac{Volume_{void}}{Volume_{cylinder}} Wood\ Volume, ft^3\right) * \left(1 - e^{-0.1307 * \frac{t}{3}}\right)$$

AquAeTer optimizing resources | water, air, earth

Project Number: 091887 Sheet No. 1 of 1
Project Name: Water Vapor Report
Prepared by: JMC Date: 5/3/2010
Checked by: PJM Date: 5/3/2010
Title: Mass of Napthalene from Cylinder Door Opening

Calculate Emissions for Example Case

Door Opening Time = 30 minutes
Wood Volume per charge = 3,500 ft^3
Cylinder Volume = 5,000 ft^3
Void Volume = 1,500 ft^3
Number of charges per year = 730

This is roughly equivalent to 2.5 million cubic feet of wood treated.

$$\frac{grams\ of\ naphthalene}{charge} = \left(53.53 + \frac{0.255}{t} * \frac{Volume_{void}}{Volume_{cylinder}} Wood\ Volume, ft^3\right) * \left(1 - e^{-0.1307 * \frac{t}{3}}\right)$$

= 45.55

Converting this to pounds (1 pound = 453.59 grams):

$$\frac{\text{lbs of naphthalene}}{\text{charge}} = 0.100427$$

For the number of charges per year, this is: 73 lbs/year, or 0.037 tons/year.

KOPPERS FIELD TEST
CYLINDER DOOR - EXHAUST CONCENTRATION

NAPHTHALENE

Scenario A: Tram Inside of Retort Background Air Concentration

Date	Time	Measured NAPH Conc ng/mL
10/5/2004	0554-0604	0.00

Scenario A: Tram Inside of Retort

Date	Time	Time (min from door opening (t=0))		Volumetric Flow Rate	Volumetric Flow Rate	Measured NAPH Conc	Measured NAPH Conc (minus background)	NAPH Mass Flow Rate	Gas Analysis Temp	NAPH Mass Flow Rate (at stp)	Notes
		start	end	cfm	scfm	ng/mL	ng/mL	g/min	F	g/min	
										1.27	Extrapolated back to time zero.
10/6/2004	0731-0736	6	11	234	210	129.07	129.07	0.77	60	0.74	
10/6/2004	0736-0746	11	21	234	210	48.43	48.43	0.29	60	0.28	
10/6/2004	0746-0756	21	31	244	211	51.01	51.01	0.30	60	0.30	
10/6/2004	0756-0806	31	41	244	211	46.35	46.35	0.28	60	0.27	

MDL =6.56 ng/mL

Scenario B: Empty Retort Background Air Concentration

Date	Time min	Time min	Measured NAPH Conc ng/mL
10/6/2004	1323-1333	NA	0.00

Scenario B: Empty Retort

Date	Time	Time (min from door opening (t=0))		Volumetric Flow Rate	Volumetric Flow Rate	Measured NAPH Conc	Measured NAPH Conc (minus background)	NAPH Mass Flow Rate	Gas Analysis Temp	NAPH Mass Flow Rate (at stp)	Notes
	min	start	end	cfm	scfm	ng/mL	ng/mL	g/min	F	g/min	
										2.40	Extrapolated back to time zero.
10/6/2004	1339-1344	1	6	262	234	143.09	143.09	0.95	60	0.92	Outlier, not included.
10/6/2004	1344-1349	6	11	262	234	304.79	304.79	2.02	60	1.96	
10/6/2004	1349-1359	11	21	261	241	237.19	237.19	1.62	60	1.57	
10/6/2004	1359-1409	21	31	261	241	188.90	188.90	1.29	60	1.25	
										0.93	Extrapolated to 41 minutes

1.10	Overall Average

AquAeTer
optimizing resources
water, air, earth

Project Number: ____ Sheet No. ____ of ____
Project Name: ____
Prepared by: PJm Date: 9/11/2008
Checked by: AEW Date: 9/11/08
Title: ____

ATTACHMENT 14

From Susquehanna Memo, the maximum concentration of Total Organic Carbon (TOC) measured in condensate collected from creosote treatment vapor from freshly treated poles is 2,200 mg/L.

In terms of percent,

$$2{,}200 \text{ mg/L} \times \frac{1\%}{10{,}000 \text{ ppm}} = 0.22\%$$

Therefore, $100\% - 0.22\% \text{ VOC} = 99.78\%$ water vapor

$$\boxed{99.8\%}$$