



Research and Development

CHARACTERIZATION OF EMISSIONS
FROM THE COMBUSTION OF WOOD
AND ALTERNATIVE FUELS IN
A RESIDENTIAL WOODSTOVE

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Characterization of Emissions from the Combustion of Wood and Alternative Fuels in a Residential Woodstove

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Abstract

Overall, oak wood is the best fuel tested, considering both emissions and stove operation. Compressed wood logs with binders and bituminous coal produce the highest emissions of SO_2 , particulate, and NO_x . Compressed wood logs without binders and treated lumber produce the highest PNA emissions. Important parameters affecting CO emission levels are fuel structure and, to a lesser degree, combustion air flow. SO_2 emission levels are related directly to fuel sulfur content. NO_x emissions are controlled by fuel nitrogen content and combustion air flow rate. Organic emissions are affected by fuel consumption rate, fuel structure, and amount of air through the stove. PNA formation is affected by combustion air flow, firebox temperature, and fuel structure. Bioassay results indicate the presence of both mutagens and promutagens in the organic extracts from flue gas samples from both wood and coal combustion tests.

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1. INTRODUCTION

The use of woodstoves for domestic heating has become popular in recent years. Woodstoves have been installed at the rate of one million per year since 1977,¹ and the trend is expected to continue because of the rising cost of oil and gas and the increased awareness of the need to find an alternative to these nonrenewable fuels. However, ambient air studies have revealed that a significant decline in air quality in certain areas is attributable to residential combustion of wood.^{2 3 4 5 6} Emissions from woodstoves and other domestic heating heating fuels have not been regulated because of the lack of Federal regulation of combustion units that produce less than 100 million Btu's per hour.⁷ Although wood will probably continue to be the dominant woodstove fuel, increased utilization of woodstoves for home heating has caused the price of wood to rise in many areas of the country while its availability has decreased. This trend may encourage a greater degree of use of coal and other alternative fuels in woodstoves.

Significant emissions from the residential combustion of carbonaceous fuels include particulates, volatile organics, CO, NO_x, and SO₂. Trace elements are also found in ash from residential combustion of coal and wood.^{8 9} There is little or no data on emissions from residential combustion of fuels other than wood and coal.

Emissions from the combustion of solid fuels for home space heating that are of primary concern are particulates, volatile hydrocarbons, and carbon monoxide, which are products of incomplete combustion. Coal and wood combustion emissions are generally higher from residential combustion sources than from other combustion units (such as industrial and utility boilers) because of the relatively low combustion efficiency of most residential units and typical operating conditions which are conducive to incomplete combustion.^{8 9} In addition, industrial combustion units are often equipped with emission control equipment, such as multiple cyclones for particulate emission reduction.¹⁰ Residential combustion of gas and oil also produces lower levels of these emissions than the use of coal or wood, which is attributable to the differences in the nature of the fuels^{8 9} and to differences in combustion conditions.

Particulates from the combustion of wood in domestic heating units consist of inorganic ash, carbon chars, and condensable organics.⁷ Particulates from residential coal-fired units consist of unburned coal and condensed hydrocarbons, in contrast to the primarily inorganic particulate matter produced during the industrial combustion of coal.⁹ Residential combustion of wood is considered to be a major source of ambient particulates in several localities.^{2 3 4 5 6} A large portion of particulate from residential combustion of wood and coal are inhalable (less than 2.5 μm in diameter).^{7 9} In Missoula, Montana, ambient particulate levels have been linked to health problems of grade school students and persons with pulmonary diseases.⁵

Levels of particulate emissions are highly variable and depend upon factors such as fuel and equipment types, firing rate, and burn rate.^{7 11 12} Organic particulate emissions from combustion of wood in woodstoves have been found to decrease with increasing burn rate, increasing log size, increasing heat release rate, and increasing stack gas temperature.^{12 13 14} The quantity of airborne particulates produced by residential coal combustion appears to be highly dependent upon coal type.^{9 10 11}

A variety of condensable organic species may be produced as a result of incomplete combustion or pyrolysis of organic materials in fuels. Polycyclic organic matter (POM), aldehydes, aliphatic hydrocarbons, and phenolic compounds are some of the organic species identified in emissions from residential combustion of wood and coal.^{8 9} POM emissions are a major concern because many POM compounds (polynuclear aromatics) have proven to be potent animal carcinogens.

In 1976, POM from residential combustion of wood counted for 80 percent of total POM from all sources, and residential combustion of coal was the biggest contributor of POM from all coal combustion sources with the exception of coke manufacturing. POM emissions from residential coal-fired units are greater than emissions from the combustion of wood in woodstoves,^{10 15} but woodstove POM emissions have been found to be higher than those from fireplaces.⁸ One reason for the relatively high levels of POM from residential stoves is that maximum thermal efficiency usually requires that air flow through the stove is reduced to a minimum. These oxygen-starved combustion conditions are favorable to the formation of POM compounds.

It must be emphasized that total POM emissions are not necessarily indicative of carcinogenic risks, since not all POM compounds are carcinogenic.¹⁶ However, several suspect carcinogens have been identified in emissions from residential combustion of wood and coal.^{9 17 18 19}

Carbon monoxide (CO) is also a byproduct of incomplete combustion. The effects of low levels of CO on the central nervous and cardiovascular systems are well-known.²⁰ CO is of particular concern because large amounts of CO enter the atmosphere from many combustion processes, and CO emissions exceed those of all other atmospheric pollutants except CO₂.²⁰ Although motor vehicles are the major source of CO, CO emissions from woodstoves are not insignificant.⁵ Emissions from woodstoves are far in excess of CO emissions from all other residential heating units,⁸ including fireplaces, as well as from industrial wood or bark boilers.²¹

Formation of nitrogen oxides (NO_x) is dependent upon fuel nitrogen content, the amount of air introduced into the stove, combustion temperature, and type of combustion equipment.⁸ NO₂ is thought to be the most toxic of the nitrogen oxides, producing local irritation at low levels and lung injury at higher levels.²² NO_x is also of environmental concern because nitric acid precipitates formed from atmospheric NO_x have had adverse effects on terrestrial and aquatic ecosystems.²³ NO_x is also known to react with environmentally prevalent amines to form N-nitroso compounds, many of which are potent animal carcinogens.²²

Total NO_x emissions from residential combustion of wood and coal are substantially lower than total emissions from domestic heating units fueled with oil and gas,⁸ reflecting the greater use of the more conventional fuels. Levels of NO_x appear to increase with increasing combustion temperature, so that the high levels of NO_x associated with combustion of oil and gas may also reflect the more complete combustion of organics.⁸

SO₂ emissions are a result of the oxidation of fuel sulfur. SO₂ is primarily an irritant but may also have bronchial and pulmonary effects.²⁴ Levels of SO₂ less than 1 ppm have caused damage to plant foliage, and aqueous systems have been detrimentally affected by acid precipitates of atmospheric SO₂.²⁴

SO₂ emissions from residential combustion of wood are low due to the low sulfur content of woods. Coal, however, has a much higher sulfur content than wood. Even though only 0.66 percent of all homes were heated by coal in 1976,

SO₂ emissions from residential coal combustion were second only to SO₂ emission from residential combustion of oil.⁸ Thus, use of coal in domestic heating is already a major source of SO₂, and increases in the use of coal for domestic heating could have relatively major environmental consequences.

The purpose of this study is to measure the emissions from the residential combustion of alternative fuels, including coal, in a conventional woodstove. Fuels tested include compressed wood, treated wood, newspapers, commercially available paper logs, and peat, in addition to untreated oak wood and bituminous coal. The pollutants discussed above were measured during the course of this study for the alternative fuels tested, and their emission levels are compared to those from wood combustion. The effects of the stove operation parameters on emission levels of these pollutants is also considered. It is hoped that this information will be useful in estimating the overall effect of these emissions from residential solid fuel units on ambient air quality.

2. FUELS

During the planning phase of this project, eight fuels were chosen as likely alternatives to wood for use in residential combustion units. The fuels chosen were coal, both bituminous and anthracite, peat, newspaper logs, cardboard logs, compressed wood chip logs, both with and without binders, and lumber pressure treated with copper salts to retard rot. Alternative fuels were chosen on the basis of availability and on the likelihood that they would be used by stove owners as a wood substitute. Except for peat, all fuels represent commercially available fuels making them likely alternatives to wood as fuel in residential woodstoves. Table 1 is a list of the fuels screened during this project and symbols used to represent each fuel.

The coal for the bituminous coal screening tests was obtained at a local coal supplier. Commonly known as bag coal, this coal is used by most homeowners with coal space heaters. Sod peat was obtained from Prulean Farms in eastern North Carolina. This peat was harvested using the sod peat harvesting technique, which extrudes the peat into cylinders which are three to four inches in diameter and about 15 inches long. It leaves the peat sods on the surface of the peat bog to dry in the sun. Although peat is not presently used in the United States for home heating, it is potentially a great energy resource in this country, and thus, someday may be employed as home heating fuel.

Compressed wood logs without binders were obtained from a local stove outlet. These logs were about 3.5 inches in diameter and about 15 inches long and were formed by pressing together woodchips and sawdust. The wood in these logs is over 90 percent hardwood. Compressed logs with binders were obtained at a local grocery store. These logs consisted of cedar shavings and sawdust held together with a paraffin binder. Copper compounds have been added to these logs to produce colorful flames.

Cardboard logs formed of compressed corrugated cardboard chips were obtained through the U.S. Environmental Protection Agency (EPA) from a manufacturer in Oregon. Newspaper logs were made in-house using a commercially available newspaper log roller. Anthracite coal was obtained from a local stove supplier. Treated lumber was obtained at a local lumber yard. Treated lumber is yellow pine pressure treated using the Wolman process.

TABLE 1. KEY: FUEL NOMENCLATURE

W	=	Oak logs
CW	=	Compressed wood logs
CWB	=	Compressed wood logs with binder
C	=	Cardboard logs
N	=	Newspaper logs
TW	=	Treated lumber (pine)
P	=	Peat
BC	=	Bituminous coal
AC	=	Anthracite coal

Two successful runs were performed for each fuel except for anthracite coal, which was not successfully burned in the stove chosen for this study. Two tests were also carried out using split and round dry oak which was obtained from a local firewood supplier. These tests were used as a baseline for comparison to tests with other fuels. Fuel analyses and information on stove operation characteristics for each fuel may be found in the discussion section of this report.

3. EQUIPMENT

The woodstove used in this study was a free standing air-jacketed design with simple open firebox. This stove represents a type of stove which is increasing in popularity. Originally designed as a fireplace insert, this type of stove is being installed in increasing numbers of new homes. Firebox dimensions are given in Figure 1. The stove flue was 8-inch, double wall, fiberglass insulated stainless steel stove pipe. The stove pipe stood unsupported, the entire stove assembly rested on a digital balance, which measured weight change (for fuel consumption) during each test.

An optional shaker coal grate was purchased with the stove along with a firebrick lining. This was necessary to burn coal, one of the alternative fuels tested. The coal grate was also used to burn peat, compressed wood logs, and cardboard logs. A second coal grate was obtained from another manufacturer because the anthracite coal did not burn well on the first grate. The second grate performed better than the first with anthracite, but it was still not possible to successfully burn anthracite coal. The stove design is such that air flow through the coal grate is not restricted enough to insure a high velocity of air through the grate, a condition which is necessary in order to successfully burn anthracite coal.

The stove firebox is enclosed on five sides by an air jacket. During stove operation air is blown through the jacket, where it is heated, and out into the room. Three blower speeds are automatically selected by a monitor of temperature in the air jacket. It was found that the blowers tended to operate at the medium speed during steady-state operation. An air jacketed stove was chosen because by monitoring temperature at the blower outlet it was possible to estimate the stove's heat output. This calculation was performed by the computer and printed out at 30 second intervals. By monitoring the heat output value test personnel could tell when conditions of steady-state stove operations were reached and could maintain these conditions throughout the tests by adjusting drafts and damper.

Air flow through the stove was controlled with sliding door drafts in the front of the stove at the bottom of the double doors and by an adjustable damper mounted at the entrance to the stove flue. The damper was closed as much as possible once steady-state conditions were reached, and most adjustments

Firebox--50.5 cm (back W) x 66.5 cm (front W)
x 55 cm (H) x 39 cm (D)

Thermocouples

R₁ - R₄ -- Blower outlets
R₅ -- Blower inlet
R₇ -- Firebox
R₈ -- Stack

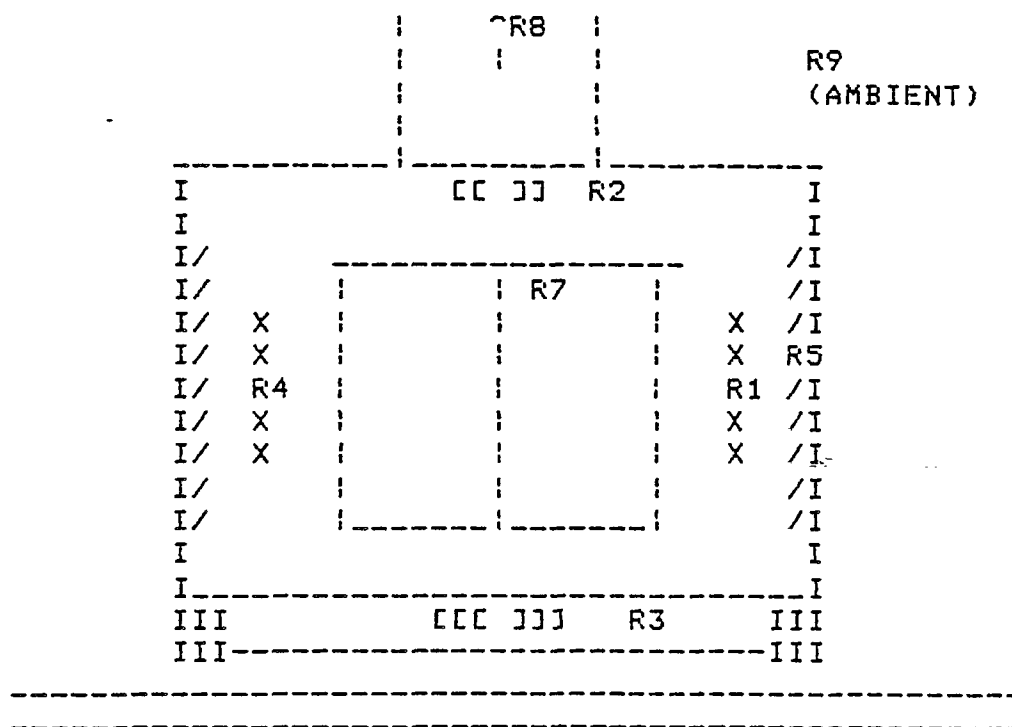


Figure 1. Stove dimensions and thermocouple placement.

to maintain these conditions were made using the sliding door drafts. The stove was not air tight, so that even with drafts and damper closed, there was still enough air flow through the stove for combustion to continue. Temperature was measured by several thermocouples which were placed in the firebox, stack, at the blower inputs and outputs, and in the test room (ambient). Thermocouple placement and numbering scheme are shown in Figure 1.

Temperature data and certain gas data were automatically recorded by the online DEC PDP-1100 computer. The computer took and retained stove operation parameter measurements at 30 second intervals. In addition, test personnel could log in comments on a computer terminal in the laboratory. The stove balance readings, stack flow turbine counts, and stove draft and damper settings were entered in the comments along with pertinent information about the test operation.

The start and stop of the Method 5 sampling train were also entered into the computer. This enabled the computer to calculate sampling period averages for the various parameters automatically recorded by the computer. At the end of each test run, the computer printed out a test run summary including these averages, sampling time, fuel type, and comments entered into the computer during the test.

Accurate measurement of flue gas velocity in wood stove flues was found to be quite problematical. Flue gas velocity was far too low to get any gas velocity measurements using conventional s-shape pitot tubes and water manometers. In another wood stove emission study funded by the U.S. EPA, Monsanto researchers utilized a micromanometer capable of being read down to 0.0002 millimeters of mercury.²⁵ An equivalent instrument was purchased, but it was found that it was also unsuitable for the gas velocity measurements. Even at maximum stack gas flows the micromanometer readings were consistently close to 0. It was felt that using such readings for the flue gas velocity measurement would be pushing the limits of the instrument.

In order to solve the problem of flue gas velocity measurements, RTI designed a turbine meter for measuring flue gas flow rates. This instrument consisted of a metal turbine mounted on a spindle in the stack above the sampling probe. The turbine rotated freely as flue gas passed through it. Two small magnets were mounted on the turbine hub; these magnets passed over a coil mounted on the spindle base, producing signals which were counted by

frequency counter. These "counts" were recorded in the comments during each run. The flow meter was calibrated by adding known amounts of CO₂ to the flue gas. By measuring the amount of dilution of the CO₂ added to the gas, it was possible to accurately estimate stack flow rate. The flow turbine was calibrated by plotting flow rates against frequency counts. The relationship between stack flow and turbine frequency counts was found to be best described by an exponential function.

Fouling of turbine by condensed organics or particulate matter during the tests was not found to be a problem except during runs with bituminous coal and compressed wood logs with paraffin binders. During these tests, it was necessary to remove and clean the stack flow turbine periodically. The stack flow turbine enabled us to get continuous flow measures of the stack during each test, which were used to flow average all gas concentrations.

4. SAMPLING PROCEDURES--ORGANICS

A whole test integrated sample of polycyclic organic matter and other organic emissions was collected by a modified Method 5 sampling train similar to the one described in the Battelle protocol.²⁶ The RTI sampling train was an all-glass/teflon construction which consisted of the following: a glass probe, a heated filter box ($\geq 204^{\circ}$ C) containing a fiberglass filter, a series of gas condensers, a water-cooled XAD-2 resin chamber, a series of ice-cooled impingers, a drying cartridge filled with silica gel, and a suitable air moving and air monitoring device. The basic method and equipment were selected in accordance with the protocol; however, the physical arrangement of the site and problems which arose during the testing necessitated some departure from the basic protocol. The main departure was in the use of a series of two condensers and a condensate trap located between the filter box and resin chamber. This section was configured in the following manner. A 90 degree ground glass joint mounted with the plane of the bend parallel to the roof brought the gas flow out of the filter box and into an Allihn condenser (300 mm). The gas then flowed through a 180 degree ground glass joint mounted with its bend perpendicular to the roof. The bottom of this glass joint was tapped to provide a connection for a 250 mL amber condensate flask. The gas was further cooled by being passed through a Graham condenser (250 mm) prior to entry into the XAD resin chamber. Any condensate was trapped ahead of the XAD. This reduced the possibility of flushing of the XAD with large quantities of water and subsequent channelling in the XAD bed. Other changes of the protocol included the use of an all-glass probe and the elimination of the particulate filter between the silica gel impinger and the dry impinger of the system. This filter was eliminated because of anticipated low flow and low particulate loading which were thought to be trapable in the front part of the system. The impinger system consisted of four impingers mounted in series. The first two impingers were filled with 100 mL of water. The second impinger was a modified Nuburg. The third impinger was dry, and the fourth contained 300 to 400 g of silica gel.

Altogether the system consisted of five subsections (See Table 2). These subsections were acid cleaned and washed with methylene chloride prior to their assembly in the laboratory. The joints were taped with teflon and clamped to facilitate transport.

TABLE 2. SAMPLE SYSTEM

-
1. Section 1. Probe Section
 - A. All glass probe
 - B. Flexible teflon connector
 - C. Ground glass joint (female)
 - D. Electrical heating tape, thermocouple, controller
 2. Section 2. Particulate Filter
 - A. Ground glass joint (male)
 - B. Glass filter holder (2 halves jointed with Bezel ring)
 - C. Sintered glass filter support with sealing gasket
 - D. Glass fiber filter
 - E. Heated box, thermocouple, and remote controller
 3. Section 3. Condenser Section
 - A. 1-300 mm Allihn condenser
 - B. 1-250 mm Liebig condenser
 - C. 2-90° ground glass T/S joint
 - D. 1-250 mL infrared shielded flask
 - E. 1-180 degree ground glass joint with condensate tap
 - F. Coolant system
 4. Section 4. XAD Resin Column
 - A. Jacket resin column with sintered glass plug (interior 2" wide, 50 g capacity)
 - B. XAD resin
 - C. Spring loaded perforated end plate
 5. Section 5. Impinger
 - A. 4 impingers
 - 1st, 100 mL water
 - 2nd, modified Nuburg with 100 mL water
 - 3rd, empty
 - 4th, silica gel (200-300 g)
 - B. Water bath cooled with ice water and portable condenser
 - D. Gas moving and monitoring attachment
-

The train was transported to the roof in sections and assembled. A standard 8-inch insulated flue was used to exhaust gas from the stove to the ambient air. The glass probe was inserted in the flue in accordance with the standard Method 5 protocol leaving 8-duct diameters ahead of the probe free of obstructions and 2 behind it before exiting to the air. The stack was cleaned prior to each test to prevent the volatilization of deposited residue which might bias the sample. Assembly and checkout were conducted according to a test protocol developed to meet RTI's situation as well as to incorporate the Battelle protocol. The filter box was heated to 205° C, the resin trap was cooled to less than 20° C, and the system was leak checked per standard procedures. The taping of the joints facilitated the leak testing and reduced the time that would have been spent in chasing down leaks. The flow meter was wired in and all the necessary cooling lines were connected to the condensers and the XAD column. The cooling water was provided by a portable condenser. The system was wrapped with insulating materials to protect it from sunlight and to maintain coolness.

Operation of the sampling equipment consisted primarily of maintaining the flow of the coolant, monitoring all temperatures, gas flow rates, and making the necessary adjustments. Backup filters and glassware were cleaned and at hand and could be rapidly installed with a minimum of downtime.

Mass emissions were collected over a 45 to 120 minute interval depending on the volume of sample required for analysis. At the conclusion of the sampling run, the train was shut down, disassembled, and transported to the laboratory for cleanup and sample recovery. Samples taken were as follows: Probe wash, filter particulate, XAD resin, XAD module and condenser wash, condensate, and impinger water. All samples were stored in amber glass bottles under refrigeration prior to analyses.

Generally, the samples were recovered immediately after the run. However, if this was not possible, the sampling train subsections were sealed and stored in a refrigerator for no more than 24 hours. The solvent system found to be most effective for sample recovery from the front half of the system (probe and condenser) was a 9:1 methylene chloride/methanol solution. If necessary, a stiff bristle, chemically inert nylon brush was used in the probe to remove any adhered particulate. Methylene chloride alone was used to rinse the XAD column and in the impinger system. The condensate was measured and

collected. Contents of the water impingers were weighed at the end of the test to determine the quantity of condensed water and were bottled for analysis. The silica gel impinger was weighed and the material discarded. All samples were labeled and refrigerated except for the filter, which was desiccated for 24 hours prior to weighing for filter particulate weight.

5. ANALYTICAL PROCEDURES

5.1 GAS ANALYSIS

Stack gas composition was continuously monitored during the tests. A separate 1/2 inch stainless steel probe was used to sample the flue gas for gas composition analysis. The probe was packed with glass wool, and a water cooled condenser was placed in the sample line to prevent fouling of the instruments. Carbon monoxide, carbon dioxide, and methane were analyzed using infrared detectors manufactured by Horiba Instruments, Incorporated. These data were recorded by the computer. Nitrogen oxides (NO_x) were measured using a photoluminescent detector manufactured by Thermo Electron Corporation. Sulfur dioxide (SO_2) was measured using a photometric detector manufactured by DuPont Instruments. Both NO_x and SO_2 concentrations were continuously recorded by a conventional stripchart recorder.

In addition to continuous gas analysis, gas bulb samples were also taken and analyzed by gas chromatography for total organic carbon. Two gas bulb samples were usually taken for each test. Orsat method measurements of oxygen were also made at intervals during the later tests using a Fyrite oxygen analyzer. Both Fyrite and gas bulb samples were taken through the same sample line as the continuous gas analysis sample. All continuous gas analyzers were calibrated per EPA standard procedure using gas mixtures of known concentrations. The instruments were calibrated prior to each test.

5.2 ORGANICS ANALYSIS

5.2.1 Sample Preparation

Modified Method 5 samples which were analyzed for organics include: probe wash ($\text{CH}_2\text{Cl}_2 + \text{CH}_2\text{OH}$), filter, condenser and XAD module wash (CH_2Cl_2), XAD-2 adsorbent, condensate catch, and impinger water. The probe wash was filtered to remove particulates captured by the probe during sampling. These particulates were weighed, and their weight was added to the weight of particulate caught on the Method 5 filter to give total particulate sampled during the test. The sampling train filter was then placed in a glass soxhlet thimble along with the probe wash filters and the XAD-2 adsorbent. The filtered probe wash and the condenser/XAD-2 module wash were poured into the soxhlet flask along with enough fresh CH_2Cl_2 to bring the volume to 500 to 700 cc. The

soxhlet apparatus was then covered with foil and allowed to reflux for 24 hours. Following extraction, the filtrate was placed into a Kuderna-Danish evaporator and concentrated to 10 to 25 cc. The resulting concentrate was stored at 4° C until analysis.

The aqueous portion in the sampling train, impingers, and condensates were added together and extracted with a separatory funnel at pH of 2.0 ± 0.5 and 12.0 ± 0.5 as described elsewhere.²⁶ Two extractions were done at each pH. The CH_2Cl_2 from each set of extractions was added together and concentrated to ~10 to 40 mL. The resulting sample was stored at 4° C until analysis.

5.2.2 Total Organics

Organic analysis were performed separately on the two types of concentrated samples described in Section 5.2.1. Total organics with a boiling point of 100 to 300° C were determined by total chromatographable organics (TCO) and gravimetric analyses described elsewhere.²⁶ Chromatograms of a hydrocarbon standard that were obtained on the same day as sample chromatograms gave retention times corresponding to the boiling point range 100 to 300° C. Calculation of TCO in each sample was based on the integrated peak area between these retention times and the area and the concentration of an internal standard (triphenyl ethylene).

Organics with a boiling point above 300° C were determined by weighing 0.5 mL samples that were evaporated to dryness. A complete description of this technique can be found elsewhere.²⁶ Results from TCO and gravimetric analyses were totaled to give total organics for the sampling period.

5.2.3 PNA Analysis

5.2.3.1 Gas Chromatography--

RTI has amassed considerable experience in the analysis of PAH in various process streams, including the aqueous condensate and tar effluents from coal gasification.^{27 28 29} During these studies, RTI encountered difficulty in characterizing these highly complex mixtures by gas chromatography-mass spectroscopy (GC/MS) in a time- and cost-effective manner. Time consuming sample fractionation procedures were necessary for good GC/MS quantitation of PNAs in these samples. Fractionation of the PNAs by these methods was not complete,⁴ and the complexity of the fractionation techniques gave rise to some sample

loss. These considerations motivated the development of a direct technique for the analysis of PNAs in complex mixtures utilizing glass capillary gas chromatography (GC²). This technique has been presented in detail in two papers.^{2 3}

Gas chromatographs of the sample extracts indicated that the samples obtained from the residential combustion unit were indeed very complex. This complexity, in conjunction with project time and cost constraints, led to the selection of GC² as the analytical method for determining PNA concentrations in the modified Method 5 sample extracts. A Varian 3700 GC² system with a flame ionization detector (FID) was used for these analyses. The system was all-glass from the injector to the detector. A wallcoated OV-101 capillary column was used in the system. All samplewetted parts were made of glass. Helium was used as the carrier gas as well as the makeup gas. Chromatographic conditions are listed in Table 3. Samples were injected using the Grob "splitless" technique,³⁰ and sample volumes ranging from 3 to 4 μ L were used. The splitless technique consists of injecting the sample and then 30 seconds later, opening the splitter to remove the excess solvent. This prevents a long solvent tail. The advantages of using this technique for polycyclic materials are well documented.³¹

Prior to GC² injection, concentrated sample extracts were internally standardized. A problem was to find a suitable internal standard for GC analysis since the extracts were substantially complex. Triphenyl ethylene (TPE) was found to be most suitable of the many internal standards tested since it was present at negligible concentrations in the extracts, was similar in nature to other aromatic compounds, and was well separated from the peaks of the compounds of interest.

PNA analyses were performed separately on the two samples described in Section 5.2.1. Aliquots were internally standardized with triphenyl ethylene. Chromatographic peaks from GC² analysis of these aliquots were compared to peaks in duplicate aliquots spiked with standard solution of 26 PNAs and TPE in order to identify the PNAs in question. Once PNA peaks were identified, compound quantitation was accomplished using the known concentration of TPE in the samples spiked with TPE only and response factors (RF) calculated from a standard composed of 25 PAHs and TPE at known concentrations. The standard was periodically run on the GC² to give response factors for each PAH. Response

TABLE 3. CHROMATOGRAPHIC CONDITIONS

Instruments	Varian 3700 with "all glass" capillary systems
Detector	FID 28° C
Column	25 m × 0.25 mm I.D. WCOT OV 101, Borosilicate capillary
Carrier	Helium, 16 psi
Temperature	50° C for 1 min, 4° C/min to 265° C, hold 20 minutes
Injection	Splitless, 1-minute delay
Detector gas flows	Optimum
Makeup gas	Helium (~29 mL/min through detector)

factors account for decreasing area counts for equally concentrated PAHs as the GC² approaches its limits for eluting high boiling point compounds and were determined from calibration curves. In addition, five samples were analyzed for PAH compounds by GC²/MS for verification of the GC² results. Overall, these results compared favorably.

5.2.3.2 Spot Tests--

The PNA sensitized fluorescence spot test³² was utilized to screen the XAD extract, condenser and probe wash, and in the methylen chloride extract from the aqueous impingers and condensate samples for the presence of PNAs. Both original and concentrated extracts were tested.

A microliter amount of sample was applied to a Whatman filter, and in another spot a microliter of naphthalene (30 mg/mL) was applied. Between these two spots, a microliter of naphthalene was superimposed on a microliter of the sample. Immediately following application of the spots, the filter paper was exposed to ultraviolet radiation in a Chromato-Vue[®] Model CC-20 ultraviolet cabinet. Differences in intensity between the sensitized spot and the sample spot relative to naphthalene were noted and recorded as one of four categories: . strong (sample spot self-fluorescent), moderate (sensitized spot considerably more intense than naphthalene), weak (sensitized spot slightly more intense than naphthalene), and none (fluorescence of sensitized spot equal in intensity to fluorescence of naphthalene).

In most cases, the qualitative spot test results compared well with the total PNAs determined by GC². Most of the aqueous (impingers and condensate) samples exhibited weak sensitized fluorescence, which is consistent with the low water solubility of PNAs. GC² analysis indicated that only the low molecular weight PNAs were present in these samples. The majority of PNAs detected by GC² were in the filter extract, XAD extract, condenser wash and probe wash samples, and these samples were also strongly or moderately fluorescent.

Several of the extracts from the aqueous samples did not exhibit sensitized fluorescence, although PNAs were identified by GC analysis. Since the spot test is 10-100 times more sensitive to PNAs than gas chromatography, the lack of fluorescence may be due to interfering species. Two of the samples, in fact, inhibited fluorescence of naphthalene, which is a clear indication of the presence of species that are capable of absorbing fluorescence. Phthalates

have been found to negatively interfere in spot tests,³³ and this type of compound has been identified in the gaseous effluent from the combustion of wood in a woodstove.²⁵ However, in a study of several different types of industrial combustion effluents, in no cases were PNAs detected by GC/MS in samples that did not also give positive spot test results.³⁴

Only one sample exhibited weak fluorescence but was not found to contain PNAs by gas chromatography. This is probably due to the sensitivity of the spot test to low levels of PNAs. A positive interference is possible, but standard samples containing a wide variety of organics, many of which would be expected to be present in these combustion samples, have not exhibited sensitized fluorescence in the PNA spot test.^{32 35}

Detection limits of individual PNAs vary with experimental conditions. For example, detection limits for B(a)P have been found to range from 1-100 pg/ μ L.^{32 34} This variation has been attributed to differences in purity of the stock materials, intensity of the ultraviolet lamp, and the subjective judgment involved in determining detection limits.^{33 34}

In this study, detection limits of B(a)P and phenanthrene were found to be 10 pg/ μ L and 10,000 pg/ μ L, respectively. The detection limits of most other PNAs are expected to be the same as B(a)P or phenanthrene or within this range.^{33 34}

Total PNAs in two of the samples were determined by the method of multiple dilutions,³² assuming an average detection limit of 100 pg/ μ L. Results are in Table 4. Although there is a good deal of uncertainty with this detection limit, it is likely that GC² and spot test results agree within an order of magnitude.³³

TABLE 4. TOTAL PNAs

Test number	Total PNAs ^a	Emission factor
CW2	41 mg	129.14 mg/kg
C2	22 mg	265.39 mg/kg

$$^a C(\text{Conc. of sample}) = 100 \text{ pg}/\mu\text{L} \times 10^{(n-1)}$$

where n = number of 1:10 dilutions required before no sensitized fluorescence.

6. EXPERIMENTAL

To properly compare the emissions of the alternative fuels tested, it was necessary to operate the woodstove as similarly as possible from test to test. Sampling only at steady-state stove operating conditions is the best way to assure reproducibility. Using considerable in-house experience in residential woodstove operation, steady-state conditions were defined to approximate conditions a typical stove owner would achieve for most of the stove's operation. The sampling period was confined to this steady-state period. However, it should be stressed that woodstove operation can vary greatly from owner to owner and that it is very difficult to determine an actual average steady-state operating conditions. In addition, startup and shutdown conditions can be very significant from an emissions standpoint when overall woodstove emission factors are considered. The major purpose of this study is to compare alternative woodstove fuels on an equal basis, and steady-state conditions were chosen for sampling periods to assure as much reproducibility as possible from test to test. Startup and shutdown conditions were judged to be too variable for reproducible testing. However, continuous gas monitoring was carried out for startup period and some of the shutdown period following sampling. It should be stressed that by sampling only at steady-state lower total emissions can be expected than if the stove was sampled from a cold start.

At the start of the test, the stove was loaded with paper and kindling (if necessary) and the fuel to be burned. Except for the compressed wood logs with binders (CWB) and the coal runs, enough fuel was added to almost fill the firebox. Two CWBs were used for each CWB test. The coal was slowly added to an existing wood fire per stove manufacturer's instructions. The fire was started with drafts and dampers open. Once the stack temperature started to rise significantly (at about 275° C), the damper was closed. The stove was allowed to reach normal operating conditions before sampling was begun. Normal steady-state conditions were with blower speeds at medium and heat output values above 50,000 Btu's/min. Once these conditions were reached, sampling was started. Sample volume varied from 0.5 to 1.7 m³ depending on the duration of the sampling period. Initially sampling periods were relatively short to avoid possible overloading the XAD adsorbent module with organics. However, it was found that longer sampling periods did not result in XAD overloading, so later tests were longer.

Draft and damper settings and fuel addition rate were adjusted for each fuel to maintain steady-state operating conditions for the entire sampling period. Descriptions of these parameters for each fuel, along with problems encountered in maintaining steady-state conditions during each test are discussed in the results.

Low flue gas velocities made isokinetic sampling unfeasible because to achieve isokinetic sampling would require extremely long sampling periods or a very large sampling probe. In addition, flow rates were variable enough during a test that achieving isokinetic sampling would be difficult if not impossible. A steady sampling rate of 0.5 cfm was used during each test. The particle size distribution from woodstove combustion was fine enough that the deviation from isokinetic sampling probably did not bias results. Personal communication and literature from other researchers in the area also implied that isokinetic conditions were not achieved during their programs. Difficulty in accurate flow measurement was the biggest reason for this problem. Although we had more accurate flow measurement than most, isokinetic sampling was still judged to be too difficult a goal to achieve. It should be noted that a steady sampling rate does weight sampling results with a bias towards periods of low flow rates. However, for most tests flow rates were consistent enough during the steady-state period to keep this bias minimal.

7. RESULTS

This section is presented in two parts. First is a discussion by pollutant describing how the fuels compared in emissions factors for each pollutant. The second part is a description of fuel burning characteristics and general emission levels of each fuel screened. Factors affecting pollutant emission levels are also discussed for each fuel.

7.1 EMISSION COMPARISON

Comparisons of the emission factors of the fuels tested are given in a table and a figure for each pollutant. Emission rates in grams per hour and emission factors in grams per kilogram of fuel consumed are graphed in each figure. The same emission results are presented in table form with the addition of the average concentration of the pollutant in the flue gas for each test. In the figures, the emissions from duplicate tests were averaged for each fuel. Sulfur and nitrogen balances are given in Table 5. This table shows that most of the sulfur and nitrogen was volatilized during combustion except for fuels with little or no sulfur or nitrogen content.

7.1.1 Pollutant Levels

7.1.1.1 Particulate--

Wood stoves are significant emitters of particulate matter. In some areas up to 73 percent of total suspended particulates has been attributable to residential wood combustion at certain times.³⁶ Also residential coal burning emits more particulate than residential wood burning.

Particulate emission results for the eight fuels successfully tested are given in Table 6 and Figure 2. Examination of these tables shows that the fuels may be ranked by particulate emissions as follows (highest to lowest):

1. Compressed wood logs with binders
2. Bituminous coal
3. Newspaper logs
4. Treated lumber
5. Peat
6. Compressed wood logs

TABLE 5. MASS BALANCES--SULFUR AND NITROGEN

	Sulfur Percent volatile	Nitrogen Percent volatile
W1 & 2	89.44	95.67
CW1	99.15	97.15
CW2	97.83	97.55
CWB1	89.40	99.40
CWB2	89.62	98.61
C1	81.40	98.37
C2	63.04	95.89
N1	88.34	<0
N2	86.48	<0
TW1	-31.40	87.82
TW2	-5.61	89.58
P1	82.60	85.18
P2	86.36	93.03
BC1	93.34	90.15
BC2	93.02	90.92

TABLE 6. EMISSION FACTORS--PARTICULATES

Fuel	Test number	g/m ³	g/hr	g/kg
Oak logs	W1	0.045	2.37	0.52
	W2	0.052	3.16	0.79
Compressed wood logs	CW1	0.182	5.14	0.93
	CW2	0.057	5.50	0.58
Compressed wood logs with binder	CWB1	0.481	51.18	16.27
	CWB2	0.296	32.00	18.20
Cardboard logs	C1	0.109	3.77	0.63
	C2	0.071	2.69	0.72
Newspaper logs	N1	0.227	17.68	5.53
	N2	0.058	5.35	1.52
Treated lumber	TW1	0.154	3.55	0.63
	TW2	0.529	10.01	2.26
Peat	P1	0.107	5.25	1.17
	P2	0.156	5.35	1.27
Bituminous coal	BC1	0.343	19.10	9.98
	BC2	0.310	13.43	5.21

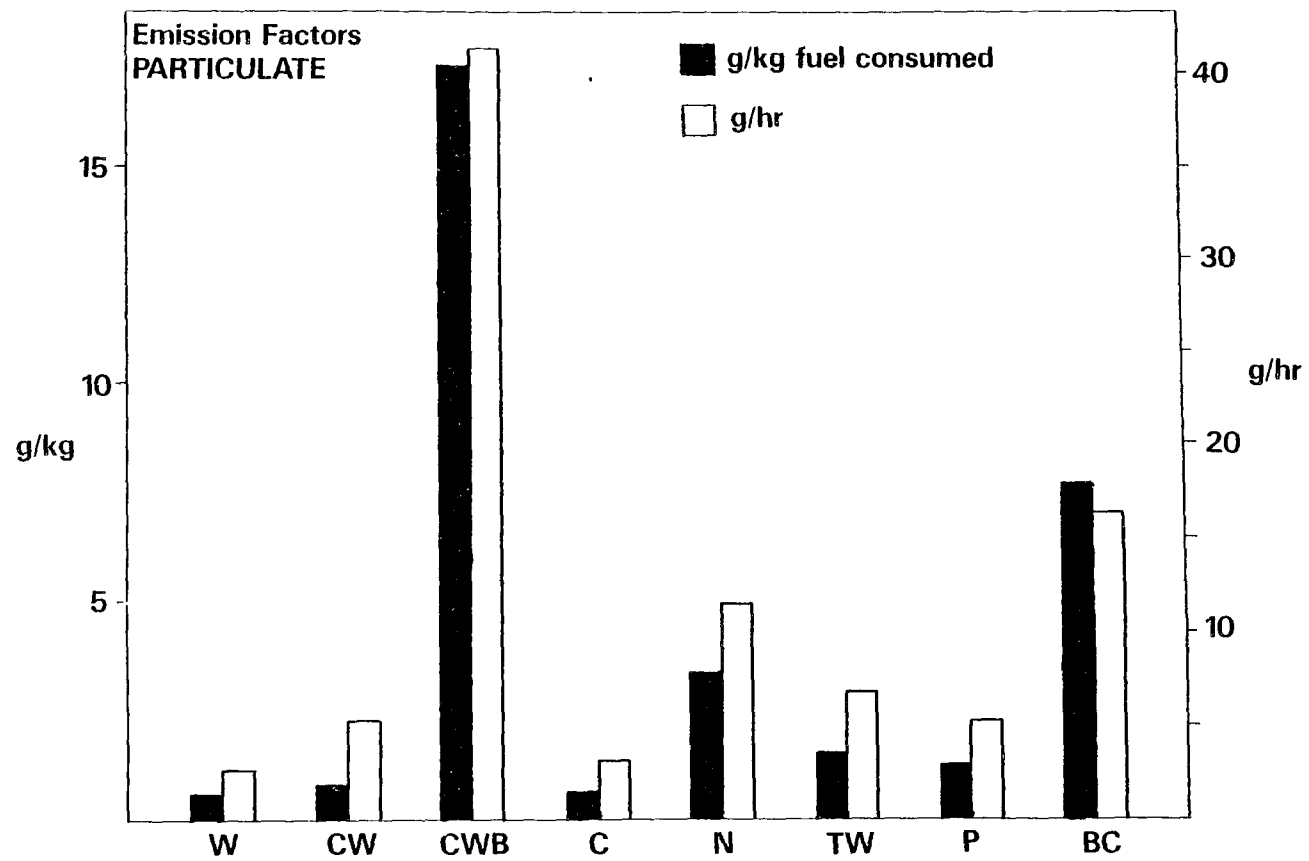


Figure 2. Emission factors: particulate.

7. Cardboard logs

8. Wood.

Wood and cardboard logs were lowest in particulate emissions and had similar particulate emission factors, although cardboard logs tended to have higher concentrations of particulate in the flue gas due to lower flow rates than the wood tests. Peat and compressed wood logs also had similar though slightly higher particulate levels, probably due to the fact that these fuels are basically compressed particulate matter and tended to disintegrate upon burning. Treated lumber was slightly higher still in particulate emissions, due to the increased amount of condensable organics in the flue gas. The treated lumber is yellow pine, which has significantly higher resin content than the aforementioned fuels. In addition, flow rates through the stove were very low during the treated lumber tests, which probably increased organic emissions. Newspaper logs were the next highest in particulate emissions. As the newspaper logs burned, burnt pieces of newspaper spalled off the rolls, contributing to the higher particulate levels. Organic emissions were very high during the newspaper tests, contributing significantly to the total particulate. Bituminous coal particulate emissions were significantly higher than the previously mentioned fuels. Most of this particulate matter was the infamous coal soot, a sticky mixture of condensed organics and carbon char. Coal particulate emitted per unit mass of fuel burned (g/kg) was over 5 times higher than for wood. However, particulate emissions rates (g/hr) were over an order of magnitude higher during coal tests than during wood tests. This discrepancy in difference is because of the higher heating value of coal which results in a lower fuel consumption rate.

The pressure drop across the orifice pressure meter in the Method 5 sampling station box was noted to decrease more rapidly immediately after coal addition than at other times during the run. This implies that the filter was collecting more particulate matter during these periods and that much of the particulate catch from the coal runs represents organic material volatilized during the pyrolysis of freshly added coal.

Compressed wood logs with paraffin binders (CWB) produced the highest particulate emissions of any fuels tested. CWB emission factors were over twice as high as coal and over 20 times higher than those for wood. The particulate catch for the CWB was largely organics, probably representing paraffin volatilization products.

Wood, compressed wood, cardboard logs and newspaper logs, and treated lumber, produced similar particulates in appearance, leaving a dark brown filter cake. Treated lumber particulate appeared to contain more organics and had a greenish tinge from copper compounds used in the lumber treatment. Fragments of burned newspapers could be seen in the particulate catch from the newspaper log tests. Peat particulate was interesting in that small sandlike particles could be seen in the filter catch. Bituminous coal and CWB produced a sooty, sticky particulate. The smoke during tests with these two fuels and tests with peat was brown to yellow, in comparison with the white to gray smoke from the other fuels. CWB particulate was especially gummy and waxy, because of the volatilization of the paraffin binders.

Table 7 is a comparison of particulate emission factors from commercial combustion units with those from residential combustion units burning wood and coal. For coal, residential stove particulate emissions are on the same order as stoker boilers, but lower than coal furnaces. It should be emphasized, however, that residential stove particulate differs qualitatively than particulate from commercial units. Commercial units emit predominantly inorganic particulate whereas residential units emit particulate composed largely of condensed hydrocarbons and unburned carbon char. Residential particulate, because of a small particle size range and trace carcinogenic hydrocarbons adsorbed on the particles, probably represents the greater health hazard.

For wood, residential stove particulate emissions are about an order of magnitude less than emissions from commercial units. This is probably due to the higher flue gas velocities in commercial units, which results in a larger amount of entrained particulate in the flue gas stream.

However, it should be noted that wood particulate emission factors have ranged to over 20 g/kg in other wood combustion studies^{11 12 13} with lower burn rates and higher organic emissions. The high particulate emission rates in these studies are largely attributable to increased total organics in the flue gas, rather than to high flue gas velocities as with commercial units.

7.1.1.2 Sulfur Dioxide (SO₂)--

Figure 3 and Table 8 gives SO₂ emission factors for the fuels tested. SO₂ emission factors vary directly with fuel sulfur content. Although SO₂ emissions are low for wood due to its low sulfur content, SO₂ emissions from

TABLE 7. COMPARISON OF PARTICULATE EMISSIONS FROM COMMERCIAL
AND RESIDENTIAL COMBUSTION UNITS BURNING WOOD AND COAL

	Particulate emission factor (g/kg fuel consumed)
Coal	
Stoker boilers ³⁷	1-6.5
Furnaces ³⁸	10-22
Residential stoves	7.60 ^a
Wood	
Stoker boiler ³⁷	2.3-6.8
Residential stoves	0.66 ^a

^aThis study, average of two tests.

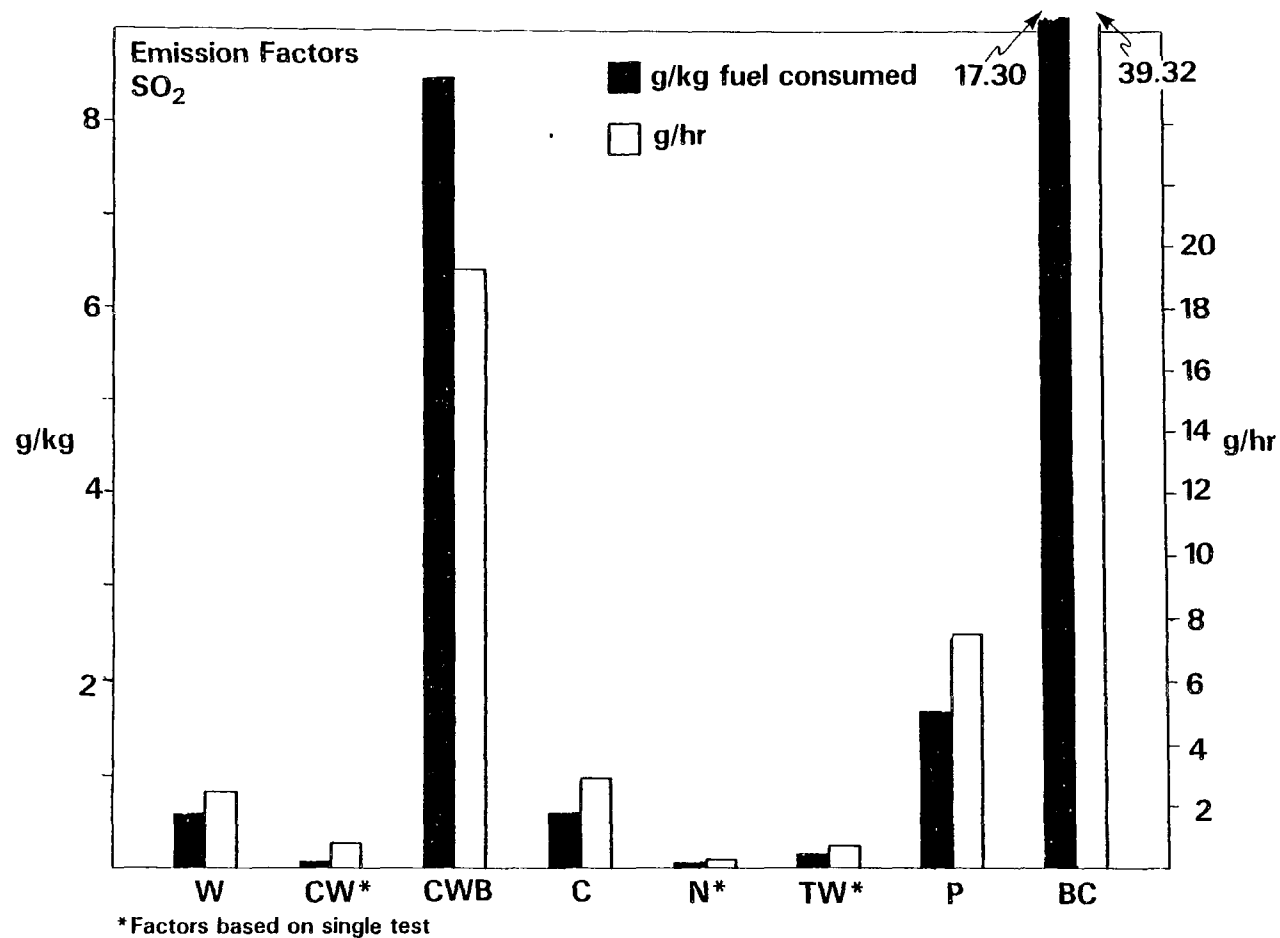


Figure 3. Emission factors: SO₂.

TABLE 8. EMISSION FACTORS--SULFUR DIOXIDE (SO₂)

Fuel	Test number	Avg. concentration μg/m ³ (ppm)		g/hr	g/kg
Oak logs	W1	4.4E4	(15.52)	2.32	0.51
	W2	4.3E4	(15.11)	2.63	0.66
Compressed wood logs	CW1	-	-	-	-
	CW2	2.9E4	(10)	0.80	0.08
Compressed wood logs with binder	CWB1	1.8E5	(64.20)	19.53	6.21
	CWB2	1.7E5	(60.65)	18.86	10.72
Cardboard logs	C1	1.3E5	(44.70)	4.42	0.74
	C2	3.4E4	(12.04)	1.31	0.35
Newspaper logs	N1	<2.9E4	(<10)	-	-
	N2	1.5E3	(0.54)	0.14	0.04
Treated lumber	TW1	<2.9E4	(<10)	<0.66	<0.12
	TW2	1.1E5	(39.98)	2.16	0.25
Peat,	P1	2.2E5	(77.46)	10.86	2.42
	P2	1.1E5	(39.91)	3.91	0.92
Bituminous coal	BC1	5.4E5	(190.20)	30.30	15.83
	BC2	1.1E6	(389.61)	48.33	18.76

combustion of coal and other fuels with high sulfur content can be significant and of concern because sulfur emission control devices for residential combustion units are not economical or available.

The eight fuels ranked as follows with regard to sulfur emissions (highest to lowest):

1. Bituminous coal
2. Compressed wood logs with binders (CWB)
3. Peat
4. Cardboard logs
5. Wood
6. Compressed wood logs without binders (CW)
7. Treated lumber
8. Newspaper logs

SO₂ emissions from treated lumber, newspaper logs, and CW were negligible. SO₂ emissions from wood and cardboard logs were higher but still quite low. Peat SO₂ emission were about twice as high as those from wood, reflecting a similar difference in sulfur content. Bituminous coal SO₂ emissions were the highest by far, with emission factors 20 to 30 times higher than those of wood, again reflecting a like difference in sulfur content. CWB had the second highest SO₂ emission factors, about an order of magnitude higher than those of wood. The reason for this high SO₂ emission is not immediately apparent from the CWB fuel sulfur analyses (0.25 percent). The sulfur content of CWB is lower than that of CW or cardboard logs, both of which had low SO₂ emissions. One reason for this discrepancy could be that standard coal analyses were performed to get sulfur content, and because these fuels are not coal, this could result in spurious fuel analysis results. Other reasons are not immediately apparent.

SO₂ concentrations generally rose slowly to a maximum as the test progressed, and then declined. Subsequent fuel additions caused additional maxima, again with SO₂ concentrations slowly rising and slowly falling off.

Table 9 is a list of SO₂ emission factors for commercial combustion units, compared with emission factors for wood and coal from this study. Examination of this table shows that the emission factors for SO₂ are similar for commercial and residential combustion units.

TABLE 9. COMPARISON OF SO₂ EMISSIONS FOR COMMERCIAL AND
RESIDENTIAL COMBUSTION UNITS BURNING WOOD AND COAL

	SO ₂ emission factor (g/kg fuel consumed)	Percent S in fuel
Coal		
Stoker boiler ³⁷	19	1.92
Furnace ³⁸	6.3-15	0.58-1.5
Residential stove	17.3 ^a	1.87
Wood		
Stoker boiler ³⁷	0.7	ND
Residential stove	0.58 ^a	0.09

^aThis study, average of two tests.

ND = No Data.

7.1.1.3 Nitrogen Oxides (NO_x)--

Nitrogen oxides (NO_x) emission factors are presented in Table 10 and Figure 4. Two rankings of fuel by NO_x emissions are possible. First, considering NO_x emission rates (g/hr), the fuels may be ranked as follows (highest to lowest):

1. Peat
2. Compressed wood logs with binder
3. Bituminous coal
4. Wood
5. Compressed wood logs (no binder)
6. Cardboard logs
7. Newspaper logs
8. Treated lumber

Considering NO_x emission factors (g/kg fuel consumed), the fuels may be ranked as follows (highest to lowest):

1. Compressed wood logs with binders
2. Bituminous coal
3. Peat
4. Wood
5. Newspaper logs
6. Cardboard logs
- 7a. Treated wood (same level as 7b)
- 7b. Compressed wood logs (no binders)

The difference in ranking between g/hr and g/kg emission factors is due to difference fuel consumption rates. Higher heating value fuels (coal and CWB) have low fuel consumption rates because less fuel has to be burned to produce a unit heat output. Hence, peat is the highest ranked NO_x emitter on a g/hr basis, but is replaced by coal and CWB on a g/kg basis because more peat is burned per unit time than coal or CWB. Similar reasoning can be used to explain changes in rank between g/hr and g/kg emission factors for the other fuels.

Two factors were found to be important in determining NO_x emission magnitude: fuel nitrogen content and stack gas flow rate. Two of the three highest NO_x emitters, peat and coal, had the highest fuel nitrogen content, 0.93 percent and 1.54 percent, respectively. This was judged to be the most important

TABLE 10. EMISSION FACTORS--NITROGEN OXIDES (NO_x)

Fuel	Test number	Avg. concentration μg/m ³ (%)	g/hr	g/kg
Oak logs	W1	5.0E4 (42.79)	3.12	0.69
	W2	5.4E4 (35.29)	3.26	0.82
Compressed wood logs	CW1	2.3E4 (15.43)	0.64	0.12
	CW2	5.7E4 (39.20)	1.61	0.17
Compressed wood logs with binder	CWB1	6.1E4 (45.31)	6.46	2.05
	CWB2	1.2E5 (88.97)	13.44	7.64
Cardboard logs	C1	5.5E4 (38.66)	1.90	0.32
	C2	4.4E4 (29.39)	1.67	0.45
Newspaper logs	N1	2.1E4 (14.50)	1.65	0.52
	N2	1.5E4 (10.44)	1.40	0.40
Treated lumber	TW1	2.8E4 (20.00)	0.65	0.11
	TW2	4.2E4 (28.58)	0.80	0.18
Peat	P1	2.9E5 (192.04)	14.11	3.14
	P2	3.1E5 (206.60)	10.58	2.50
Bituminous coal	BC1	1.8E5 (126.58)	10.24	5.35
	BC2	1.4E5 (98.92)	6.27	2.43

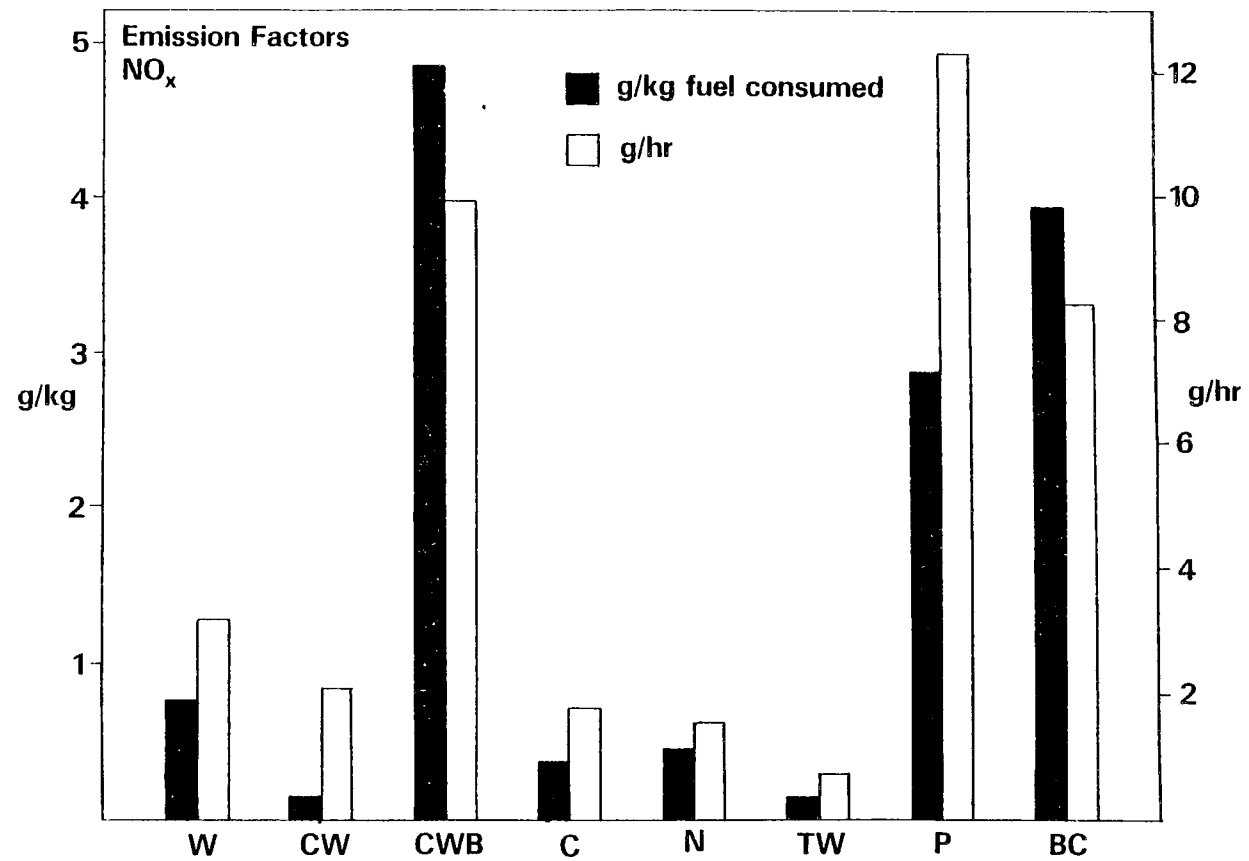


Figure 4. Emission factors: NO_x.

cause of high NO_x emissions from the combustion of these fuels. The other fuel with exceptionally high NO_x emissions, CWB, had the highest stack flow rates of all the fuels tested. Omitting the fuels with high nitrogen content, a correlation of NO_x emission rate (g/hr) and stack flow rate was apparent. The linear correlation coefficient for stack flow rates versus NO_x emission rate for tests using fuels was 0.717. Increasing stack flow rate, which is indicative of increased air flow through the stove, thus increases NO_x emissions. This agrees with conclusions drawn by other researchers. No correlation was found between firebox temperature and NO_x emissions, however, which disagrees with conclusions drawn by other researchers. It could be that firebox temperature did not vary enough during these tests to affect NO_x emissions.

Maximum NO_x concentrations generally occurred a few minutes after fire start. Other maxima occurred following fuel additions. Air flow changes through the stove could be detected on the NO_x chart. Following door opening to poke the fire, NO_x readings dropped immediately and then rose to levels above the level prior to opening the doors. The initial decrease reflects dilution of the NO_x in the stack gas from the large amount of air introduced into the stove following door openings. The subsequent increase in NO_x levels reflects a higher emission of NO_x due to increased air flow through the stove through the open doors. NO_x concentrations also increased with increased draft opening and damper opening, again reflecting increased NO_x formation because of increased air flow through the stove.

During several tests, the NO_x detector was switched to the NO detection mode to determine the percentage of NO_2 versus NO in the flue gas. NO_2 is generally considered to be more of a problem than NO from environmental and health standpoint. NO proportions are given in Table 11. It may be seen that NO accounted for most of the total NO_x measured during these tests, accounting for an average of 76.09 percent of the total NO_x .

Table 12 is a comparison of NO_x emission factors (g/kg) from the coal and wood tests in this study with emission levels from coal and wood combustion in commercial units. Coal stoker units produce NO_x emission factors similar to those from residential stoves. Coal furnaces are slightly higher in NO_x emission factors. Commercial wood units are significantly higher in emission factors than residential wood stoves, however. This difference can be attributed to differences in amounts of combustion air. Commercial wood burning

TABLE 11. PERCENT NO IN NO_x EMISSIONS

Test number	NO _x level (ppm)	NO level (ppm)	Percent NO ^a
W1	116.74	51.77	44.35
	101.52	43.65	43.00
	53.80	41.11	76.42
	50.25	38.02	75.76
	39.59	26.39	66.67
	40.61	27.41	67.50
	45.68	35.02	76.67
	46.19	31.98	69.23
W2	63.96	45.68	71.43
	46.19	31.47	68.13
	43.14	33.50	77.65
	34.52	28.93	83.82
	36.04	26.90	74.65
	33.50	27.92	83.33
CWB2	50.18	48.20	96.05
	42.73	38.26	89.53
	33.29	27.33	82.09
	30.81	25.84	83.87
C2	49.74	40.61	81.63
	30.96	20.81	76.21
	34.01	21.83	64.18
	26.39	20.81	78.85
	25.38	20.81	82.00
N2	21.50	14.85	69.05
	16.90	13.82	81.82
	13.31	11.26	84.62
	12.80	10.75	84.00
TW2	24.50	19.50	79.59
	26.00	29.50	75.00
	19.00	14.50	76.32
	19.00	14.50	76.32

^aAverage percent NO is 76.09.

TABLE 12. COMPARISON OF NO_x EMISSION FACTORS FOR
COMMERCIAL AND RESIDENTIAL COMBUSTION
UNITS BURNING WOOD AND COAL

	NO _x emission factor (g/kg)	Percent N in fuel
Coal		
Stoker boiler ³⁷	3-7.5	ND
Furnace ³⁸	6.3-15	ND
Residential stove	3.89 ^a	1.54
Wood		
Stoker boiler ³⁸	4.5	ND
Residential stove	0.76 ^a	0.29

^aThis study, average of two tests

ND = No data.

units operate with high excess of air, a condition conducive to NO_x formation. Starved air conditions used in most residential units minimizes NO_x formation. The same effect was not seen for coal because fuel nitrogen appears to have a greater effect on NO_x emissions than stack flow for high nitrogen content fuels such as coal or peat.

7.1.1.4 Carbon Monoxide (CO)--

CO emission factors are given in Table 13 and Figure 5. CO emissions for the various fuels tested did not vary as much as with the previously discussed pollutants. Ranking fuels according to CO emission factors (g/kg) fuel consumed is as follows (highest to lowest):

1. Newspaper logs
2. Compressed wood logs with binders
3. Peat
4. Bituminous coal
5. Cardboard logs
6. Compressed wood logs without binder
7. Treated lumber
8. Wood

Ranking of fuels according to CO emission rates (g/hr) is as follows (highest to lowest):

1. Newspaper logs
2. Compressed wood logs without binders
3. Peat
4. Cardboard logs
5. Compressed wood logs with binders
6. Treated lumber
7. Wood
8. Bituminous coal

Reasons for the change in ranking between emission factors (g/kg) and emission rates (g/hr) are related to fuel consumption rates and fuel heating values as discussed in the previous section on NO_x emissions.

CO emission levels could not be successfully correlated with stove operating parameters, including stack flow rates, firebox temperatures, stack temperatures, fuel consumption rate, and heat output. Examination of Figure 5 reveals

TABLE 13. EMISSION FACTORS--CO

Fuel	Test number	Avg. concentration $\mu\text{g}/\text{m}^3$ (%)		g/hr	g/kg
Oak logs	W1	2.5E6	(0.20)	130.57	28.90
	W2	2.9E6	(0.23)	175.31	44.00
Compressed wood logs	CW1	1.4E7	(1.12)	395.93	71.51
	CW2	8.9E6	(0.71)	248.63	26.09
Compressed wood logs with binder	CWB1	2.1E6	(0.17)	226.15	71.88
	CWB2	2.0E6	(0.16)	216.37	123.02
Cardboard logs	C1	9.4E6	(0.75)	323.97	54.42
	C2	5.1E6	(0.41)	195.08	52.43
Newspaper logs	N1	4.8E6	(0.38)	369.49	115.49
	N2	3.3E6	(0.36)	298.09	84.94
Treated lumber	TW1	9.0E6	(0.72)	208.22	37.01
	TW2	5.4E6	(0.43)	101.71	22.97
Peat	P1	5.3E6	(0.43)	257.71	57.31
	P2	8.4E6	(0.67)	286.73	67.82
Bituminous coal	BC1	2.0E6	(0.16)	111.41	58.22
	BC2	3.0E6	(0.24)	130.17	50.52

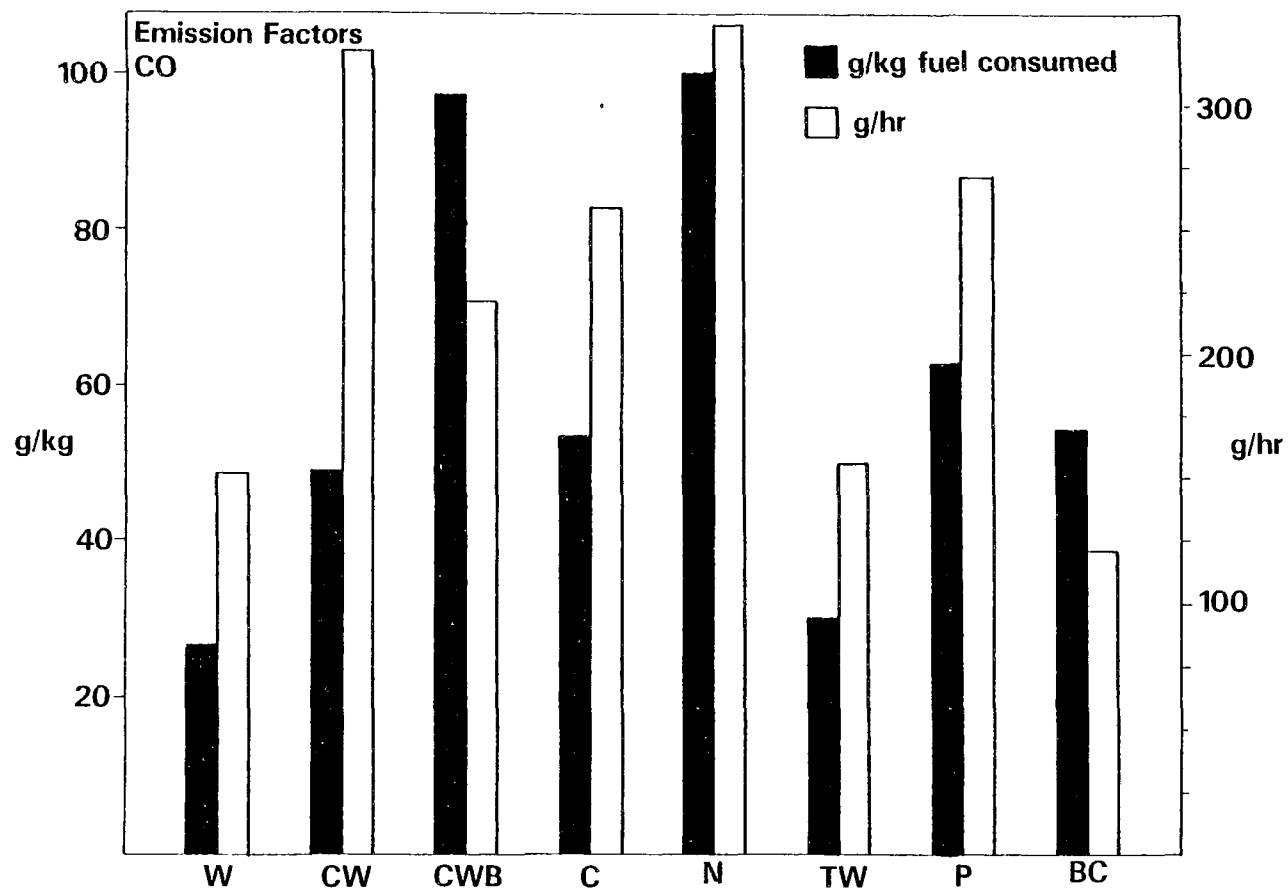


Figure 5. Emission factors: CO.

that the fuels with the lowest CO emissions are wood, treated lumber, and bituminous coal. This is significant because all the other fuels with higher CO emissions are manmade. They represent either compressed particulate or chips (CW, peat, cardboard logs) cemented particulate (CWB), or rolled newspaper. The physical structure of these fuels probably is the major cause of their higher CO emissions. The tightness of these fuel structures probably prevents air from reaching the inner portions of the fuel as it is burned, resulting in incomplete combustion and higher CO emissions. Newspaper logs have a tightly rolled structure of many sheets and the tightness of these logs prevents air from reaching the inner layers before the outer layers burn off. There is probably an oxygen concentration gradient across the log as it burns. Paraffin impregnated CWB also is a very tight fuel which burns slowly and does not crack open during burning as does coal or wood. The particulate formed fuels (peat, CW, and cardboard logs) tended to fall apart when burned, forming a pile of smoldering particulate matter in the stove. Oxygen starved conditions almost certainly exist in the center of the pile, leading to increased CO emissions in these fuels as compared to wood.

Maximum CO concentrations were generally a few minutes after fire start. Other CO maxima occurred following fuel additions during each test.

Table 14 compares CO emission factors from commercial combustion units with those from residential units (this study) for wood and coal. It may be seen that CO emissions from residential stoves are significantly higher than those from commercial combustion units. This can be attributed to the starved air combustion conditions in residential wood stoves.

7.1.1.5 Carbon Dioxide (CO₂)--

CO₂ emission factors for the fuels tested are given in Table 15. CO₂ emissions were highest for compressed wood logs with binders. CO₂ emissions for the other fuels were fairly uniform.

Maximum CO₂ concentrations generally occurred a few minutes after the fire start. Other maxima occurred after each fuel addition. CO₂ maxima usually lagged behind CO maxima by 2-3 minutes.

7.1.1.6 Organics--

Table 16 is a listing of emission factors for total organics. A compilation of results from total chromatographical organics and gravimetric analyses

TABLE 14. COMPARISON OF CO EMISSIONS FROM COMMERCIAL AND RESIDENTIAL COMBUSTION UNITS BURNING WOOD AND COAL

	CO emission factors g/kg fuel consumed
Coal	
Stoker boiler ³⁷	1-5
Furnace ³⁸	4.4-13
Residential stove	34.45 ^a
Wood	
Stoker boiler ³⁷	0.9-27
Residential stove	54.36 ^a

^aThis study, average of two tests.

TABLE 15. EMISSION FACTORS--CO₂

Fuel	Test number	Avg. concentration μg/m ³ (%)		g/hr	g/kg
Oak logs	W1	1.2E8	(5.90)	6.1E3	1.3E3
	W2	8.6E7	(4.39)	5.3E3	1.3E3
Compressed wood logs	CW1	2.2E10	(11.13)	6.1E3	1.1E3
	CW2	1.7E8	(8.46)	4.7E3	4.9E2
Compressed wood logs with binder	CWB1	1.5E8	(7.44)	1.6E4	4.9E3
	CWB2	1.0E8	(8.46)	1.1E4	6.5E3
Cardboard logs	C1	1.8E8	(9.34)	6.3E3	1.1E3
	C2	1.2E8	(5.95)	4.4E3	1.2E3
Newspaper logs	N1	5.1E7	(2.58)	3.9E3	1.2E3
	N2	4.8E7	(2.44)	4.4E3	1.3E3
Treated lumber	TW1	1.9E8	(9.92)	4.5E3	8.0E2
	TW2	1.9E8	(9.74)	3.6E3	8.2E2
Peat	P1	1.2E8	(6.32)	6.1E3	1.4E3
	P2	1.9E8	(9.52)	6.4E3	1.5E3
Bituminous coal	BC1	7.2E7	(3.66)	4.0E3	2.1E3
	BC2	7.2E7	(3.69)	3.1E3	1.2E3

TABLE 16. EMISSION FACTORS--TOTAL HYDROCARBONS (+100° C^a) (g/kg)

Run	TCO (100-300°C ^a)	Gravimetric (+300°C ^a)	Total
W1	1.35	3.54	4.89
W2	1.80	4.67	6.47
CW1	3.10	3.67	6.77
CW2	0.85	1.15	2.00
CWB1	1.28	1.45	2.73
CWB2	1.56	1.28	2.84
C1	1.40	3.06	4.46
C2	3.15	6.13	9.28
N1	4.80	21.13	25.93
N2	3.40	13.43	16.83
TW1	1.71	1.28	2.99
TW2	1.00	5.77	6.77
P1	7.00	17.58	34.58
P2	0.83	8.52	9.35
BC1	0.74	7.52	8.26
BC2	0.18	0.70	0.88

^aBoiling point

and represents total organics with boiling points greater than 100° C. It may be seen in this table that total organic emissions in the flue gas were similar for all fuels except for newspaper logs and peat, which had higher organic emission factors. Newspaper logs showed a high amount of high boiling point (+300° C) compounds, contributing to a high level of total organics. This is somewhat surprising since newspaper logs had the lowest PNA emission factors (see Fuels Comparison). Peat also had fairly organic emission factors, again with high boiling organics contributing a large portion of the total organics. Coal, with organic emissions comparable to most other fuels, had the highest proportional contribution of heavy organics. The second coal run was suspiciously low in organics. Very low emission factors were also seen for PNAs for this test. The disagreement with the first coal run, along with high organic concentrations in coal flue gas reported by other researchers, implies that the organic results for this test should be held in question.

Results of the gas bulb analyses are presented in Table 17.

7.1.1.7 Polynuclear Aromatic Hydrocarbons (PAH)--

Emission factors for the 24 polynuclear aromatic hydrocarbons analyzed in this study are presented in Table 18. Figure 6 is a comparison of benz(a)pyrene (B(a)P) emission factors for the eight fuels tested. It may be seen from this table that B(a)P emission factors are lowest for newspaper logs. Wood and coal have similar levels, contrary to results of other researchers. This may be due to fairly low firebox temperatures and heat output during the coal run, combined with good air circulation through the stove during the coal run. Stove design may also be a factor. Other fuels had higher B(a)P emission factors probably due to burning characteristics which reduce air to the fuel (particulate fuels) or a high resin content combined with very low air flow through the stove (treated lumber).

Some of the wood and coal PNA emission factors were compared to emission factors from combustion of coal and wood in other types of residential units (Table 19). The PNA emissions from wood combustion differ by an order of magnitude, which reflects the difference in stove type and combustion conditions. Emissions from bituminous coal combustion in the wood stove and in a residential hot water boiler, however, are in much closer agreement.

TABLE 17. GAS BULB ORGANIC CARBON CONCENTRATION

Run	Concentration (ppm)
W1	173
	336
W2	310
	82
CW1	
CW2	1,100
CWB1	456
	158
CWB2	99
	354
C1	773
	620
C2	1,140
	810
N1	
N2	680
	270
TW1	170
	303
TW2	2,800
P1	807
	16
P2	230
BC1	206
	100
BC2	178
	69

TABLE 18. PAH EMISSION FACTORS (mg/kg)

Compound	W1	W2	CW1	CW2	CWB1	CWB2	C1	C2
Naphthalene	30.19	43.29	53.48	27.94	335.01	260.52	70.90	108.34
Biphenyl	13.32	9.46	7.88	2.29	16.35	29.70	8.21	8.71
Acenaphthene	NA	8.03	3.13	0.56	1.39	1.48	1.62	4.24
Fluorene	4.75	4.59	6.18	1.94	1.65	10.53	3.52	8.76
Phenanthrene	8.19	11.32	23.27	8.16	48.80	42.66	19.82	21.89
Anthracene	4.69	7.38	8.72	1.88	ND	7.02	1.62	2.71
Carbazole	NA	ND	0.10	ND	ND	4.45	0.29	ND
1-Methyl phenanthrene	9.50	19.85	6.32	1.11	15.44	25.11	3.11	5.37
9-Methyl anthracene	3.13	1.29	6.04	ND	20.05	ND	6.34	ND
Fluoranthene	2.94	4.37	16.74	5.38	24.22	17.01	15.01	9.79
Pyrene	2.44	2.80	11.56	4.10	14.05	12.01	9.25	3.21
Benz(a)anthracene	0.13	ND	5.66	1.39	ND	1.75	2.65	2.08
Chrysene	2.00	1.15	2.57	1.28	5.06	1.35	1.99	2.03
12-Methyl benz(a)anthracene	NA	0.07	ND	ND	ND	ND	ND	0.04
6-Methyl chrysene	NA	0.50	1.88	0.24	3.61	0.41	0.37	1.17
7-Methyl benz(a)anthracene	NA	0.50	1.88	0.24	3.61	0.41	0.37	1.17
7,12-Dimethyl benz(a)anthracene	1.13	1.79	6.04	2.12	8.25	ND	2.70	3.07
Benzo(b)fluoranthene	ND	ND	ND	ND	ND	0.94	ND	ND
Benzo(k)fluoranthene	ND	ND	ND	ND	ND	0.94	ND	ND
Benzo(e)pyrene	0.44	0.65	2.47	2.08	3.08	0.54	2.70	1.41
Benzo(a)pyrene	0.69	0.57	2.74	1.94	5.72	0.67	1.82	1.17
Perylene	0.44	1.22	1.18	0.83	14.60	0.67	0.70	0.54
3-Methyl cholanthrene	0.31	0.22	1.53	ND	ND	0.54	ND	0.90
Dibenz(a,h)anthracene	ND	NA	NA	NA	NA	NA	NA	NA
Benzo(g,h,i)perylene	ND	0.07	0.90	2.05	ND	0.013	1.62	0.14
Coronene	NA	ND	0.90	ND	1.24	ND	ND	ND

NA = Not analyzed.

ND = Not detected.

TABLE 18. (continued)

Compound	N1	N2	TW1	TW2	P1	P2	BC1	BC2
Naphthalene	64.44	142.64	115.87	297.89	82.98	36.46	67.01	26.96
Biphenyl	33.22	21.03	11.67	54.40	18.36	8.21	12.08	3.59
Acenaphthene	NA	7.60	2.35	15.01	NA	3.55	ND	0.15
Fluorene	17.27	6.35	5.96	31.92	13.53	7.33	10.75	1.57
Phenanthrene	23.92	21.24	18.30	48.57	18.84	7.33	24.29	7.822
Anthracene	13.12	4.16	4.98	35.42	13.47	3.77	6.56	1.673
Carbazole	NA	ND	1.18	1.04	NA	0.04	NA	0.49
1-Methyl phenanthrene	5.48	4.16	3.44	17.97	10.68	7.46	10.12	4.43
9-Methyl anthracene	ND	ND	ND	1.02	8.91	4.74	ND	ND
Fluoranthene	9.22	9.27	7.67	17.49	12.72	7.50	8.59	2.71
Pyrene	0.08	2.60	6.35	13.58	8.22	3.77	7.05	1.67
Benz(a)anthracene	1.83	0.21	1.99	4.87	6.33	ND	1.95	+
Chrysene	1.74	3.33	1.29	1.63	6.60	1.97	2.51	0.30
12-Methyl benz(a)anthracene	NA	ND	ND	ND	ND	ND	NA	ND
6-Methyl chrysene	NA	0.10	0.34	0.39	NA	0.26	NA	0.15
7-Methyl benz(a)anthracene	0.50	0.21	4.03	6.31	0.07	ND	1.75	0.74
Benzo(b)fluoranthene	ND	0.21	ND	ND	0.07	0.22	ND	ND
Benzo(k)fluoranthene	0.33	0.42	1.93	3.42	3.67	0.48	0.99	0.54
Benzo(e)pyrene	0.25	0.31	1.54	3.20	5.78		0.77	0.20
Benzo(a)pyrene	0.17	ND	0.62	ND	6.33	3.16	0.27	3.05
Perylene	NA	0.94	5.15	8.44	0.07	ND	ND	0.20
3-Methyl cholanthrene	ND	NA	NA	NA	ND	NA	ND	NA
Dibenz(a,h)anthracene	ND	ND	0.20	0.39	1.43	ND	ND	ND
Benzo(g,h,i)perylene	NA	ND	ND	1.13	NA	ND	NA	ND
Coronene								

NA = Not analyzed.

ND = Not detected.

+ = May be present; peak interference.

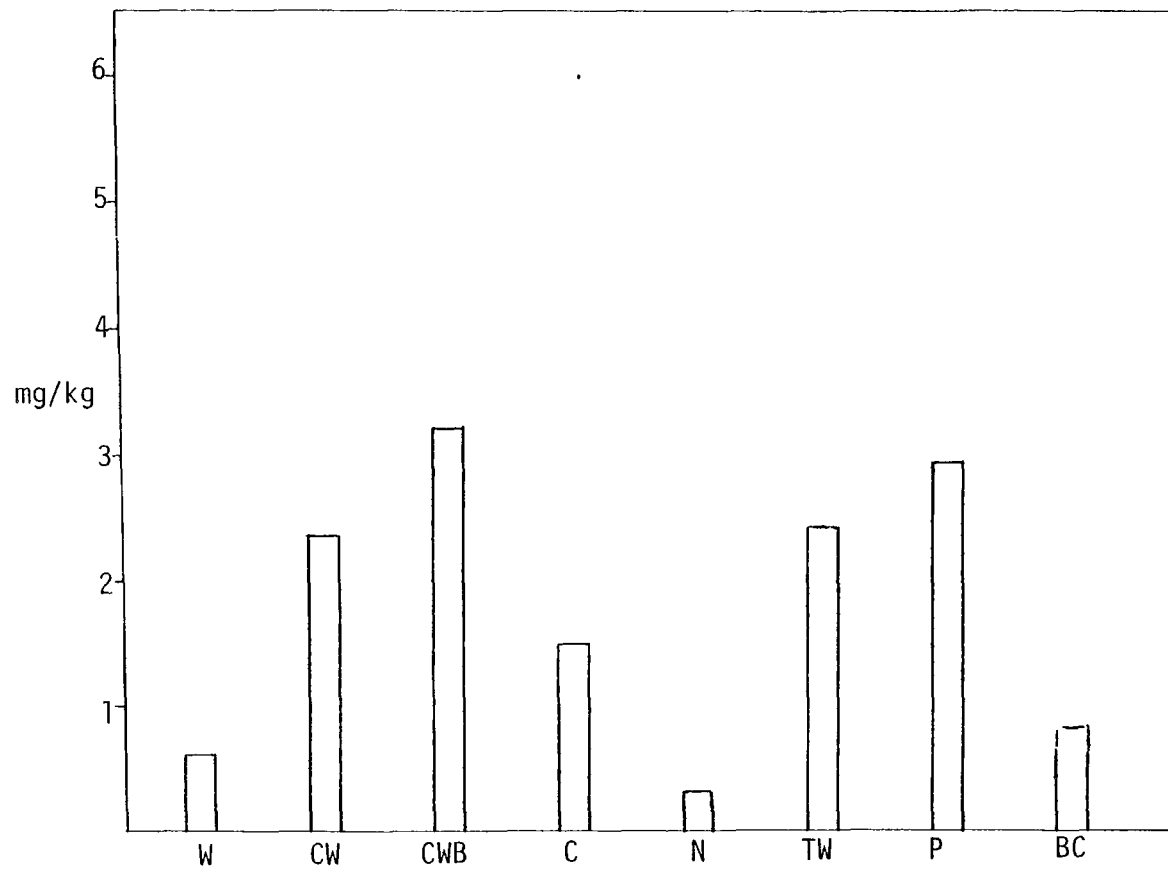


Figure 6. Emission factors: benz(a)pyrene.

TABLE 19. COMPARISON OF EMISSION FACTORS OF PNAs (g/kg)

	Oak, this study	Oak, ²⁵ Baffled stove	Bituminous coal, this study	Coal, ³⁸ Hot water boiler
Naphthalene	0.0367	0.2729	0.0670	0.28
Biphenyl	0.0114	0.0228	0.0121	0.009
Fluorene	0.0047	0.0224	0.0108	0.048
Anthracene/phenanthrene	0.0158	0.0745	0.0309	0.029
Fluoranthene	0.0037	0.0180	0.0086	0.01
Pyrene	0.0026	0.0156	0.0071	0.009
Chrysene/benz(a)anthracene	0.0017	0.0125	0.0045	0.007
7,12-Dimethyl benz(a)- anthracene	0.0015	-	0.0018	0.15
Benzopyrenes and perylene	0.002	0.0083	0.0020	0.006
3-methyl cholanthrene	0.0003	0.00007	ND	0.003

ND = Not detected.

7.2 FUELS COMPARISON

Table 20 gives results of proximate and ultimate analysis of the nine fuels tested. Heating values (dry and wet basis) for each fuel are also given in this table. Table 21 is a listing of important stove operating parameters for each fuel test run. Note that heat output estimates are only used for test comparisons and are not accurate estimates of actual heat output. Following is a discussion, by fuel, of conditions encountered in each test, the effects of these conditions on emissions, and any problems encountered in reaching and maintaining steady-state stove operation. Table 22 is a listing of ash analyses for all 16 tests.

Wood (Oak)

Wood (oak) was the best fuel tested in this program on the basis of emissions and ease of stove operation. The stove chosen for this study was designed to burn wood, and this was reflected by stove operating parameters. Examination of Table 21 shows that there was the least amount of variation of these parameters between the duplicate test runs than for any other fuel tested. This is also reflected in the emission factors, which are very consistent between the two duplicate tests (Tables 6, 8, 10, and 13).

Because of this similarity between tests, it was not possible to determine the effect of stove operating parameters on emissions for the wood tests. As discussed under emission comparisons, wood was among the lowest emitting fuels for all pollutants except for NO_x . NO_x emissions from wood were significantly lower than the high NO_x emitting fuels, however, with NO_x levels more comparable to the four low NO_x emitting fuels (Figure 4). Maximum NO_x , CO, and SO_2 levels for the wood tests are given in Table 23 along with the time in each test these maxima occurred. It may be seen from this table that pollutant emission maxima occurred shortly after the fire was started or after wood addition to the fire.

Total organic emissions were similar for the two duplicate tests with wood (Table 16). Organic emissions were also similar for wood and all other fuels except peat and newspaper logs, which had significantly higher organic emissions. Heavy organics ($+800^\circ\text{C}$ boiling point) accounted for about 2/3 of the total organic emissions. PNA emission factors were also comparable for the duplicate wood tests. Wood PNA emission factors were generally lower than those from other fuels, especially considering the heavier PNAs (those with

TABLE 20. FUEL ANALYSES

	W ^a	CW	CWB	C	N	TW	P	BC	AC
Proximate analysis (as received)									
Percent moisture	10.87	10.45	2.70	9.23	8.54	9.16	12.74	2.37	4.08
Percent ash	0.99	0.42	0.71	1.17	0.51	1.14	2.20	10.97	10.22
Percent volatile	74.14	76.62	89.77	77.93	78.68	77.32	56.85	32.61	4.54
Percent fixed carbon ^b	14.01	12.51	6.82	11.67	12.27	12.38	28.21	54.05	81.16
Btu's/lb (as received)	7310	7946	13925	7331	7805	7890	8668	12731	12178
(dry basis)	8201	8873	14311	8077	8534	8686	9933	13040	12696
Ultimate analysis (dry basis)									
Percent carbon	50.90	53.30	67.56	49.96	53.06	52.19	54.89	73.36	84.04
Percent hydrogen	6.20	6.12	9.92	6.01	6.04	6.20	5.98	4.72	2.00
Percent nitrogen	0.29	0.44	0.34	0.37	0.00	0.43	0.93	1.54	1.14
Percent chlorine	0.00	0.00	0.29	0.00	0.02	0.00	0.05	0.06	0.01
Percent sulfur	0.09	0.89	0.25	0.35	0.16	0.005	0.21	1.87	0.57
Percent ash	1.11	0.47	0.73	1.29	0.56	1.25	2.52	11.24	10.65
Percent oxygen ^b	41.41	38.78	20.97	42.02	40.16	39.93	30.42	7.21	1.59

^aAverage of two analyses.^bBy difference.

TABLE 21. OPERATING PARAMETERS--SAMPLING PERIOD AVERAGES

		Flow rate (dry) (scfm)	Fuel consumption rate (kg/hr)	Stack tempera- ture (°C)	Firebox tempera- ture (°C)	Sample volume (scm)	Estimated heat output Btu's/hr
Oak logs	1	30.73	4.518	286	515	1.392	65477.1
	2	35.88	3.984	248	537	1.375	62053.7
Compressed wood	1	16.64	5.490	197	601	0.787	72975.6
	2	16.49	9.530 ^a	262	570	0.933	59706.2
Compressed wood w/binders	1	62.62	3.128	254	644	1.140	77406.3
	2	63.62	1.750	250	516	1.302	62218.3
Cardboard logs	1	20.34	5.953	284	633	0.889	61181.6
	2	22.40	3.711	238	531	0.850	64320.6
Newspaper logs	1	45.78	3.199	219	400	1.155	19644.5
	2	53.97	3.510	253	430	1.344	53334.4
Treated wood	1	13.62	5.648	279	483	1.659	-
	2	11.14	4.427	188	554	1.688	66197.8
Peat	1	28.89	4.497	300	565	0.473	61273.7
	2	20.15	4.227	273	529	1.222	64502.9
Bituminous coal	1	32.78	1.914	288	464	1.343	35937.5
	2	25.54	2.580	335	597	1.646	52499.7

^aExtrapolated.

TABLE 22. ASH ANALYSIS

	W1 & 2	CW1	CW2	CWB1	CWB2	C1	C2
Proximate (as received)							
Percent moisture	1.15	1.85	8.08	0.29	2.18	6.17	2.26
Percent ash	57.52	54.93	25.50	93.10	81.82	61.37	73.67
Percent volatile	35.17	35.15	27.63	16.22	27.17	27.99	24.88
Percent fixed carbon ^a	6.16	8.07	38.79	-9.61	-11.17	4.47	0.81
Btu's/lb (as received)							
(dry basis)	2209	2701	7513	245	1170	699	2066
	2235	2752	8173	346	1196	745	2114
Ultimate (dry basis)							
Percent carbon	22.82	25.93	55.07	4.64	11.41	9.06	16.06
Percent hydrogen	0.25	0.65	1.59	0.15	0.40	1.63	0.37
Percent nitrogen	0.45	0.40	0.58	0.45	0.63	0.36	0.45
Percent chlorine	0.04	0.00	0.05	0.84	0.84	0.33	0.25
Percent sulfur	0.34	0.24	1.04	5.86	5.13	3.89	3.83
Percent ash	58.19	55.97	27.74	93.37	83.64	65.41	75.38
Percent oxygen ^a	17.91	16.81	13.93	-5.31	-2.05	19.32	3.66

^aBy difference.

(Continued)

TABLE 22. (continued)

	N1	N2	TW1	TW2	P1	P2	BC1	BC2
Proximate (as received)								
Percent moisture	10.94	22.72	6.45	8.72	2.37	2.56	1.80	2.23
Percent ash	31.11	29.45	33.43	36.42	28.32	40.14	47.71	61.69
Percent volatile	23.44	22.05	15.67	6.10	13.23	10.77	6.61	5.98
Percent fixed carbon ^a	34.51	25.78	44.46	48.76	56.08	46.53	43.88	30.10
Btu's/lb (as received)								
(dry basis)	6348	4961	8225	7363	9163	7593	6864	4892
	7128	6420	8792	8066	9385	7793	6990	5004
Ultimate (dry basis)								
Percent carbon	48.77	44.60	58.90	53.86	62.64	51.92	47.06	21.06
Percent hydrogen	1.43	1.16	0.72	0.89	0.95	0.69	0.88	0.47
Percent nitrogen	0.59	0.59	1.77	1.86	1.66	1.29	0.95	0.90
Percent chlorine	0.12	0.13	0.00	0.00	0.07	0.07	0.03	0.02
Percent sulfur	1.00	1.00	0.22	0.22	0.44	0.57	0.78	0.84
Percent ash	34.93	38.11	35.72	39.90	29.01	41.19	48.58	63.09
Percent oxygen ^a	13.16	14.41	2.67	3.27	5.23	4.27	1.72	13.62

^aBy difference.

TABLE 23. EMISSION MAXIMA--WOOD TESTS

	Test number	Maximum concentration	Time of maximum
NO _x	W1	254.74 ppm	3 min after fire start
	W2	68.24 ppm	9 min after 22.6 lb wood addition; 2 min after draft/damper opening
SO ₂	W1	None	Levels uniform throughout test
	W2	None	Levels uniform throughout test
CO	W1 and 2	1.0%	2 min after fire start

boiling points greater than that of perylene). Wood PNA emission factors were similar to those for bituminous coal and higher than those from newspaper logs, the fuel with the lowest PNA emissions.

The wood used in this study was fairly dry (11 percent moisture) and was obtained from a local firewood supplier. It is representative of firewood available in North Carolina. The burn rate (about 4 kg/hr) was higher than other studies using wetter wood,^{11 12 13 14} which resulted in lower particulate emission factors for this study. Wood with high moisture has been shown to have higher particulate emissions, with emission factors reaching over 20 g/kg.¹³ Because of the great variability of reported particulate emission rates for woodstoves, under certain conditions wood particulate emission factors could be higher than for the other fuels in this study. However, during this study the burn rate for each fuel was controlled (when possible) to provide equal heat output from the stove for each test. Thus, we feel that the comparison between the alternate fuels' particulate emission factors and the emission factors for dry oak are valid. Care should be taken when comparing the wood particulate emission factors in this study with those from other studies with different stoves, wood types, wood moisture content, and burn rates.

Compressed Wood Logs (without binders)

These logs, formed of compressed wood chips, were determined to be unsuitable for use in residential wood stoves on several grounds. First, it was impossible to control the fire with draft and damper settings. Even with the stove closed up as completely as possible, the flame remained very high. The fact that the stove used in this study was not airtight contributed to this problem, but with an airtight stove, drafts would have to be so restricted that increased pollutant production including CO, particulate, and condensable organics, would almost certainly result. In addition, immediately following ignition these logs swelled and fell apart, resulting in a pile of smoldering sawdust in the stove. On the first test with these logs, test personnel, unaware of this problem, opened the doors of the stove to add more fuel and received a lapful of burning sawdust which had piled up against the doors as the log disintegrated. The use of the coal grate in the second test alleviated this problem, but it is still felt that these logs represent a definite safety hazard for woodstove use.

In addition, compressed wood logs (CW) had higher CO emission factors than wood, related to their tendency to fall apart when burned. NO_x and SO₂ emissions were low for CW. Particulate emissions from CW were higher than wood or treated lumber but lower than other fuels.

In spite of an attempt to keep conditions constant between duplicate tests with CW, the two tests differed some in stove operating parameters (see Table 21). Although average flow rate for the sampling period was similar for the two tests, other parameters show that the runs were different. These differences can be used to show some of the effects of changing stove operation parameters on emissions. CW1 had lower fuel consumption but a higher relative heat output than CW2. Comparison of stack and firebox temperatures for the two tests reveals the reason behind this difference. Higher firebox temperatures and lower stack temperatures for CW1 indicate that flow through the stove was more restricted during CW1 than during CW2, resulting in lower stack heat loss, higher amounts of heat radiated into the room by the stove, and lower fuel consumption for this test compared to CW2. Higher fuel consumption resulted in a lower g/kg particulate emission factor for CW2, in spite of a similar emission rates (g/hr) for the two tests (Table 6). CO emission factors (g/kg) and emission rates (g/hr) were both significantly higher for CW1 than for CW2. The more restricted flow during CW1 is probably responsible for these high CO emission levels. Although NO_x emissions were low for both CW tests, lower NO_x emission factors and emission rates for CW1 also reflect the more restricted air flow through the stove during this test.

Total organic emissions for the CW tests are similar to those from tests with most other fuels (Table 16). Heavy organics (boiling points >300° C) accounted for a slightly larger portion of total organics than the light organics (boiling point 100° C-300° C); but levels of both were fairly similar. Total organic emissions were higher for CW1 than for CW2, again reflecting more restricted air flow during this test and have lower combustion efficiency.

PNA emission factors were higher than for wood tests and were similar to those from tests of other composite fuels (except newspapers) and to tests of treated lumber. This reflects relatively low combustion air availability attributable to structural characteristics of the fuel and low air flow through the stove, as for the treated lumber tests. PNA emissions factors for CW1 were generally higher than those for CW2, although this difference was less

apparent for the higher molecular weight PNAs. Again this is probably related to more restricted air flow through the stove for CW1 compared to CW2. PNA discharge severities were highest for CW than any other fuel, reflecting higher PNA production and low flow rates which result in a more concentrated flue gas effluent.

Compressed Wood Logs (with binders)

It should be noted that package directions on this product specifically warned against using these logs in a woodstove and burning more than one of these logs at a time, and that both recommendations were not followed during the tests with compressed wood logs with binders (CWB). Compressed wood logs with binders produced a thick, greenish gray smoke when burned. Emission factors for CWB were, except for total hydrocarbons, were among the highest of all fuels for all the pollutants measured. Particulate emission factors for CWB were by far the highest of all fuels (Figure 2). The particulate produced during the combustion of CWB was sooty and sticky, similar to that from coal, and probably represents organic volatilization products from the paraffin binder used in the fuel. Buildup of this particulate resulted in a high pressure drop across the Method 5 filter during the later state of sampling. NO_x emission factors (g/kg) were also highest for CWB and NO_x emission rates (g/hr) were second only to peat. This switch in ranking is due to the lower fuel consumption rates for CWB. Because CWB fuel nitrogen content was moderate, high NO_x emissions from CWB are probably attributable to the high air flow through the stove during the CWB tests, highest for all fuels, and to the relatively high average firebox temperatures (644°C and 516°C) during the tests. SO_2 emissions from CWB were second only to bituminous coal. The reason for this is not immediately apparent because the CWB sulfur content was only 0.25 percent. It is possible that the fuel analysis is in error since these analyses were designed for coal samples, and CWB is not very similar to coal.

CO emissions factors for CWB were comparable to those from other fuels, although once again comparing emissions on a g/kg basis produced a different ranking (2nd) for CWB than for emissions on a g/hr basis (5th). This is because of the high heating value and hence low fuel consumption rate for CWB.

Total organic emissions were surprisingly low (Table 16) considering the waxy, organic appearance of the particulate. It is possible that methylene chloride was not completely effective in dissolving the filter organics. PNA emissions were fairly high for CWB, however, on a mg/kg basis, being very high for naphthalene and biphenyl, compared to other fuels, and highest in B(a)P emissions on a mg/kg basis.

Test conditions were similar for the two duplicate tests with CWB except that the damper was half open during CWB2 and closed during CWB1. This resulted in higher firebox temperatures for the first test because of more restricted air through the stove, also reflected by the lower flow rate for CWB1 and higher heat output for CWB1. Some interesting conclusions about the combustion characteristics of CWB may be arrived at from examining the differences in operation parameters and emissions for the two tests. Fuel consumption was lower for the second test than for the first in spite of a higher air flow through the stove during CWB2. This implies that fuel consumption rate is controlled more by combustion temperature than availability of excess air for combustion. It follows that the physical structure of CWB is the most important limiting factor on air supply for combustion. In other words, the availability of oxygen to the site of combustion of the on the CWB is limited by the diffusion of air to the combustion area, and the rate of this diffusion controls combustion. The CO emission rates (g/hr) reflect this, since CO emission rates are remarkably similar in spite of difference in firebox temperature, combustion air flow, and fuel consumption rates.

Particulate emission rates (g/hr) are higher for CWB1 than for CWB2, reflecting the higher fuel consumption rate for CWB1. Indeed, putting particulate emissions on a g/kg basis, shows that a similar amount of particulate is emitted per unit mass of CWB burned, although particulate emissions factors are slightly higher than for CWB2, probably reflecting the lower firebox temperatures which encourage less complete combustion. NO_x emissions were higher on both a g/hr and a g/kg basis for CWB2, reflecting the increased air flow through the stove for this test. Since firebox temperatures are lower for CWB2 than for CWB1, this observation supports the conclusion that combustion air flow has a greater effects on NO_x emissions than firebox temperature.

Comparison of PNA emission factors (Table 18) mg/kg for CWB2 shows that, although the emission factors for the lighter PNAs are similar for two runs,

emission factors for the heavier PNA (chrysene on) are about an order of magnitude lower than CWB2 than for CWB1, in spite of lower fuel consumption rate for CWB2. The lower average firebox temperature and the higher flows through the stove during CWB2 seems to have reduced the amount of cyclization reactions in the firebox during this test.

Cardboard Logs

Except for wood, cardboard logs (C) were about the best fuel tested in this particular stove. Cardboard logs burned similarly to wood being easy to start and keep burning during the tests. No problems were encountered keeping heat outputs constant at sufficiently high levels during the cardboard logs tests. Emissions from cardboard logs also compared favorably with those of wood. Particulate emissions were low, comparable but slightly higher than those from wood combustion. Carbon monoxide emissions were higher for cardboard logs than for wood or coal, but were the lowest among the manmade particulate type fuels. As discussed before, elevated CO levels for cardboard logs compared to wood were probably due to the compressed particulate nature of this fuel. NO_x emission factors were lower for cardboard logs than for wood. SO_2 emissions were low, at about the same level as SO_2 emissions from wood combustion.

Total organics from the combustion of cardboard logs were comparable to most other fuels. As with wood, about two thirds of the total organics were heavy organics with boiling points greater than 300°C . PNA emission factors for cardboard logs were higher than those for wood combustion, but similar to those from other formed particulate type fuels. Again this reflects the burning characteristics of the cardboard logs which results in local oxygen starved conditions in the combustion zone and higher CO and PNA emissions than for naturally formed fuels like wood.

Stove operating parameters for the duplicate tests for cardboard logs were comparable except that a higher firebox temperature was achieved during C1, probably because the flow rate through the stove was lower during this test. This higher firebox temperature was concurrent with a higher fuel consumption rate during C1. As with CWB, increased air flow through the stove did not result in increased fuel consumption because increased flow also reduced firebox temperature. Emission factors (g/kg) were very similar for

all pollutants during C1 and C2. However, slightly lower emission factors for CO and heavy PNAs for C2 probably reflect the higher air flow through the stove during C2, as does the slightly higher NO_x emission factor. The higher total organic emission factors for total organics for C2 also reflect the lower firebox temperatures during this test. Pyrolysis products were not burned as completely during C2 as during C1 because of the lower temperatures and a decreased residence time in the stove from the higher flow rates. This reasoning also can explain the lower PNA formation since lower residence time, lower temperatures, and higher amounts of combustion air can tend to inhibit PNA formation through cyclization reactions.

Newspaper Logs

As a stove fuel, newspaper logs (N) were not up to par with the other fuels considering stove operation parameters. Although newspaper logs compared well with wood in heating value per unit mass, it was difficult to achieve satisfactory heat outputs from the stove during the tests with newspaper logs. Firebox temperatures remained low during the newspaper log tests. This was primarily because of the construction of the newspaper logs. These logs were formed from tightly rolled newspapers, a construction which restricted air circulation into the logs, resulting in a slow burn rate. In addition, the outer layers tended to burn and remain on the surface of the newspaper logs, insulating the remaining logs and further inhibiting its combustion. Very high air flows had to be maintained through the stove to assure continued combustion. Rolling the logs less tightly may be a partial solution to this problem.

Newspaper logs had negligible SO₂ emissions. NO_x emissions were also low, in spite of the high air flows through the stove during the newspaper tests. Low firebox temperatures are thought to be partially responsible for the low NO_x emissions. Firebox temperatures simply were not high enough for appreciable NO_x formation. Another reason for low NO_x emissions is that fuel nitrogen content for newspapers was zero. Thus, all of the NO_x emissions during the newspaper tests are from the oxidation of atmospheric nitrogen.

Newspaper logs ranked third in particulate emission factors. Much of this particulate represents pieces of burnt paper which spall off the newspaper logs as they burn. The shape of these particles (platelike) enhances their

entrainment in the flue gas stream. High, heavy organic emissions from newspaper logs contributed to the high particulate levels.

Newspaper logs produced the highest CO emissions, in spite of high combustion air flows through the stove. High CO emissions for the newspaper logs thus seem to be because of the newspaper log construction, which, as previously discussed, prevents sufficient combustion air from reaching the fuel.

Newspaper logs had, on the average, emitted the highest amount of total organics during combustion. However, PNA emission factors from newspaper combustion were the lowest, especially for the heavier PNAs. Comparing the fuels, B(a)P emission factors were lowest for newspaper logs. This discrepancy points to some interesting conclusions about PNA formation. Firebox temperatures were lowest for newspaper logs than for any other fuels and stack flow rates were second highest. These conditions seem to have inhibited the cyclization reactions necessary for forming PNA compound to the extent that not much of the heavier more condensed PNAs were formed. Most of the organics (75 percent) collected by the modified Method 5 train were heavy organics (boiling points greater than 300° C). These probably represent pyrolysis and distillation products evolved from the newspapers. At the combustion site in the newspaper logs, these products evolved because insufficient combustion air was present in the combustion zone. These conditions were also responsible for high CO levels during the newspaper tests. As these pyrolysis products evolved from the burning logs, a combination of low firebox temperatures and low firebox residence time (from high flow rates) prevented extensive combustion or cyclization of these compounds. This led to high total organic concentration but low concentrations of heavy PNAs in the flue gas stream.

Comparison of the stove operating parameters for the duplicate tests with newspaper logs reveals that the two tests were similar except for a lower firebox temperature and much lower heat output during N1 (Table 21). The very low heat output for N1 reflects the fact that medium blower speed was never achieved during this test, and blower speed was factored in when calculating heat outputs. The newspaper logs simply would not burn fast enough during N1 to heat the stove up to normal operating temperature. Better results were achieved for the second test by not rolling the newspaper logs as tightly as for the first test.

CO and total hydrocarbon emission factors were lower for N2 than for N1 (Tables 13 and 16). This reflects higher firebox temperatures which resulted in more complete combustion of these emissions during N2. PNA emission factors were slightly higher for N2 than for N1. Again this reflects the higher firebox temperatures during N2, which seems to increase PNA formation through cyclization reactions.

Treated Lumber (TW)

Treated lumber (TW), like CW, burned very readily in the woodstove with a very high flame spread. This required both draft and damper setting to be closed as much as possible in order to try to control the burning of TW. Even with draft and dampers completely closed, flames were still visible in the firebox during the combustion of TW. However, combustion was not as violent as with CW, so that flow rates through the stove were lower than the tests with CW, and were the lowest encountered for any fuel tested.

SO₂ emissions were negligible for TW. NO_x emission were lowest for TW as compared to other fuels. This reflects the low flow rate through the stove during the treated wood test. In spite of this low flow rate, CO levels were very similar to those on the combustion of wood. This supports the conclusion that fuel structure is important in determining CO emissions from different fuels, because treated wood and wood (oak) are similar in structure and dissimilar in structure from the fuels formed of compressed particulates all of which had high CO emissions. Particulate emissions from TW ranked fourth among fuels when expressed as g/kg. TW ranked higher in particulate emissions factors than other fuels because of an increased amount of condensed organic on the filter during the tests with TW. The two tests with TW varied considerably in their particulate emission factors. The first test had emission factors for particulates similar to those from the wood combustion test. However, the second test had much higher particulate emission factors. Examination of total organic emissions for the TW tests (see Table 16) shows that organic emissions during TW2 were indeed higher than those during TW1. Most of the organics in TW2 were heavy organics. Higher amounts of heavy organics for TW2 reflects the lower flow rates for this test than for TW1. Relatively high ranking of TW in particulate emission factor is largely due to the high heavy organic loading on the filter during the TW2 test.

Examination of those operating parameters for the TW tests shows that flow rates were higher for TW1 than for TW2. This resulted in a higher firebox temperature and lower stack temperature than for TW2 and a slightly lower fuel consumption rate. Unlike particulate fuels, the fuel consumption for TW seems to be controlled by the flow rate of air through the stove during stove operation. As mentioned before, the lower flow rate during TW2 resulted in higher particulate and hydrocarbon emission factors for this test compared to TW1. It appears that air flow was restricted enough during TW2 to prevent combustion of the heavy organics evolved from the wood as pyrolysis products during combustion. These heavy organics deposited on the filter in modified Method 5 train resulting in higher particulate emission factors and higher organic emission factors for TW2.

Overall organic emissions compared favorably with most of the other fuels for the TW tests. However, the second TW test had a higher proportion of heavy organics than did most of the other fuels. PNA emission factors were fairly high for the TW tests. PNA emission factors were lower for TW1 than for TW2, reflecting higher flow rates through the stove than for TW1. This, in combination with a lower firebox temperature for TW1, seems to have led to lower PNA formations for TW1 compared to TW2.

The high flame spread from TW, probably resulting from high resin content of this fuel, which was treated pine, makes this fuel unsuitable for wood stove use. In addition, contact with the manufacturer of this product revealed that the lumber was pressure treated with copper oxides compounds to retard rot. Trace amounts of arsenic and chromium compounds at ppm levels are also added to this wood to enhance its resistance to fungus and insect damage. Examination of the Modified Method 5 sampling train after the TW tests revealed that the XAD module had turned a rather bright shade of green. This is visual evidence of a rather significant copper volatilization during the tests with TW. Since copper is a less volatile element than arsenic, it can be expected that most or all of the arsenic present in the wood will be volatilized during the combustion of the wood. Other studies have shown that in the combustion of chlorophenol-treated wood products polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are emitted.³⁹ For this reason, it is recommended that TW not be burned under any circumstances including residential applications such as woodstoves and fireplaces.

Peat

From the stove operating standpoint, peat was a fairly satisfactory fuel. Although the sod peat burned in this test was a particulate fuel, and thus fell apart when burned, it did not have much flame spread as did the CW. Therefore, stove draft and damper settings similar to those used with wood could be also used with peat. Using the coal grate for the peat combustion test prevented the problem of particulates falling out of the stove when the doors were opened. Flames were fairly low off the burning peat and after a while, all that could be seen in the firebox were red glowing remains of the peat sod. Normal stove operating temperatures and heat output were easily achieved using the peat. The smoke from peat combustion was very fragrant. Opinions differed on whether this fragrance was pleasant or decidedly unpleasant. Peat combustion in residential installations may therefore have problems from an aesthetic standpoint.

NO_x emissions for peat were the highest among all the other fuels tested on a g/hr basis and were third highest on a g/kg basis (Figure 4). The high NO_x emission from peat combustion can be attributed to the high nitrogen content in the peat (0.93 percent). Nitrogen fuel content for peat was lower than that for bituminous coal but considerably higher than nitrogen contents for the other fuels. Peat ranked third in SO_2 emissions. CO emissions were relatively high for peat combustion, compared to those from other particulate fuels, and higher than those from the naturally structured fuels, coal, treated, wood, and wood (oak). High CO emissions factors for peat are probably due to its particulate structure, as explained for the other particulate fuels. Particulate emissions from peat were similar to those from CW. Peat ranked fifth in particulate emission factors.

Examination of the stove operating parameters (Table 21) shows the two test with peat were similar. Differences in emission factors for the various pollutants measured during these tests cannot be readily explained by difference in stove operating parameters during duplicate tests with peat.

Peat ranked second in total organic emissions. Most of the total organics from peat combustion were heavy organics (boiling points greater than 300° C). PNA emission factors were fairly high for P1 but were low for P2. No explanation is immediately apparent for this discrepancy.

Bituminous Coal

In order to burn bituminous coal in the stove used for this study, a special optional shaker grate was purchased from the stove manufacturer. Although this grate did make it possible to burn bituminous coal in the stove, it is felt that the grate design in combination with the stove design prevented the most efficient combustion of this fuel. The shaker grate sat in the middle of the stove's firebox. One to two inches of space was around the grate on all sides. This enabled much of the air entering the stove to flow up and around the grate, thus bypassing the burning fuel bed. This resulted in a less than efficient combustion of the bituminous coal.

SO₂ emissions from combustion of bituminous coal were higher than for any other fuel tested. This is a reflection of the fact that bituminous coal had the highest fuel sulfur content (1.87 percent) of all fuels tested. NO_x emissions from coal were also very high. Bituminous coal ranked second in NO_x emissions on a g/kg basis and third in NO_x on g/hr basis. These relatively high NO_x concentrations in flue gas from bituminous coal combustion are largely due to the high fuel nitrogen content of bituminous coal (1.54 percent). CO emission factors for bituminous coal were moderate, slightly higher than those from the combustion of wood or treated wood but lower than emission factors for CO for the particulate structured fuels. Again this reflects the natural structure of bituminous coal versus the composited particulate structure of the particulate fuels. Bituminous coal ranked second in total particulate emissions. This particulate is the infamous coal soot, a sticky mixture largely composed of unburned carbon particles with some adsorbed volatile organics.

Organic emissions from coal were surprisingly low. Total organics were largely composed of heavier organics (boiling points greater than 300° C). PNA emission factors were also low, comparable or a bit lower than those for wood, depending on which bituminous coal test was compared to the wood test. This may be because of the stove in which the bituminous coal was burned.

Examination of stove operating parameters for bituminous coal tests (Table 21) shows that there was some difference between the two duplicate tests. Stove drafts were fairly open during the first test of bituminous coal per manufacturer's instruction. This resulted in lower burn rate for this

test and a fairly low heat output for this test. Firebox temperatures for BC1 were also lower than those for BC2. During BC2, the stove was closed off more so that it could reach proper operating temperatures. This resulted in a lower flow rate through the stove at a higher fuel consumption, probably because of the higher firebox temperature. Dampers were left halfway open for both tests resulting in stack temperatures considerably higher than those from the other tests. SO₂ and CO emission factors were similar in BC1 and BC2, NO_x emission factors were higher in BC1 than for BC2, however. This reflects higher flows through the stove during BC1. Particulate and total organic emissions were higher for BC1 than for BC2. These are believed to be related since most of the extra organic matter in BC1 compared to BC2 seems to come from heavy organics (boiling point greater than 300° C). Thus high boiling organic compounds contributed to the particulate catch for BC1, resulting in a higher emission particulate factor for this test. PNA emission factors were higher for BC1 than for BC2 (Table 18). Since most of the heavy organics emitted during BC1 probably represent pyrolysis product from the coal and since higher firebox temperatures and lower flow rates during BC2 would seem to favor formation of PNA during combustion of BC2, lower levels of PNA actually detected in the flue gas samples for BC2 imply that PNAs from bituminous coal combustion are primarily pyrolysis products from bituminous coal. This is supported by the fact that bituminous coal has a much more condensed aromatic structure than the other fuels tested. However, PNA concentrations in the sample extract for BC2 are admittedly suspiciously low. Analytical problems thus cannot be ruled out. For this reason, in calculating the PNA discharge severities only the values for BC1 were used.

Anthracite Coal

Anthracite coal could not be burned successfully in the stove chosen for this study. The coal grate designed for the stove did not perform well with anthracite. Air flowed around the grate instead of through it, and after the kindling loaded in the stove died down, the coal smoldered and went out. On a subsequent test, an oak fire was started and a good bed of coals was established before adding coal. Although the coal was added to the coal bed in small amounts, it did not burn with any flame and as soon as the wood coals died, so did the fire. A second coal grate was obtained from another manufacturer who

said it could successfully burn anthracite in a stove very similar to the one used in this study. This grate was designed so that most of the air coming into the stove went through the grate. This grate performed better, but a self-sustaining anthracite fire still could not be established. Air was forced through the grate using a blower during one test, and a small blue flame could be established on the coal bed. However, with the removal of the forced air, this flame quickly died out, and the coal once again did not burn. It was therefore concluded that it is very difficult to burn anthracite in a conventional woodstove and that a stove specifically designed to produce high air velocities through the coal grate is necessary for successful anthracite combustion. This is due to the high fixed carbon content and low volatile content of anthracite (see Table 20).

7.3 BIOASSAY RESULTS

Method 5 sample extracts from one wood combustion (W1) and one coal combustion test (BC1) were subjected to an Ames Salmonella mutagenicity assay to measure their mutagenic potential. Although IERL Level I Environmental Assessment and the protocol of Ames and others⁴⁰ specify testing with five Salmonella strains, only two strains (TA98 and TA100) were utilized for this study because of limited sample size and economic considerations.

The results of bioassay analysis suggest the presence of frameshift and base pair substitution mutagens in both samples. Both samples were highly mutagenic with TA98 and moderately mutagenic with TA100. Both samples demonstrated an increase in mutagenic activity with the addition S9, a metabolic activator of promutagen compounds. Therefore, both samples contain direct-acting mutagens and promutagens.

The coal combustion sample was more mutagenic than the wood combustion sample, based on the slope of the dose/response curves in units of revertants/mg of sample. Putting bioassay results on a revertants/kg of fuel consumed basis, the coal extract is more mutagenic than the wood extract by a factor of two. Since emission factors (g/kg) for the PNAs analyzed in this report are only slightly higher for BC1 than for W1, this suggests that compounds other than the 24 PNAs analyzed in this report may be contributing to the mutagenicity of these samples.

Complete bioassay methods and test results are presented as a separate report. In this report, 11020I is the wood sample and 11007 is the coal sample. These correspond to samples W1 and BC1 discussed in this report.

8. CONCLUSIONS

1. Overall oak wood was the best fuel, considering both emissions and stove operation. Cardboard logs (C) were almost as good as wood. Although they did emit more CO and PNAs than wood, levels of these pollutants were lower than for most other fuels, and stove operation was easier with C than with other fuels.
2. Compressed wood logs with binders (CWB) and bituminous coal (BC) produced the highest emissions (g/kg fuel consumed) of SO₂, particulate, and NO_x. In addition, CWB emissions were high in CO and PNAs.
3. Compressed wood logs without binders (CW) were determined to be unsuitable for stove use on safety grounds. CW also emitted large amounts of CO.
4. Treated wood (TW) should not be burned under any circumstances because of the presence of arsenic compounds which probably volatilize during combustion.
5. Peat (P) emissions had relatively high levels of NO_x, SO₂, CO, and PNAs.
6. Particulate matter from BC and CWB combustion was sooty and sticky. These fuels produced the highest particulate emission by far. Composite fuels (CW, C, P, newspaper (N)) produced particulate emissions higher than those of wood. High particulate levels for N and TW were largely attributable to condensed organics.
7. Important parameters affecting CO emission levels were fuel structure and, to a lesser degree, combustion air flow. Fuels with a manmade, compressed particulate structure (CW, CWB, C, P) and rolled newspapers had high CO emissions because their structure inhibited air flow to the combustion zone. Wood, treated lumber, and coal had the lowest CO emissions as these fuels would shrink and crack when burned, permitting sufficient air to reach the burning fuel. Results from duplicate tests for each

fuel suggest that air flow through the stove is also a factor affecting CO emissions, with reduced air flow leading to increased emissions. CO emissions were significantly high and of concern for all fuels.

8. SO₂ emission levels generally could be related to fuel sulfur content, with higher fuel sulfur content causing higher SO₂ emissions. SO₂ emissions were at levels of environmental concern only for P, BC, and CWB.
9. NO_x emissions were controlled by fuel nitrogen content and combustion air flow rate. High nitrogen content fuels (P and BC) had highest NO_x emissions. Increased air flow through the stove also led to increased NO_x emissions. NO_x levels were generally low and as a result were not as much of a concern as other pollutants.
10. Organic emission levels were comparable for all fuels except peat and newspaper logs, which had high levels of organics in the flue gas effluent stream. Organic emissions were affected by fuel consumption rate, fuel structure, and amount of air through the stove. Higher fuel consumption sometimes led to increased organics. Lowering air flow through the stove increased organic emissions. Newspaper logs had high organic emissions because of their physical structure, which inhibited air from reaching the combustion zone leading to increased pyrolysis products.
11. PNA formation was affected by combustion air flow, firebox temperature, and fuel structure. Composite structured fuels had higher PNA formation except for newspaper logs, which, in contrast to high total organic emissions, had very low emissions of heavier PNAs. It was concluded that during the tests with newspaper logs firebox temperatures were too low for extensive cyclization reactions leading to PNA formation. Also flow rates through the stove were high for newspaper logs decreasing the pyrolysis products residence time in the combustion zone and hence inhibiting PNA formation. Other composite fuels had relatively high PNA production rates. This is attributable to their structure, which limits the availability of air during combustion and creates starved air conditions favorable to PNA production. Tests with treated wood also had relatively

high levels of PNAs in the flue gas effluent stream, attributable to low air flow through the stove during these tests. Wood and coal had similar PNA emissions, with coal emitting less PNAs than wood. PNA emissions from coal could possibly be pyrolysis products from the coal itself.

12. Bioassays on organic extracts from one wood test and one coal test demonstrated the presence of both mutagens and promutagens in the sample extracts. Organics from coal combustion were about twice as mutagenic as those from wood combustion on a mutagenicity per unit mass of fuel consumed basis.

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APPENDIX

Final Report

Ames Testing of Stove Combustion Products

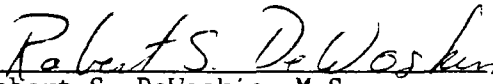
FINAL REPORT

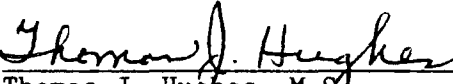
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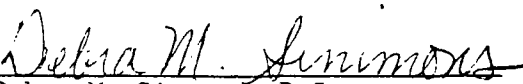
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1.0 Introduction

The Ames/Salmonella mutagenicity assay measures the mutagenic potential of chemical compounds (Ames et al., 1975). The molecular basis of this assay is the interaction of a chemical mutagen with the DNA of a Salmonella bacterium carrying a mutation in a gene whose normal function is to allow the de novo synthesis of the essential amino acid histidine. These mutant bacteria are unable to grow in a medium deficient in this amino acid. However, when a chemical mutagen interacts with the DNA of this bacterium in such a way as to introduce a second mutation in the histidine operon which corrects the original mutation, the bacterium can then survive in a histidine deficient medium, giving rise to a visible colony on histidine deficient agar. The frequency of mutational reversion is proportional to the concentration and potency of the chemical mutagen. Therefore, the number of colonies produced after addition of mutagen is directly proportional to its mutagenic potential (McCann et al., 1975). This test is normally conducted with five tester strains of Salmonella bacteria expressing frameshift (TA98, TA1538, TA1537) and base-pair substitution (TA100, TA1535) mutations in the histidine operon. The combustion samples in this study were only tested with TA98 and TA100. Since many substances are not active mutagens unless metabolically transformed (promutagens), the in vitro assay has been modified to provide this transformation function by adding a rat liver microsomal fraction (S9) which is rich in mixed-function oxidases (P450 and P448), the enzyme systems which are mainly responsible for biotransformation of promutagens. The relationship between the potency of a chemical as a mutagen to its potency as a carcinogen has been the subject of considerable controversy and study with regard to the utility of the bacterial assay as a predictor of carcinogenic potential (Rinkus and Legator, 1979). However, this assay has been shown to predict known carcinogens as mutagens with an accuracy approaching 90% (McCann et al., 1975; Brusick, 1979).

This study tested organic compound extracts from the combustion products of a residential wood stove for mutagenic activity in the Ames Salmonella/mutagenicity assay. General information about the study is shown in Table 1. The samples were supplied by the Process and Chemical Engineering Division, Research Triangle Institute and consisted of a Soxhlet (SOX) extract in dichloromethane and an aqueous extract (AQ) for each of two fuels (wood and coal). The SOX and AQ extracts were generated from different stages of the sampling train, but were combined as a composite sample for testing.

These composite samples were tested for toxicity to determine the dose levels for the mutagenicity assays. It should be noted that the mutagenicity protocols of Ames et al. (1975) and IERL-RTP Level I Environmental Assessment Manual Brusick and Young, 1980) specify testing with five Salmonella strains (TA98, TA100, TA1535, TA1537 and TA1538). Because of the limited sample amount and minor emphasis on the bioanalysis of the stove combustion products, only strains TA98 and TA100 were utilized.

TABLE 1. GENERAL PROJECT INFORMATION

Title of Project

Ames Mutagenicity Testing of Stove Combustion Products

Objective of Project

To assess the mutagenic potential of extracts of the organic compounds from the combustion of wood and coal in a residential type stove.

Sponsor

Process and Chemical Engineering Division, Research Triangle Institute, Research Triangle Park, NC 27709.

Project Number

RTI Task No. 47U-1914-39

Test Substance Identification

<u>Test Substance</u>	<u>Sample No.</u>	<u>State/Purity/Stability/Solvent</u>
Wood - DCM Extract	11020I KD	Solid/unknown/light-heat sensitive/ DMSO
Wood - Aqueous Extract	11020I pH Extract	Solid/unknown/light-heat sensitive/ DMSO
Coal - DCM Extract	11007 Sox	Solid/unknown/light-heat sensitive/ DMSO
Coal - Aqueous Extract	11007 pH Extract	Solid/unknown/light-heat sensitive/ DMSO

Storage Location of Results

Original Data: RTI Archives

Final Report: RTI Archives

Storage Location of Samples

Returned to Dr. Robert Truesdale, Process and Chemical Engineering Division, Research Triangle Institute.

Dates

Samples Received: 01/12/82
 Testing Initiated: 01/18/82
 Testing Completed: 01/26/82
 Preliminary Results Reported: 02/05/82
 (via telephone)
 Final Report Completed: 02/22/82

2.0 Summary

Sample 11020I yielded 56 mg of extracted solid; 42 mg from the soxhlet extract and 14 mg from the aqueous extract. Sample 11007 yielded 121 mg of extracted solid; 120 mg from the soxhlet extract and 0.6 mg from the aqueous extract.

Sample 11020I and sample 11007 demonstrated mutagenic activity with Salmonella tester strains TA98 and TA100. The MEC value for both samples was 50 µg/plate with TA98 and 500 µg/plate for TA100. This result suggest the presence of frameshift and base pair substitution mutagens. Based upon the MEC values the samples were categorized as highly mutagenic with TA98 and moderately mutagenic with TA100. Both samples demonstrated an increase in mutagenic activity with the addition of S9 with strains TA98 and TA100. Therefore, both samples contain direct-acting mutagens and promutagens. The presence of promutagens in organic compound extracts from residential stove combustion products has been previously reported (Austin et al., 1982, Appendix A).

Sample 11007 was more active than sample 11020I for both strains, with or without the addition of S9. This comparison was based upon the slope of the dose-response curves in units of revertants/µg of sample. A more relevant comparison might be based on revertants/Joule of heat generated.

3.0 Laboratory Facilities and Quality Control

3.1 Ames Mutagenesis Laboratories

The bacteriological section of Research Triangle Institute's In Vitro Environmental Toxicology Laboratory is completely equipped for large-scale Ames/Salmonella testing, as well as research and development studies. This facility is equipped with automated plate pouring and colony counting apparatus and large-capacity plate incubation equipment for high-volume testing. The four mutagenesis laboratories are equipped with three Baker NCB-6 laminar flow carcinogen hoods and one Lab Con exhaust hood. The Class II Type-B (Baker NCB-6) hoods and the exhaust hood are vented through charcoal filters on the roof of the testing facility. Plate incubation and counting equipment are vented for personnel protection. The incubators used in the evaluation of hazardous materials are vented to the roof before the doors of the incubators are opened. All laboratory personnel are appropriately garbed with laboratory clothing, safety apparatus and two pairs of gloves while working with hazardous materials. Gloves and laboratory waste are double-bagged (plastic bags) and stored in 55 gallon drums until disposal. Drums are disposed of at a certified burial site. An OSHA approved, negative pressure, Toxic Substances Laboratory is employed for the handling of mutagenic, carcinogenic and radioactive materials. A central bacteriological media preparation and glassware cleaning facility is contained adjacent to one of the mutagenesis laboratories. Two 80 ft² walk-in constant temperature incubators are used for large-scale bacteriological cell preparations. The Ames mutagenesis laboratories also include adequate refrigeration and freezing facilities (two 90 ft² walk-in cold rooms; Kelvinator Ultracold Freezer -70°C, two Liquid Nitrogen Freezers) for separate storage of media, test substances (including known carcinogens), and Salmonella strain storage. The laboratories are subject to timer controlled ultra-violet sterilization daily. Each laboratory is equipped

with adequate storage and disposal facilities. All wastes are incinerated (2,500°F) at Duke University Medical Center, an approved carcinogen waste disposal site. Room for housing animals associated with the proposed work is available in the RTI Animal Research Facility. The Animal Research Facilities have received full accreditation from AALAC, and are located in a separate (10,000 square foot) building adjacent to the laboratory building.

The Ames facility has computerized the data collection and handling system in order to subject test results to rigorous statistical assessment. The data is entered at RTI and analyzed by the TUCC (Triangle University Computation Center) IBM computer. Analysis of results and interpretation of the data are then performed by the project leader.

3.2 Quality Control

Quality control is an important part of the Ames assay. Tester strains are checked for the proper characteristics, positive controls are prepared fresh for each assay and the equipment is inspected before use. The S9 activation preparation is tested for activation potential with known promutagens and is compared with RTI's historical data base. The spontaneous revertant rate for Salmonella tester strains should be within the recommended range (deSerres and Shelby, 1979). The quality control information, for this assay, along with a listing of equipment and the sources of chemical controls, are given in Table 2.

TABLE 2. QUALITY CONTROL INFORMATION

Sponsor:

Process and Chemical Engineering Division, Research Triangle Institute,
Research Triangle Park, NC.

Project No.

RTI Task No. 47U-1914-39

Testing Facility

Research Triangle Institute, Post Office Box 12194, Research Triangle
Park, NC 27709.

Test Substance

Organic compound extracts (RTI No. 11020I and 11007)
Source: Combustion products from residential stove; wood or coal
was utilized as fuel
Physical State: solid residue
Purity: unknown
Composition: unknown
Stability: assume light and heat sensitivity
Storage conditions: 4°C in closed glass vials protected from light

Bioassay

Ames/Salmonella/mammalian microsome mutagenicity assay (Ames et al.,
1975).

Controls

Solvent: Dimethylsulfoxide (Fisher Scientific)
Positive: TA98: +S9 - 2-Aminoanthracene (IITRI)
 -S9 - 2-Nitrofluorene (IITRI)
 TA100: +S9 - 2-Aminoanthracene (IITRI)
 -S9 - Sodium azide (IITRI)

Activation Mixtures

Source: Fischer 344 male rats, 200 grams, induced with Aroclor 1254
at 500 mg/kg i.p. per Ames et al. (1975)
Lot No.: RLI002
QC Assay Date: 5-14-81

TABLE 2. (continued)

Strain Marker Verification

<u>Strain</u>	<u>Spont. Rev. Range</u>	<u>rfa Mutation</u>	<u>R-factor</u>	<u>UV Sensitivity</u>
TA98	15-40	+	+	+
TA100	150-220	+	+	+

Equipment

<u>Description</u>	<u>Manufacturer</u>	<u>Date last checked</u>
Laminar flow hoods	Baker NCB-6	Feb., 1982
Freezer	Kelvinator Ultracold	Feb., 1982
Incubator	Fisher Model 307	Feb., 1982
Colony Counter	Artek Systems Corp.	Feb., 1982

4.0 Experimental Procedure

This section describes the sample preparation and the procedure for the Ames Salmonella/mammalian microsome mutagenesis assay including the procedure for analyzing, interpreting and presenting the data.

4.1 Sample Preparation

Organic compound extracts from residential stove combustion products were received from PCED in clear glass sample vials at room temperature. The sampling train for each test condition generated two extracts; a Soxhlet extract of the particulate matter in dichloromethane (DCM) and an aqueous extract from an impinger. Both extracts were transferred to preweighed scintillation vials, the solvent was removed by evaporation with a stream of nitrogen, residues were weighed, and resuspended in dimethylsulfoxide (DMSO) for the Ames test.

The residue from extracts of sample 11020I weighed 56 mg: 42 mg from the soxhlet extraction and 14 mg from the aqueous extraction. These two residues were combined and serially diluted with DMSO to dose levels of: 1,000, 500, 100, 50 and 10 μ g of extract per plate. The residue from extracts of sample 11007 weighed 121 mg: 120 mg from the soxhlet extraction and only 0.6 mg from the aqueous extraction. These two residues were also combined and serially diluted with DMSO to dose levels of 1,000, 500, 100, 50 and 10 μ g of extract per plate.

Prepared samples were protected from light and stored at 4°C prior to testing. Table 3 lists the sample receipt and storage information for these samples.

4.2 Protocol for Testing

The procedures for handling the strains and preparing media components were those of Ames et al. (1975). The S9 microsomal preparation was obtained from Fischer 344 male rats injected with Aroclor 1254; protein was measured by the method of Lowry et al. (1951).

TABLE 3. SAMPLE RECEIPT AND STORAGE

Sample Receipt:

Sponsor Dr. Robert Truesdale, Process and Chemical Engineering Div., RTI
 Sponsor Code 11020I, 10007
 Method of Fabrication or Source Residential stove
 Date Received 1-12-82
 Storage Location Ames lab freezer (4°C), Rm 215, Bldg. 3, RTP, NC
 RTI Code 11020I, 11007

Sample Description:

11007 Sox (13.2 ml): AQ (pH extract 4.9 ml)
 Identity 11020I Sox (KD 10 ml): AQ (pH extract 5.2 ml)
 Lot No. -
 State/Color/Purity solid residue/clear to dark yellow/unknown
 Density unknown
 Stability assume light and heat sensitive
 Solubility >1% in dimethylsulfoxide
 *Safety Data potential mutagens

Test Performed:

Bioassay/Date toxicity prescreen 1-18-82; mutagenicity 1-22-82
 Date Sample Prepared 1-18-82
 Storage Location of Prepared Sample Ames lab (No. 215) freezer 4°C
 Length of Time in Storage Prior to Assaying Tox-1 day; Mut-4 days

The standard assay was divided into four parts as follows.

4.2.1 Toxicity Testing, Plate Incorporation Method (see Table 4)

Approximately 500 cells per dish were plated on nonselective media (histidine-positive overlay). Tests were performed with and without addition of Aroclor-induced S9 at five dose levels. Due to a limited amount of sample some doses were tested without replicate plates. The viability ratio (VR) was calculated as the fraction of surviving colonies with sample to surviving colonies without sample. A viability ratio of less than one indicated toxicity of the sample compound; a value of one or greater indicated no toxicity. A dose that produced a VR of less than .5 was considered a toxic dose. All toxicity determinations were performed in duplicate except where sample amount was limited. Bioassay quality control was accomplished with solvent controls, positive controls and strain controls, with and without microsomal S9.

4.2.2 Mutagenicity Testing, Plate Incorporation Method (see Table 5)

Cells were plated at 10^8 cells/plate with selective media (histidine-negative overlays). All mutagenic determinations were performed in triplicate with and without S9 addition.

4.2.3 Positive Mutagen Control Testing, Plate Incorporation Method

Approximately 10^8 cells were plated in each dish on histidine-negative overlays. Known mutagens were tested to assure that the strains were active and the S9 preparation was activating promutagens to the desired levels. If known positive controls did not demonstrate proper mutagenic activity, the test components (cultures and/or S9) were rejected. Control compounds were:

<u>Strain</u>	<u>Without S9</u>	<u>With S9</u>
TA 98	2-Nitrofluorene 10, 5 µg/plate	2-Anthramine 5, 1 µg/plate
TA 100	Sodium Azide 5, 1 µg/plate	2-Anthramine 5, 1 µg/plate

Positive control tests were performed in triplicate.

TABLE 4. STANDARD PROTOCOL FOR TOXICITY DETERMINATIONS IN AMES/SALMONELLA BIOASSAY

Added to 2.0 ml agar, histidine (+), before layering onto plates ^a						
Lab Code ID and Tube No. ^a	Sample in Vehicle ml	S-9 Micronomes ^b per ml of S-9 Mix	S-9 Mix in H ₂ O ml	Activation Prep. Medium Phosphate Buffer ml	Vehicle ml	Bacteria ml (10,000 cells/ml)
1-1	.1 (1000 µg)/plate	0.1	0.5	0	0	0.1
1-2	.1 (500 µg)/plate	0.1	0.5	0	0	0.1
1-3	.1 (250 µg)/plate	0.1	0.5	0	0	0.1
1-4	.1 (100 µg)/plate	0.1	0.5	0	0	0.1
1-5	.1 (10 µg)/plate	0.1	0.5	0	0	0.1
1-6	.1 (1000 µg)/plate	0	0	0.5	0	0.1
1-7	.1 (500 µg)/plate	0	0	0.5	0	0.1
1-8	.1 (250 µg)/plate	0	0	0.5	0	0.1
1-9	.1 (100 µg)/plate	0	0	0.5	0	0.1
1-10	.1 (10 µg)/plate	0	0	0.5	0	0.1
1-11	0	0	0	0.5	0.1	0.1
1-12	0	0.1	0.5	0	0.1	0.1
1-13	0	0	0	0.5	0	0.1
1-14	0	0.1	0.5	0	0	0.1
1-15	0	0	0	0	0	0.1

^a Each done in triplicate.

^b In 0.15 M KCl.

TABLE 5. STANDARD PROTOCOL FOR MUTAGENESIS DETERMINATIONS IN AMES/SALMONELLA BIOASSAY

Added to 2.0 ml agar, histidine (-), before layering onto plates ^a						
Lab Code ID and Tube No. ^b	Sample in Vehicle ml	S-9 Microsomes ^b per ml of S-9 Mix	S-9 Mix in H ₂ O ml	Activation Prep. Medium Phosphate Buffer ml	Vehicle ml	Bacteria ml (10 ⁹) cells/ml
2-1	.1 (1000 µg)/plate	0.1	0.5	0	0	0.1
2-2	.1 (500 µg)/plate	0.1	0.5	0	0	0.1
2-3	.1 (250 µg)/plate	0.1	0.5	0	0	0.1
2-4	.1 (100 µg)/plate	0.1	0.5	0	0	0.1
2-5	.1 (10 µg)/plate	0.1	0.5	0	0	0.1
2-6	.1 (1000 µg)/plate	0	0	0.5	0	0.1
2-7	.1 (500 µg)/plate	0	0	0.5	0	0.1
2-8	.1 (250 µg)/plate	0	0	0.5	0	0.1
2-9	.1 (100 µg)/plate	0	0	0.5	0	0.1
2-10	.1 (10 µg)/plate	0	0	0.5	0	0.1
2-11	0	0	0	0.5	0.1	0.1
2-12	0	0.1	0.5	0	0.1	0.1
2-13	0	0	0	0.5	0	0.1
2-14	0	0.1	0.5	0	0	0.1
2-15	0	0	0	0	0	0.1

^a Each done in triplicate.

^b In 0.15 M KCl.

4.2.4 Sterility Testing, Plate Incorporation Method

Sterility tests were conducted with histidine-positive overlay plates, with the identical components employed in the tests. Components tested were sample(s), positive controls, solvent(s), water, direct-acting mix, S9 mix, and agar plates. Sterility testing was performed in duplicate.

4.3 Formulation of NADPH Generating System (see Table 6)

Components	M.W.	Concentration/ml S9 Mix
1. NADP	765.4	4 μ moles
2. G6P	282	5 μ moles
3. $MgCl_2$	203.3	8 μ moles
4. KCl	74.5	33 μ moles
5. Sodium phosphate buffer pH 7.4		100 μ moles
6. Organ homogenate (S9 fraction)		100 μ liters

Make-up following stock solutions:

0.2 M NADP	Millipore filter
0.2 M G6P	Millipore filter
0.4 M $MgCl_2$	Sterilize by autoclaving
1.65 M KCl	Sterilize by autoclaving
0.2 M Na Phosphate buffer pH 7.4	Sterilize by autoclaving

- A. 2.0 ml and 0.2 ml aliquots of 0.2 M NADP is dispensed into sterile vials and kept frozen at $-70^{\circ}C$ until used.
- B. 2.5 ml and 0.5 ml aliquots of 0.2 M G6P is dispensed into sterile vials and kept frozen at $-70^{\circ}C$ until used.
- C. S9 mix is then produced following the formulas in Table 5 S9 is added to the S9 mix in a 1:10 part ratio.

Toxicity and Mutagenicity Preparation (see Figure 1)

1. Add 1.8 ml of the appropriate suspension to a dram vial and keep on ice.
2. Add 0.3 ml of the test material to the dram vial. Shake on vortex.
3. Dispense 0.7 ml/2.0 ml overlay, vortex and plate.

4.4 Salmonella Strain Validation (from Ames' Methods Paper, 1975)

The cells are taken from oxoid broth inoculated and grown overnight.

TABLE 6. AMES ACTIVATION SYSTEM

Component	M	MW	Supplier	Stock Preparation	Volume of Stock added/ml of Final Mix	Per 100 ml	Final Concentration of Component/ml in Mix
1. NADP ^a	0.2	765.4	ICN	76.6 g/500 ml H ₂ O	20 1	2.0	4 moles
2. Glucose-6-phosphate dibasic	0.2	282	Sigma	28.2 g/500 ml H ₂ O	25 1	2.5	5 moles
3. Sodium ^b phosphate	0.2	142 DI 138 Mono	Sigma	2 liter dibasic ^c 300 ml mono ^d	500 1	50.0	100 moles
4. MgCl ₂	0.4	203.3	Sigma	40.7 g/500 ml H ₂ O	20 1	2.0	8 moles
5. KCL	1.65	74.5	Sigma	61.5 g/500 ml H ₂ O	20 1	2.0	33 moles
6. Homogenate	-	-	-	Standard KCl 9,000 x g supernatant	100 1	10.0	Approximately 25 mg of fresh tissue equivalent
7. H ₂ O					315 1	31.5	

^aAM mix is 1-7 with the addition of bacteria.

^bSodium phosphate is used as NM mix plus bacteria, pH 7.4.

^c2 liter dibasic = 56.8 gm/2000 ml.

^d300 ml mono = 8.28 gm/300 ml.

Components 1 and 2 are prepared in sterile distilled water and maintained at -20°C.

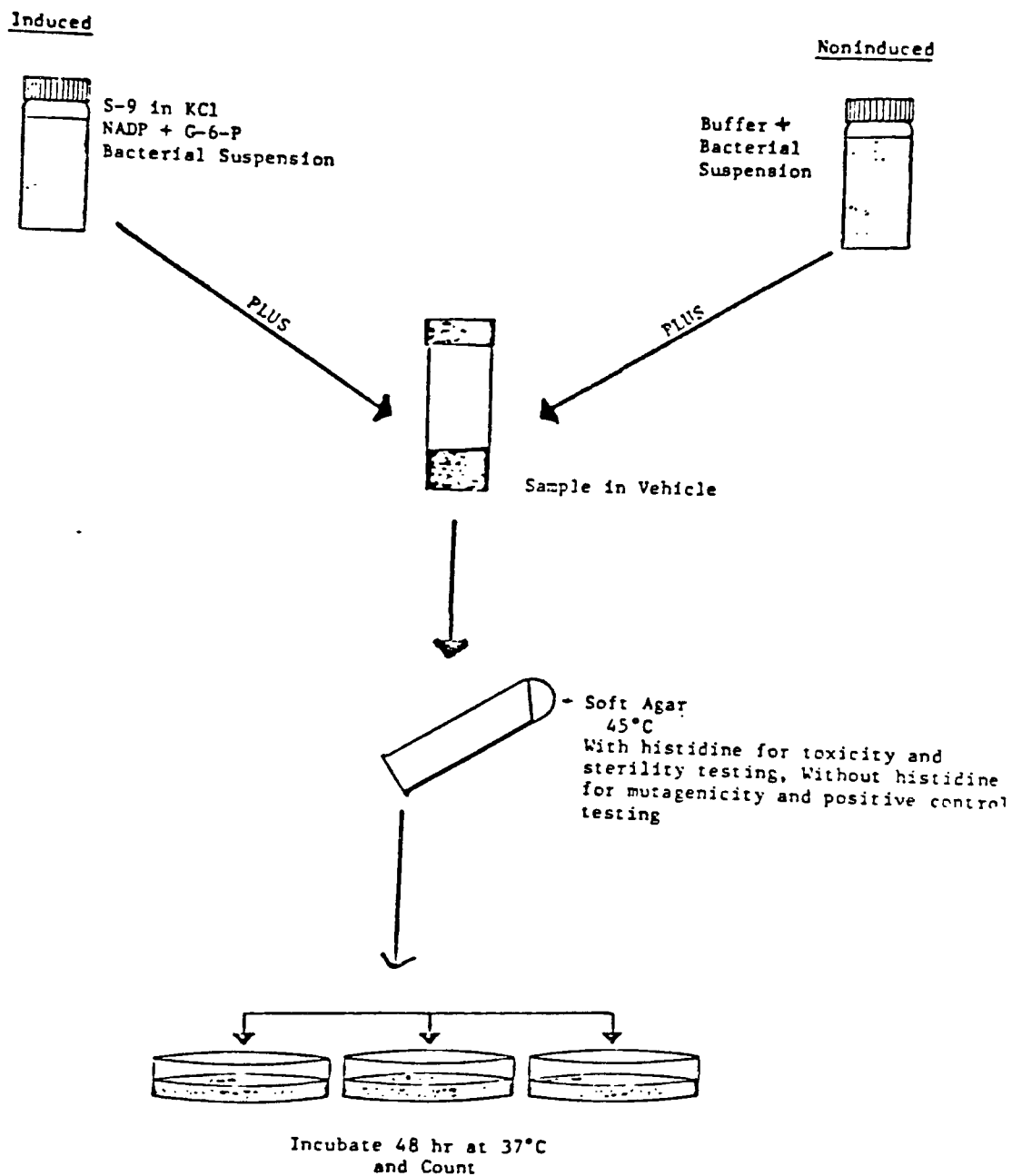
Components 3, 4, and 5 are prepared in distilled water, sterilized, and maintained at 4°C.

Component 6 is prepared and stored at -80°C until used.

Components 1-5 combined = core reaction mixture. MW = Molecular weight.

Components 1-6 combined = complete S-9 mixture.

Figure 1. Ames protocol.



1. Histidine Requirement

Base Layer Plates, total needed = 30

5 strains - .1 ml/plate

Overlays - H^+ (1A) and H^- (1B)

A. Cells should grow with addition of histidine, heavy cloudy background.

B. Spontaneous Background - must be within acceptable limits.

2. Crystal Violet/rfa Character

Base Layer Plates, total needed = 15

5 strains - .1 ml/plate

Overlays - H^+

10 μ l of crystal violet on filter paper disc

Place disc + cv on plate after pouring overlay with bacteria

A clear zone of inhibition should be present around the disc indicating that rfa cell wall mutation is present.

3. Ampicillin Resistant R Factor (Qualitative)

Base Layer Plates, total needed = 15

5 strains - .1 ml/plate

H^+ overlays

Pour overlays and cells; using q-tip, streak fresh ampicillin down middle of plate

(Ampicillin - 100 μ l of 8 mg/ml in .02 N NaOH)

Strains 98 and 100 - No zone of inhibition around ampicillin streak

Strains 37, 35, 38 - Zone of inhibition around ampicillin streak

4. UV Sensitivity/ Δ uvrB Deletion

Base Layer Plates, total needed = 15

5 strains - .1 ml/plate

Overlays - H^+

Pour plates, irradiate plates: with screen with T - cut out

Strains 98 and 100 - 8 sec

Strains 35, 37, 38 - 6 sec

Cells should be present only on non-irradiated area.

5. Ampicillin Resistant R. Factor (Quantitative Assay)

Base Layer Plates, total needed = 15

5 strains - 0.1 ml/plate after dilution in NB

5/100 → 1/100 → 10/100 → 20/100

Overlays - H⁺

Place 0.1 ml of diluted cells and 100 ml ampicillin in H⁺
overaly

Strains 98 and 100 - full growth

Strains 35, 36, and 38 - no growth

6. Control for Ampicillin

Same as #5, but no ampicillin is used.

7. Sterility

Plates - 3 each

Overlays - H⁺ - 3 each

Overlays - H⁻ - 3 each

4.5 Date Handling and Presentation

Raw data for both the toxicity and mutagenicity assays were analyzed by computer. The results are presented in tabular and graphical form in Appendix A. The information presented includes the counts from each plate, the average count, the standard deviation, a quality control check for an acceptable spontaneous revertant count, and either a viability ration (VR) for the toxicity assay or a mutagenic ratio (MR) for the mutagenicity assay. The MEC (minimum effective concentration) is also indicated by an asterisk if the sample was mutagenic.

4.6 Data Analysis and Interpretation

4.6.1 Toxicity Assay/Data Analysis and Interpretation

The results from the toxicity assay for the combustion samples determined the doses utilized in the mutagenicity assay. The expression utilized to assess a toxic effect is called the viability ration (VR) and was calculated as follows:

$$\text{Viability Ratio} = \frac{\text{no. of surviving colonies in sample}}{\text{no. of surviving colonies in solvent}}$$

A toxicity assay dose that resulted in a 50% reduction in bacterial growth (i.e., a viability ratio of 0.50) became the highest dose tested in the

mutagenicity assay. If the viability ratio is below 0.50 the sample at that dose was considered toxic. An asterisk will appear in the table column headed "TOX" for the lowest concentration that demonstrated a toxic effect. A viability ratio greater than 1.0 indicated that the sample at that dose was nontoxic. The interpretation of the VR considers the values for testing both with and without S9 activation, and whether the toxic effect was dose responsive.

4.6.2 Mutagenicity Testing/Data Analysis an Interpretation

The mutagenicity of a test compound can be quantified as the mutagenic ratio (MR). The MR is calculated as follows:

$$\text{Mutagenic Ratio} = \frac{\text{no. of revertant colonies in sample}}{\text{no. of revertant colonies in solvent}}$$

The sample was considered mutagenic with strains TA98 and TA100 if the MR was 2.0 or greater and the response increased at three increasing doses. The sample can be further categorized as having high or low mutagenicity based upon the smallest amount of sample required to produce a MR of 2.0 or greater. This lowest dose is called the Minimum Effective Concentration (MEC) and was identified in the tables by an asterisk under the column with the "MEC" heading. Table 7 list the criteria used for categorizing a sample's mutagenic activity based upon the MEC. This study used the criteria in the column labeled "Solids."

The slope of the linear portion of the dose-response curve is also utilized for categorizing a sample's mutagenic activity. The slope is expressed in revertants per microgram of sample. Because the Salmonella tester strains respond differently to mutagens, the slopes of the dose-response curves should only be compared within and not between strains.

TABLE 7. IERL/LEVEL I AMES ASSAY EVALUATION CRITERIA

Mutagenic Activity	Criteria Used		
	Solids (MEC in µg/plate)	Liquids (MEC in µl/plate)	Organic Extracts (MEC in µl/plate)
High	<50	<2	<2
Moderate	.50-500	2-20	2-20
Low	500-5000	20-200	20-200
Not detectable	5000	>200	>200

NOTE: These categories at these doses are based upon a mutagenic ratio of 2.0 for strains TA98 and TA100 and 3.0 for strains TA1535, TA1537, and TA1538.

5.0 Results and Discussion

Table 8 summarizes the toxicity and mutagenicity results. The raw data and statistical analysis can be found in Appendix A. In the front of the Appendix is a legend key for the computer printout headings.

5.1 Toxicity Pre-Screen

The toxicity pre-screen was performed on strain TA98 with and without S9 activation. The results are listed in Tables A1-2 and Graphs A1-4 in Appendix A. The asterisk in the "TOX" column denotes a viability ratio of less than 50% survival. Sample 11020I was more toxic to TA98 than sample 11007 and was toxic at the 500 µg/plate dose with or without the S9 homogenate. Sample 11007 was toxic at the 1000 µg/plate dose in the absence of S9 and demonstrated a reduced toxic activity in the presence of S9. Because of a limited amount of sample only one plate was poured with sample 11020I and duplicate plates were poured for sample 11007. A toxicity prescreen was not performed on strain TA100. The analysis of the toxicity results suggested the following doses for mutagenicity testing: 1,000, 500, 100, 50, 10 µg/plate. Adequate amounts of sample were available for triplicate plates in the mutagenicity test for these samples. Triplicate plates are recommended for quality control purposes.

5.2 Mutagenicity Testing

The results from the mutagenicity testing are listed in Tables A4-5 and Graphs A5-8 for TA98 and Tables A5-6 and Graphs A9-12 for TA100. Under the heading, "Activation," a batch code (i.e., RLI002) will appear if the S9 activation system was added to the test mixtures. Under the column headed, "MEC," an asterisk appears by the minimum dose which produced a mutagenic ratio (MR) of 2.0 or greater. The MEC value can then be categorized to rank the sample for mutagenic activity.

Sample 11020I demonstrated mutagenic activity with strains TA98 and TA100 both with and without the addition of a S9 rat liver activation system. The MEC necessary to produce a MR of 2.0 or greater was 50 µg/plate

TABLE 8. MUTAGENICITY OF 11020I AND 11007 TA98 (DETECTS
FRAMESHIFT MUTAGENS), DETERMINED AT NONTOXIC
DOSES

Sample Code	S9 Activation	MEC ($\mu\text{g}/\text{plate}$)	Mutagenicity ^a Ranking	Slope (rev/ μg)
11020I	-	50	H	0.47
	+	50	H	0.74
11007	-	50	H	0.67
	+	50	H	0.97

TA100 (DETECTS BASE PAIR SUBSTITUTION MUTAGENS)

Sample Code	S9 Activation	MEC ($\mu\text{g}/\text{plate}$)	Mutagenicity ^a Ranking	Slope (rev/ μg)
11020I	-	500	M	0.79
	+	500	M	1.28
11007	-	500	M	0.96
	+	500	M	1.74

^aH = high mutagenic activity; M = moderate mutagenic activity.

with TA98 and 500 µg/plate with TA100. The MRs at these doses were greater than 2.0. Based upon the criteria listed in Table 7, sample 11020I was categorized as highly (H) mutagenic with strain TA98 (frameshift mutagens) and moderately (M) mutagenic with strain TA100 (base pair substitution mutagens).

The mutagenic activity of the samples with or without the addition of a S9 rat liver activation system was analyzed by comparing the slopes from the linear portion of the sample's dose-response curves. The mutagenic activity demonstrated in the absence of S9 was interpreted as activity from direct-acting mutagens. Direct-acting mutagens do not require the addition of a S9 activation system to produce a mutation in the histidine operon. An increase in the mutagenic activity with the addition of the S9 activation system was interpreted as increased activity from promutagens.

Sample 11020I clearly demonstrated mutagenic activity with both strains TA98 and TA100 in the absence of S9 and therefore contains direct-acting mutagens. This sample demonstrated a greater mutagenic activity with the addition of S9. The greater activity of sample 11020I with the addition of S9 suggests that this sample also contained promutagens. Promutagens have been previously detected in stove combustion products by Austin et al. (Appendix B).

Sample 11007 was also categorized as highly mutagenic with strain TA98 (MEC of 50 µg/plate) and moderately mutagenic with strain TA100 (MEC of 500 µg/plate) with or without the addition of S9. As in sample 11020I, greater activity occurred with the addition of S9 suggesting the presence of both direct-acting mutagens and promutagens. Comparing the two samples for mutagenic activity by comparing the slopes of the dose-response curve demonstrates that sample 11007 was more mutagenic than sample 11020I under all conditions tested.

6.0 References

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- McCann, J., Choi, E., Yamasaki, E. and B. N. Ames. Detection of Carcinogens or Mutagens in the Salmonella/Microsome Test: Assay of 300 Chemicals, Proc. Nat. Acad. Sci. 72, 5135-5139 (1975).
- Rinkus, R. and N. Legator. Chemical Characterization of 465 Known or Suspected Carcinogens and Their Correlation with Mutagenic Activity in the Salmonella typhimurium System, Cancer. Res. 39, 3289-3318 (1979).

APPENDIX A

COMPUTER PRINTOUT LEGEND

EXP Date = Date of the experiment.

Test Type = Pour or preincubation test (left blank or 01).

Dilution = Milligrams of S9 to milligrams of S9 mix.

Mixture = Microliters of S9 mix per plate.

Chemical = Code for chemical tested.

Strain = Salmonella strain used.

Plated = Microliters of S9 mix plated for sterility plate.

Technician = Code for the technician performing the work.

Contract No. = Contract number of project.

Activation = Code number for the batch of S9 mix. Blank for the testing without S9.

Batch = Code for the strain batch.

Colonies - Number of colonies on S9 sterility plate. Generally blank if S9 was sterile.

S054 = Solvent (dimethylsulfoxide).

P = Positive controls.

P-01 = Sodium azide.

P-02 = 9-aminoacridine.

P-03 = 2-nitrofluorene.

P-04 = 2-aminoanthracene.

STD DEV = Standard deviation of duplicate plate counts.

Q/C = Quality control column.

A = acceptable i.e., within the ranges specified for each project.

NA = not acceptable.

VR = Viability ratio, the ratio of surviving colonies with sample to the surviving colonies of the solvent control.

COMPUTER PRINTOUT LEGEND (continued)

TOX = Toxicity - an asterisk appears in this column for the lowest dose with

a viability ratio of 0.5 or less.

MR = Mutagenic ratio - the ratio of the number of revertants with sample over

the number of revertants with the solvent control.

MEC = Minimum effective concentration, the lowest dose with a MR of 2.0 or greater.

The units for the dose are in microliters/plate for liquid samples and in micrograms/plate for solids. Please note that for the mutagenicity data the positive controls and the samples are in microgram units while the solvent control is in microliter units.

TABLE A1. TOXICITY OF 110201 - TA98

TOXICITY
EXP DATE: 011882
TEST TYPE: 01
DILUTION= :
MIXTURE=

CHEMICAL: 110201
STRAIN: TA98
PLATED=
TECHNICIAN= RDE

CONTRACT NO.: 2075
ACTIVATION:
BATCH: A172
COLONIES=

SOLVENT/ POSITIVE	DOSE LEVEL	PLATE A: COUNT BG	PLATE B: COUNT BG	PLATE C: COUNT BG	AVERAGE COUNT	STD DEV COUNT	VR	TOX
S1 54	0.00	438	387		412.5	36.1	1.0	
	10.00	572			572.0		1.4	
	50.00	552			552.0		1.3	
	100.00	499			499.0		1.2	
	500.00	82			82.0		0.2	*
	1000.00	0			0.0		0.0	

TOXICITY
EXP DATE: 011882
TEST TYPE: 01
DILUTION= 1: 10
MIXTURE= 500

CHEMICAL: 110201
STRAIN: TA98
PLATED= 100
TECHNICIAN= RDE

CONTRACT NO.: 2075
ACTIVATION: RL1002
BATCH: A172
COLONIES=

SOLVENT/ POSITIVE	DOSE LEVEL	PLATE A: COUNT BG	PLATE B: COUNT BG	PLATE C: COUNT BG	AVERAGE COUNT	STD DEV COUNT	VR	TOX
S1 54	0.00	579	592	589	586.7	6.8	1.0	
	10.00	572			572.0		1.0	
	50.00	552			552.0		0.9	
	100.00	499			499.0		0.9	
	500.00	82			82.0		0.1	*
	1000.00	0			0.0		0.0	

TABLE A2. TOXICITY OF 11007 - TA98

TOXICITY
EXP DATE: 011882
TEST TYPE: 01
DILUTION= :
MIXTURE=

CHEMICAL: 11007
STRAIN: TA98
PLATED=
TECHNICIAN= RDE

CONTRACT NO.: 2075
ACTIVATION:
BATCH: A172
COLONIES=

SOLVENT/ POSITIVE	DOSE LEVEL	PLATE A: COUNT BG	PLATE B: COUNT BG	PLATE C: COUNT BG	AVERAGE COUNT	STD DEV COUNT	VR	TOX
S1 54	0.00	438	387		412.5	36.1	1.0	
	10.00	491	518		504.5	19.1	1.2	
	50.00	473	458		465.5	10.6	1.1	
	100.00	553	461		507.0	65.1	1.2	
	500.00	307	320		313.5	9.2	0.8	
	1000.00	131	141		136.0	7.1	0.3	*

TOXICITY
EXP DATE: 011882
TEST TYPE: 01
DILUTION= 1: 10
MIXTURE= 500

CHEMICAL: 11007
STRAIN: TA98
PLATED= 100
TECHNICIAN= RDE

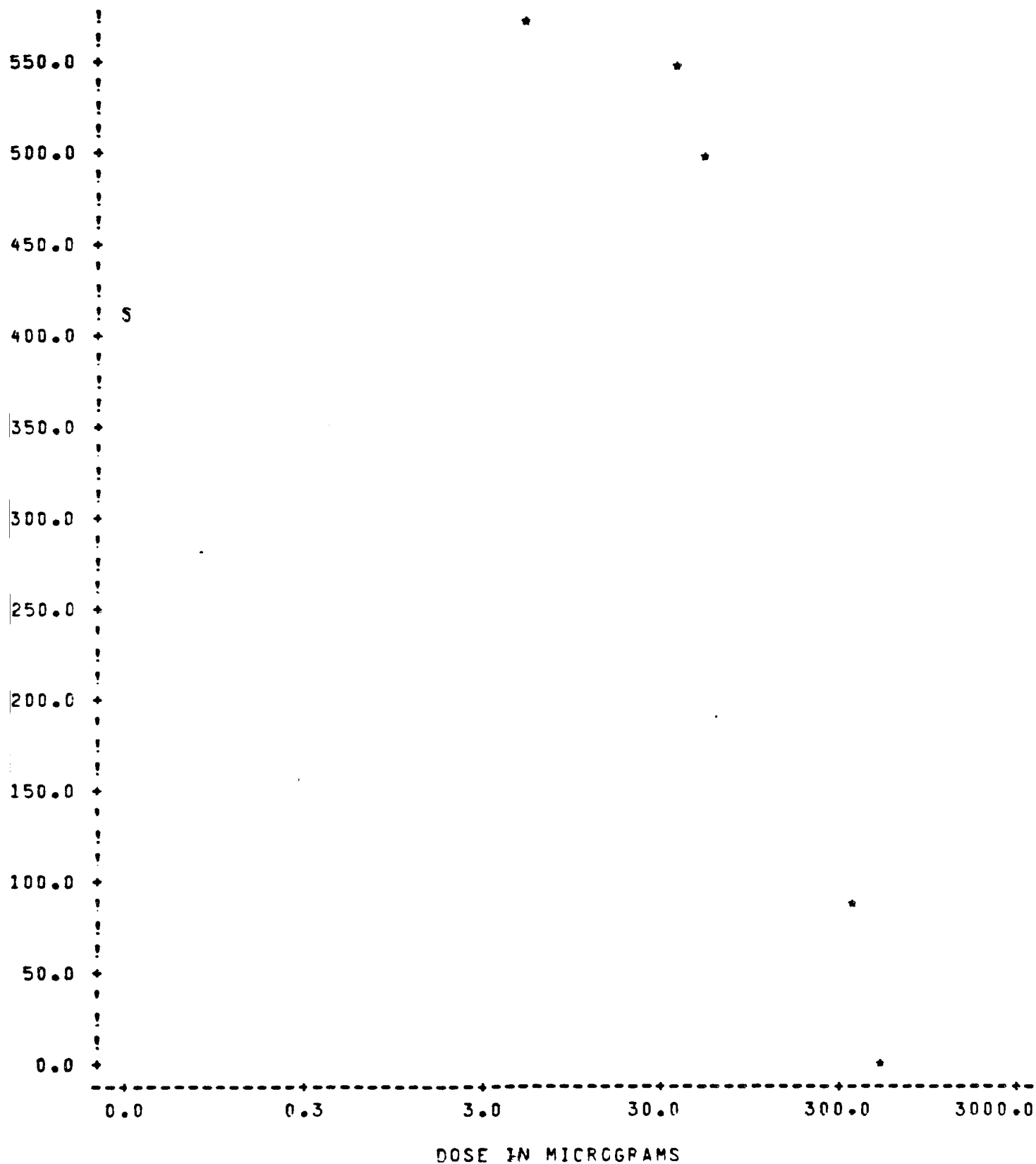
CONTRACT NO.: 2075
ACTIVATION: RL1002
BATCH: A172
COLONIES=

SOLVENT/ POSITIVE	DOSE LEVEL	PLATE A: COUNT BG	PLATE B: COUNT BG	PLATE C: COUNT BG	AVERAGE COUNT	STD DEV COUNT	VR	TOX
S1 54	0.00	579	592	589	586.7	6.8	1.0	
	10.00	625	658		641.5	23.3	1.1	
	50.00	657	353		505.0	215.0	0.9	
	100.00	728	568		648.0	113.1	1.1	
	500.00	441	572		506.5	92.6	0.9	
	1000.00	367	435		411.0	33.9	0.7	

GRAPH A1. TOXICITY OF 110201 - TA98 -S9

S=SOLVENT P=POSITIVE N=ANTHRAMINE W/O S9 *=TEST COMPOUND
 CONTRACT=2075 CHEMICAL=110201 STRAIN=98 DATE=011882 ACTIVATN=

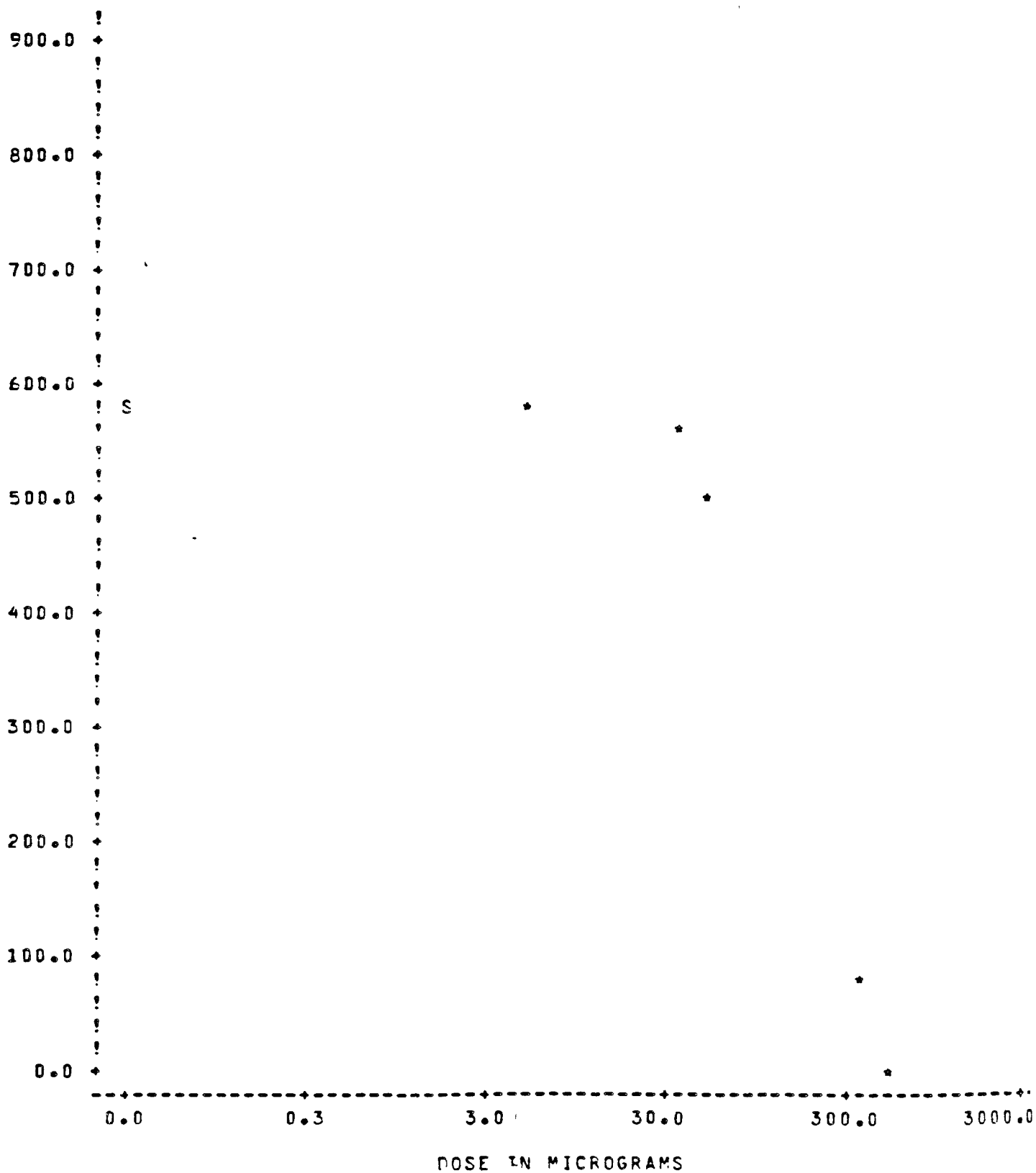
PLOT OF AVGCOUNT*DOSE SYMBOL IS VALUE OF SPIND



GRAPH A2. TOXICITY OF 11020I - TA98 +S9

S=SOLVENT P=POSITIVE N=ANTHRAMINE W/O S9 +=TEST COMPCUND
 CONTRACT=2075 CHEMICAL=11020I STRAIN=98 DATE=011882 ACTIVATN=RLI002

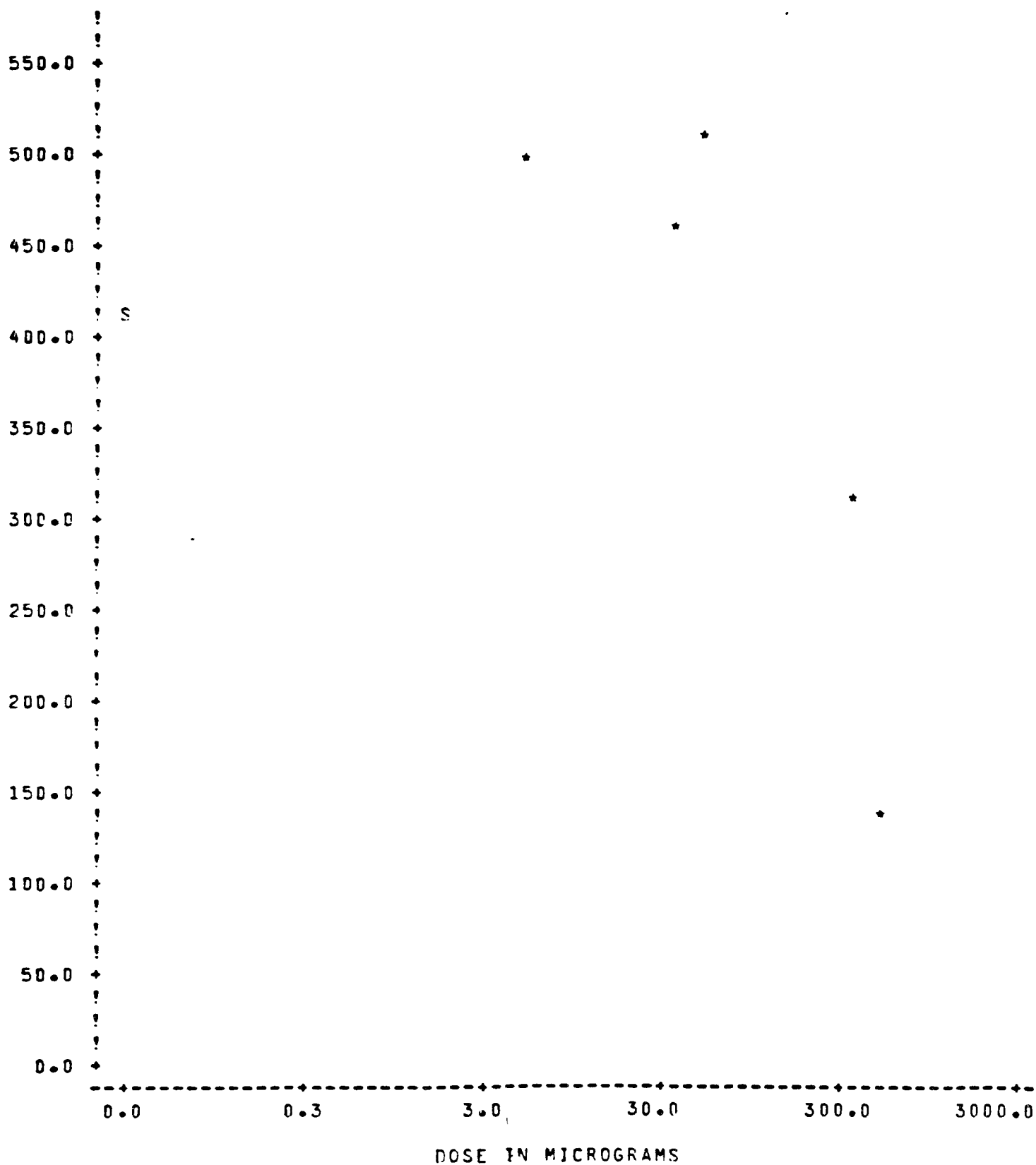
PLOT OF AVGCOUNT*DOSE SYMBOL IS VALUE OF SPIND



GRAPH A3. TOXICITY OF 11007 - TA98 -S9

S=SOLVENT P=POSITIVE N=ANTHRAMINE W/O S9 *=TEST COMPOUND
 CONTRACT=2075 CHEMICAL=11007 STRAIN=98 DATE=011882 ACTIVATN=

PLOT OF AVGCOUNT*DOSE SYMBOL IS VALUE OF SPIND



GRAPH A4. TOXICITY OF 11007 - TA98 +S9

S=SOLVENT P=POSITIVE N=ANTHRAMINE W/O S9 +=TEST COMPOUND
 CONTRACT=2075 CHEMICAL=11007 STRAIN=98 DATE=011882 ACTIVATN=RL1002

PLOT OF AVGCOUNT*DOSE SYMBCL IS VALUE OF SPIND

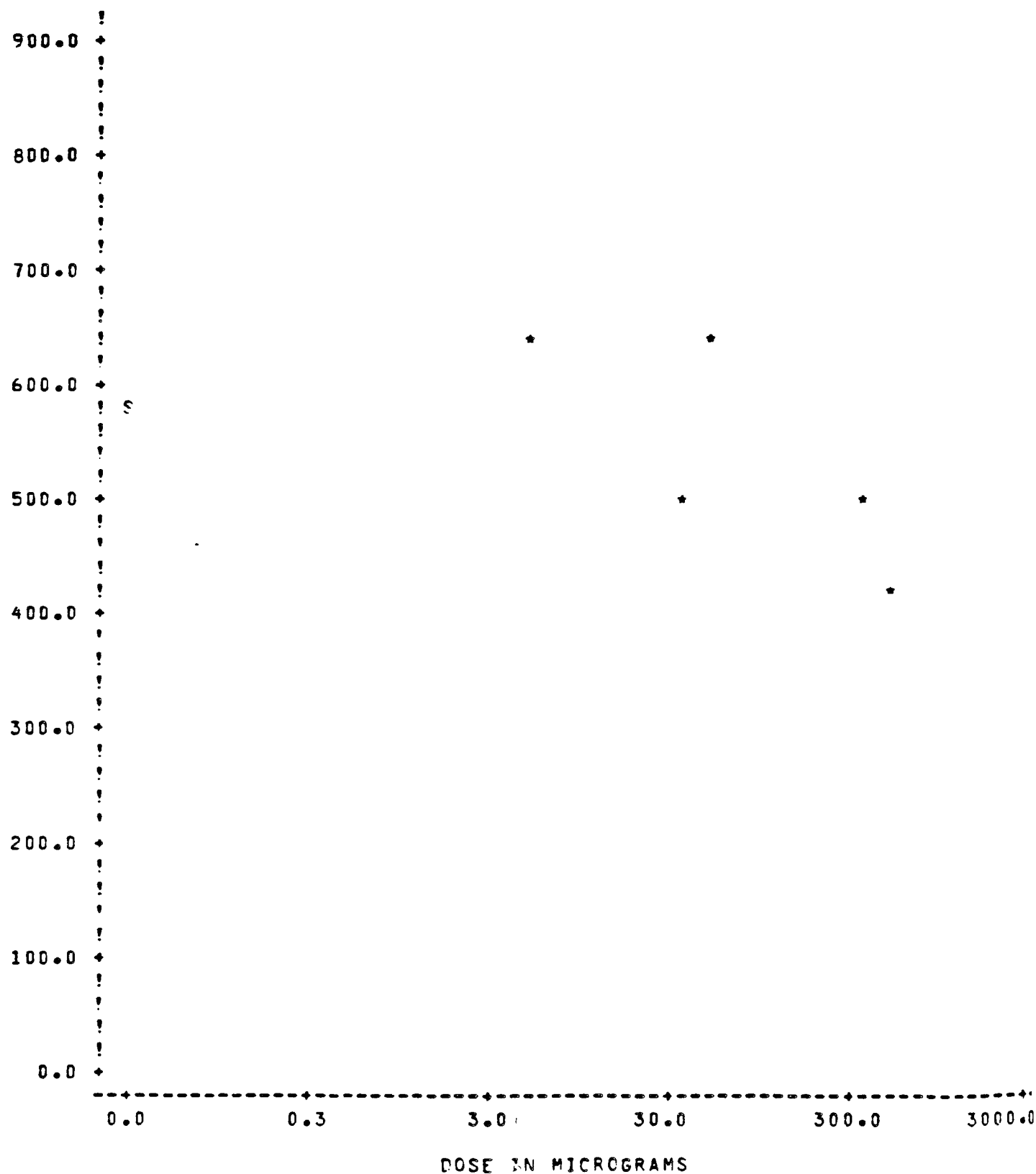


TABLE A3 MUTAGENICITY OF 110201 - TA98

M U T A G E N I C I T Y

EXP DATE: 012282 CHEMICAL: 110201
 TEST TYPE: 01 STRAIN: TA98
 DILUTION= : PLATED= :
 MIXTURE= : TECHNICIAN= RDE

CONTRACT NO.: 2075

ACTIVATION:
 BATCH: A212
 COLONIES=

SOLVENT/ POSITIVE	DOSE LEVEL	PLATE A: CCUNT BG	PLATE B: COUNT BG	PLATE C: CCUNT BG	AVERAGE COUNT	STD DEV CCUNT	G/C	MR	MEC
S1 54	0.00	19	20	19	19.3	0.6	A	1.0	
P1 04	5.00	30	31	39	33.3	4.9		1.7	
P2 03	5.00	402	340	368	370.0	31.0	A	19.2	
P3 03	10.00	795	858	771	808.0	44.5	A	41.5	
	10.00	18	27	19	21.3	4.9		1.1	
	50.00	56	60	58	58.0	2.0		3.0	*
	100.00	94	77	108	93.0	15.5		4.8	
	500.00	184	180	200	188.0	10.6		5.7	
	1000.00	247	246	238	243.7	4.5		12.6	
	2000.00	0	0	0	0.0	0.0		0.0	

M U T A G E N I C I T Y

EXP DATE: 012282 CHEMICAL: 110201
 TEST TYPE: 01 STRAIN: TA98
 DILUTION= 1: 10 PLATED= 100
 MIXTURE= 500 TECHNICIAN= RDE

CONTRACT NO.: 2075

ACTIVATION: RL1002
 BATCH: A212
 COLONIES=

SOLVENT/ POSITIVE	DOSE- LEVEL	PLATE A: CCUNT BG	PLATE B: COUNT BG	PLATE C: CCUNT BG	AVERAGE COUNT	STD DEV CCUNT	G/C	MR	MEC
S1 54	0.00	22	34	20	25.3	7.6	A	1.0	
P1 04	1.00	178	229	221	209.3	27.4	A	8.3	
P2 04	5.00	1361	1328	1400	1363.0	36.0	A	53.5	
	10.00	46	43	33	40.7	6.8		1.6	
	50.00	85	52	95	50.7	5.1		3.6	*
	100.00	147	146	143	145.3	2.1		5.7	
	500.00	251	261	278	263.3	13.7		10.4	
	1000.00	342	306	321	323.0	18.1		12.8	
	2000.00	281	267	277	275.0	7.2		10.5	

TABLE A4 MUTAGENICITY OF 11007 - TA98

M U T A G E N I C I T Y

EXP DATE: C12282 CHEMICAL: 11007
 TEST TYPE: 01 STRAIN: TA98
 DILUTION= : PLATED=
 MIXTURE= TECHNICIAN= RDE

CONTRACT NO.: 2075

ACTIVATION:

BATCH: A212

COLONIES=

SOLVENT/ POSITIVE	DOSE LEVEL	PLATE A: COUNT BG	PLATE B: COUNT BG	PLATE C: COUNT BG	AVERAGE COUNT	STD DEV COUNT	G/C	MR
S1 54	0.00	15	20	19	15.3	0.6	A	1.0
P1 04	5.00	30	31	35	33.3	4.5		1.7
P2 03	5.00	402	340	368	370.0	31.0	A	19.2
P3 03	10.00	795	858	771	808.0	44.5	A	41.9
	10.00	27	26	31	28.0	2.6		1.5
	50.00	60	65	68	65.7	4.5		3.4
	100.00	87	105	89	95.0	12.2		4.5
	500.00	306	308	293	302.3	8.1		15.7
	1000.00	110	57	93	100.0	8.9		5.2
	2000.00	176	165	165	168.7	6.4		8.7

M U T A G E N I C I T Y

EXP DATE: C12282 CHEMICAL: 11007
 TEST TYPE: 01 STRAIN: TA98
 DILUTION= 1: 10 PLATED= 100
 MIXTURE= 500 TECHNICIAN= RDE

CONTRACT NO.: 2075

ACTIVATION: RL1002

BATCH: A212

COLONIES=

SOLVENT/ POSITIVE	DOSE LEVEL	PLATE A: COUNT BG	PLATE B: COUNT BG	PLATE C: COUNT BG	AVERAGE COUNT	STD DEV COUNT	G/C	MR
S1 54	0.00	22	34	20	25.3	7.6	A	1.0
P1 04	1.00	178	225	221	209.3	27.4	A	8.3
P2 04	5.00	1361	1328	1400	1363.0	36.0	A	53.5
	10.00	37	28	39	34.7	5.9		1.4
	50.00	62	55	46	54.3	8.0		2.1
	100.00	70	67	55	72.0	14.1		2.8
	500.00	245	271	260	258.7	13.1		10.2
	1000.00	364	351	330	348.3	17.2		13.8
	2000.00	247	240		243.5	4.9		9.6

TABLE A5. MUTAGENICITY OF 110201 - TA100

MUTAGENICITY CONTRACT NO.: 2075
 DATE: 012282 CHEMICAL: 110201 ACTIVATION:
 TYPE: 01 STRAIN: TA100 BATCH: A212
 DILUTION= : PLATED= COLONIES=
 DURE= TECHNICIAN= RDE

INT/ DIVE	DOSE LEVEL	PLATE A: COUNT BG	PLATE B: COUNT BG	PLATE C: COUNT BG	AVERAGE COUNT	STD DEV COUNT	G/C	MR	MEC
54	0.00	198	193	225	205.3	17.2	A	1.0	
54	5.00	302	289	272	287.7	15.0		1.4	
51	1.00	547	516	578	547.0	31.0	A	2.7	
51	5.00	974	963	931	956.0	22.3	A	4.7	
	10.00	216	187	217	206.7	17.0		1.0	
	50.00	266	282	268	272.0	8.7		1.3	
	100.00	288	277	266	277.0	11.0		1.3	
	500.00	436	474	435	448.3	22.2		2.2	*
	1000.00	514	506	414	478.0	55.6		2.3	

MUTAGENICITY CONTRACT NO.: 2075
 DATE: 012282 CHEMICAL: 110201 ACTIVATION: RLI002
 TYPE: 01 STRAIN: TA100 BATCH: A212
 DILUTION= 1: 10 PLATED= 100 COLONIES=
 DURE= 500 TECHNICIAN= RDE

INT/ DIVE	DOSE LEVEL	PLATE A: COUNT BG	PLATE B: COUNT BG	PLATE C: COUNT BG	AVERAGE COUNT	STD DEV COUNT	G/C	MR	MEC
54	0.00	158	168	167	164.3	5.5	A	1.0	
54	1.00	345	374	349	356.0	15.7		2.2	
54	5.00	1300	1298	1290	1296.0	5.3	A	7.9	
	10.00	228	217	216	220.3	6.7		1.3	
	50.00	352	319	307	326.0	23.3		2.0	
	100.00	400	365	410	391.7	23.6		2.4	
	500.00	519	497	480	498.7	19.6		3.0	*
	1000.00	454	461	428	447.7	17.4		2.7	

TABLE A6. MUTAGENICITY OF 11007 - TA100

MUTAGENICITY
 EXP DATE: 012282 CHEMICAL: 11007
 TEST TYPE: 01 STRAIN: TA100
 DILUTION= : PLATED=
 MIXTURE= TECHNICIAN= RDE

CONTRACT NO.: 2075
 ACTIVATION:
 BATCH: A212
 COLONIES=

SOLVENT/ POSITIVE	DOSE LEVEL	PLATE A: COUNT BG	PLATE B: COUNT BG	PLATE C: COUNT BG	AVERAGE COUNT	STD DEV COUNT	G/C	MR	PEC
S1 54	0.00	198	193	225	205.3	17.2	A	1.0	
P1 04	5.00	302	289	272	287.7	15.0		1.4	
P2 01	1.00	547	516	576	547.0	31.0	A	2.7	
P3 01	5.00	974	963	931	956.0	22.3	A	4.7	
	10.00	201	220	203	208.0	10.4		1.0	
	50.00	237	272	227	245.3	23.6		1.2	
	100.00	338	323	330	330.3	7.5		1.6	
	500.00	667	645	691	667.7	23.0		3.3	*
	1000.00	227	289	322	279.3	48.2		1.4	
	2000.00	270	281	282	277.7	6.7		1.4	

MUTAGENICITY
 EXP DATE: 012282 CHEMICAL: 11007
 TEST TYPE: 01 STRAIN: TA100
 DILUTION= 1: 10 PLATED= 100
 MIXTURE= 500 TECHNICIAN= RDE

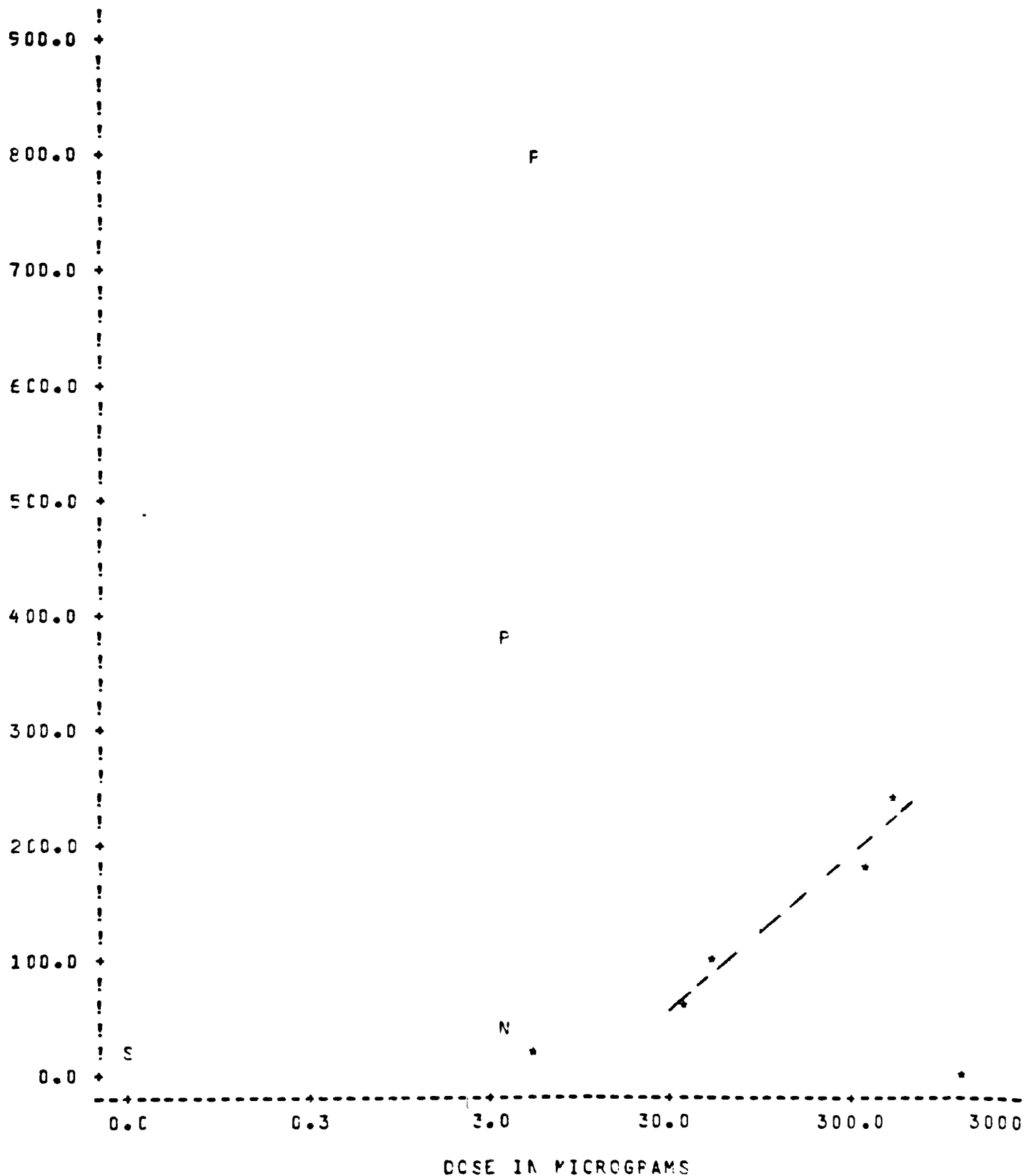
CONTRACT NO.: 2075
 ACTIVATION: RL1002
 BATCH: A212
 COLONIES=

SOLVENT/ POSITIVE	DOSE LEVEL	PLATE A: COUNT BG	PLATE B: COUNT BG	PLATE C: COUNT BG	AVERAGE COUNT	STD DEV COUNT	G/C	MR	PEC
S1 54	0.00	158	168	167	164.3	5.5	A	1.0	
P1 04	1.00	345	374	349	356.0	15.7		2.2	
P2 04	5.00	1300	1298	1290	1296.0	5.3	A	7.9	
	10.00	159	140	166	155.0	13.5		0.9	
	50.00	214	239	233	226.7	13.1		1.4	
	100.00	277	274	279	276.7	2.5		1.7	
	500.00	568	569	658	596.3	51.7		3.6	*
	1000.00	863	838	763	821.3	52.0		5.0	
	2000.00	467	497	491	485.0	15.9		3.0	

GRAPH A5 MUTAGENICITY OF 110201 - TA98 S9

S=SOLVENT P=POSITIVE N=ANTHRAMINE W/O S9 *=TEST COMPOUND
 CCNTRACT=2075 CHEMICAL=110201 STRAIN=58 DATE=012282 ACTIVATR=

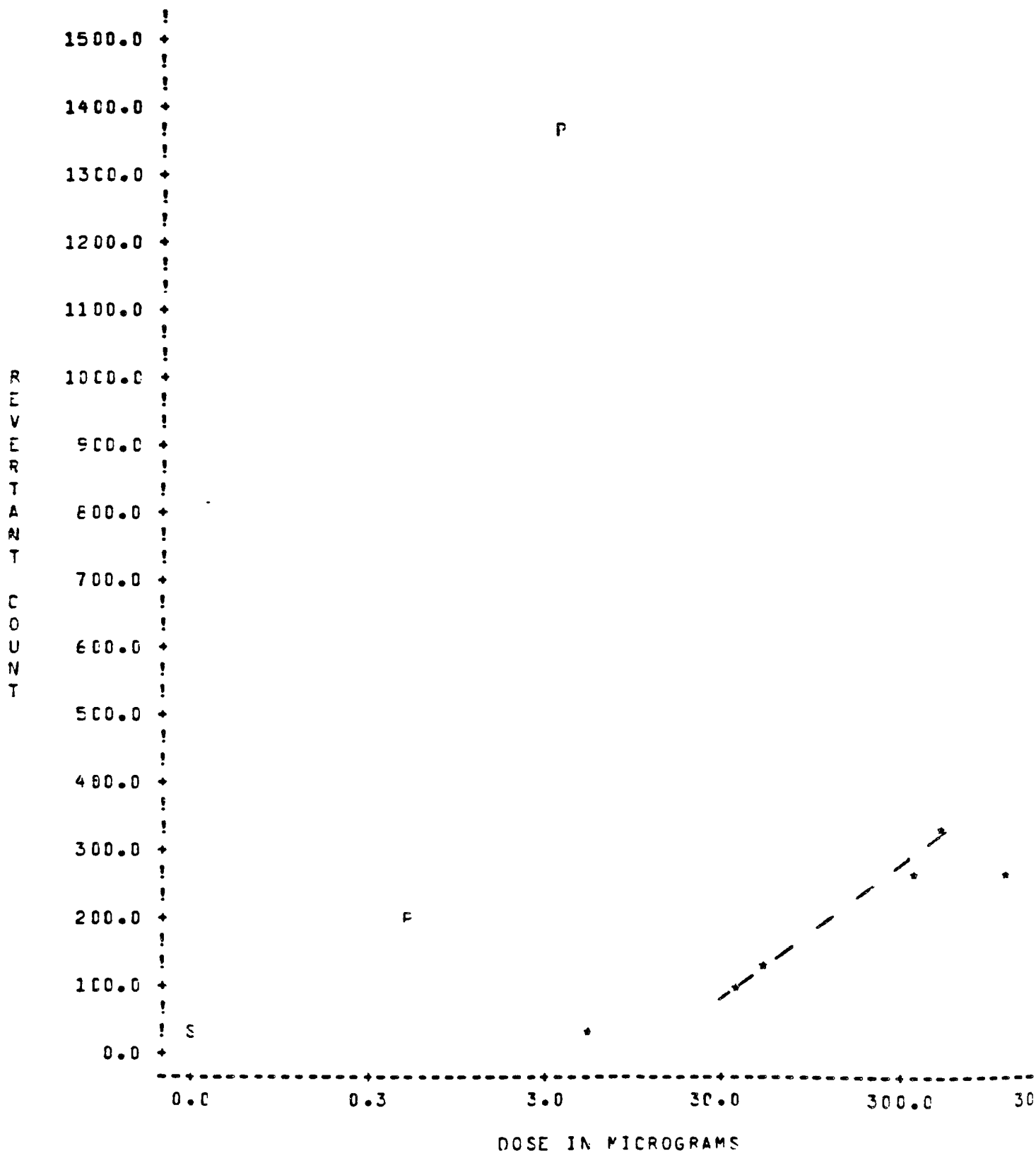
PLOT OF AVGCOUNT*DOSE SYMBOL IS VALLE OF SPIND



GRAPH A6 MUTAGENICITY OF 110201 - TA98 S9

S=SOLVENT P=POSITIVE N=ANTHRACENE W/O S9 *=TEST COMPOUND
 CONTRACT=2075 CHEMICAL=110201 STRAIN=98 DATE=012282 ACTIVATN=RL100

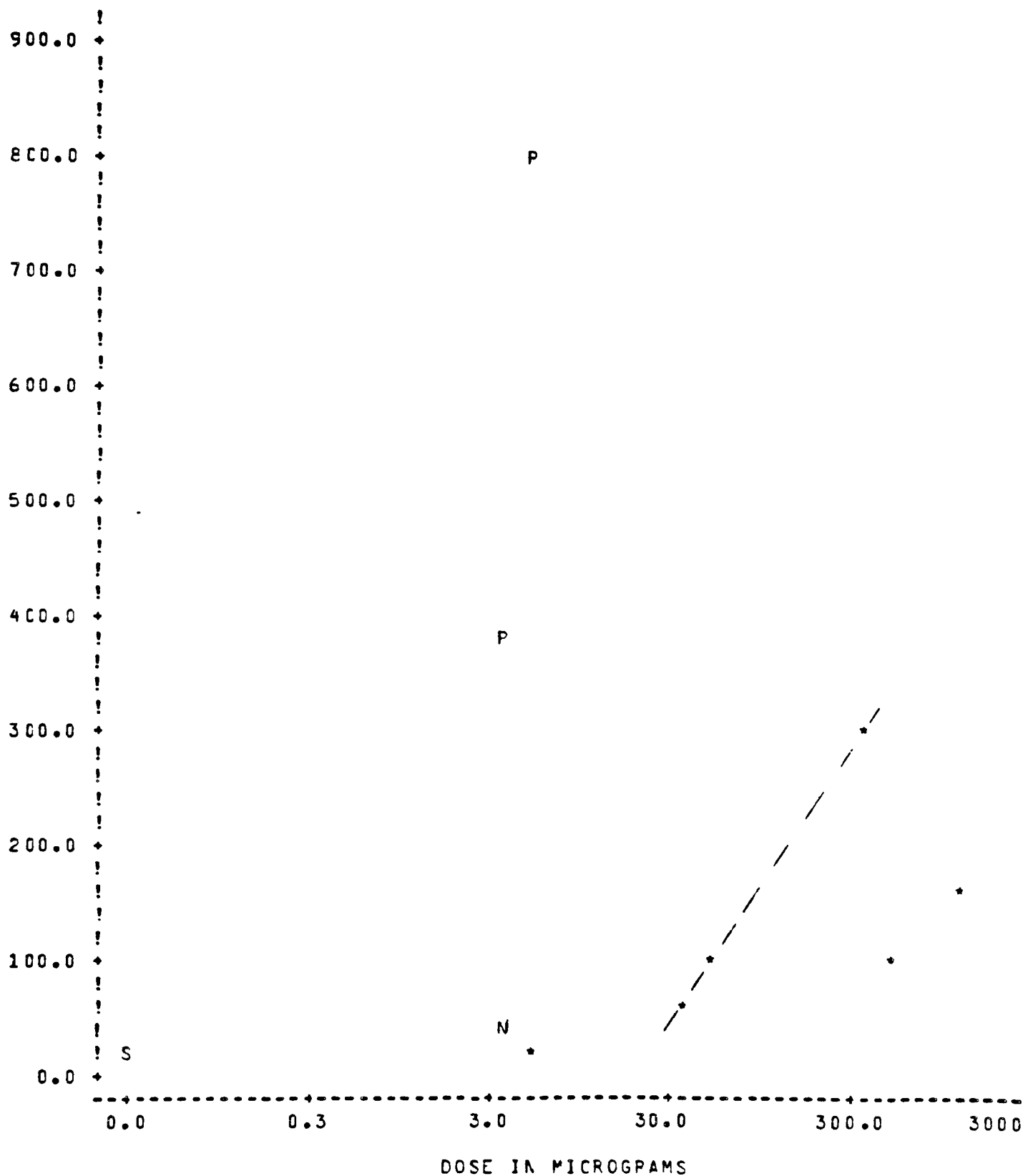
PLOT OF AVGCCOUNT*DOSE SYMBOL IS VALUE OF SPIND



GRAPH A7 MUTAGENICITY OF 11007 - TA98 S9

S=SOLVENT P=POSITIVE N=ANTHRACENE W/O S9 *=TEST COMPOUND
 CONTRACT=2075 CHEMICAL=11007 STRAIN=58 DATE=012282 ACTIVATN=

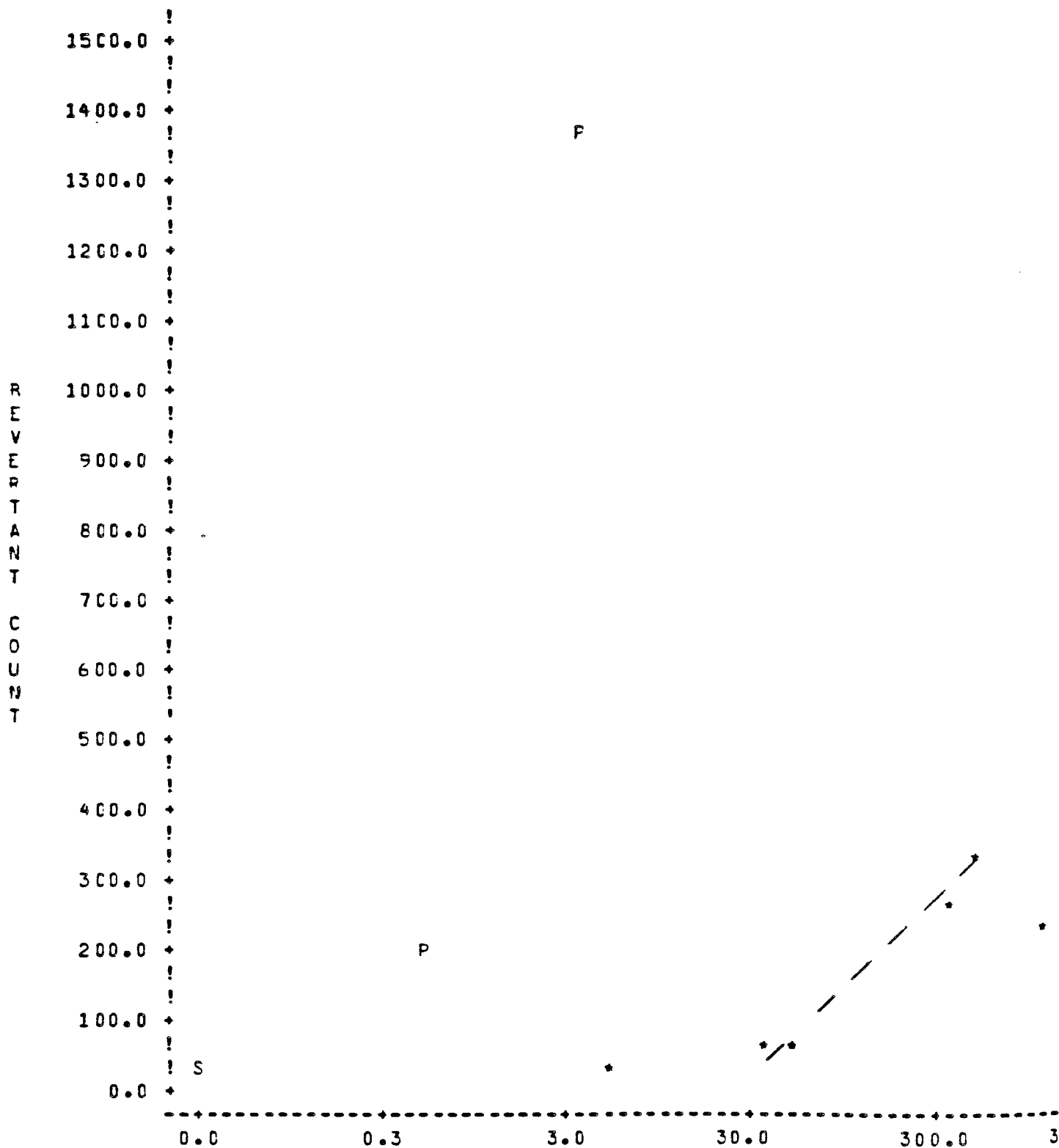
PLCT CF AVGCCUNT*DCSE SYMBOL IS VALUE OF SPIND



GRAPH A8 MUTAGENICITY OF 11007 - TA98 S9

S=SOLVENT P=POSITIVE N=ANTHRAMINE W/O S9 *=TEST COMPOUND
 CONTRACT=2075 CHEMICAL=11007 STRAIN=98 DATE=012282 ACTIVATN=RLIC

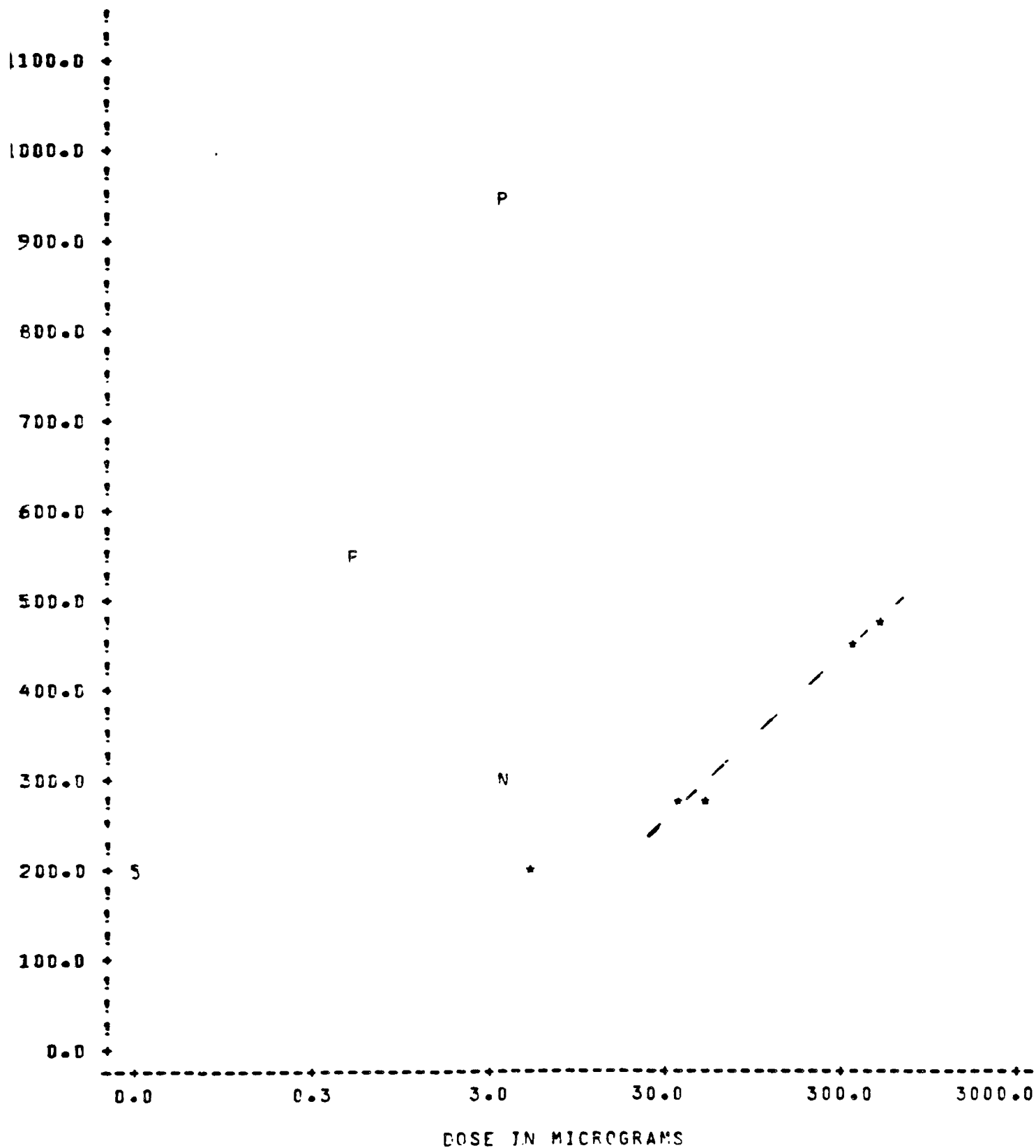
PLCT OF AVGCCUNT*DCSE SYMBOL IS VALUE OF SPIND



GRAPH A9. MUTAGENICITY OF 110201 - TA100 -S9

S=SOLVENT P=POSITIVE N=ANTHRAMINE W/O S9 *=TEST COMPOUND
 CONTRACT=2075 CHEMICAL=110201 STRAIN=100 DATE=012282 ACTIVATN=

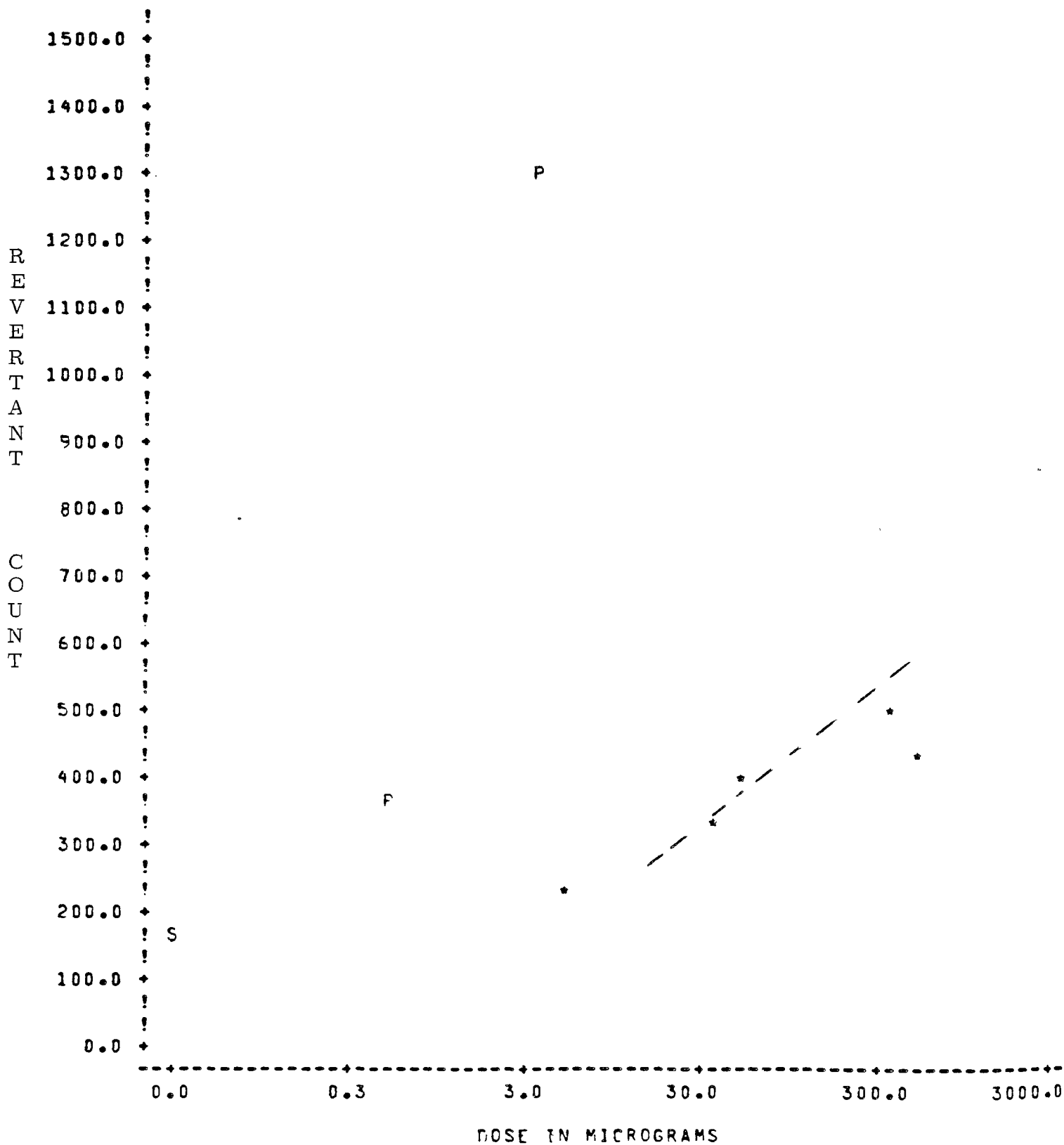
PLOT OF AVGCOUNT*DOSE SYMBOL IS VALUE OF SPIND



GRAPH A10. MUTAGENICITY OF 11020I - TA100 +S9

S=SOLVENT P=POSITIVE N=ANTHRAMINE W/O S9 *=TEST COMPOUND
 CONTRACT=2075 CHEMICAL=11020I STRAIN=100 DATE=012282 ACTIVATN=RLI002

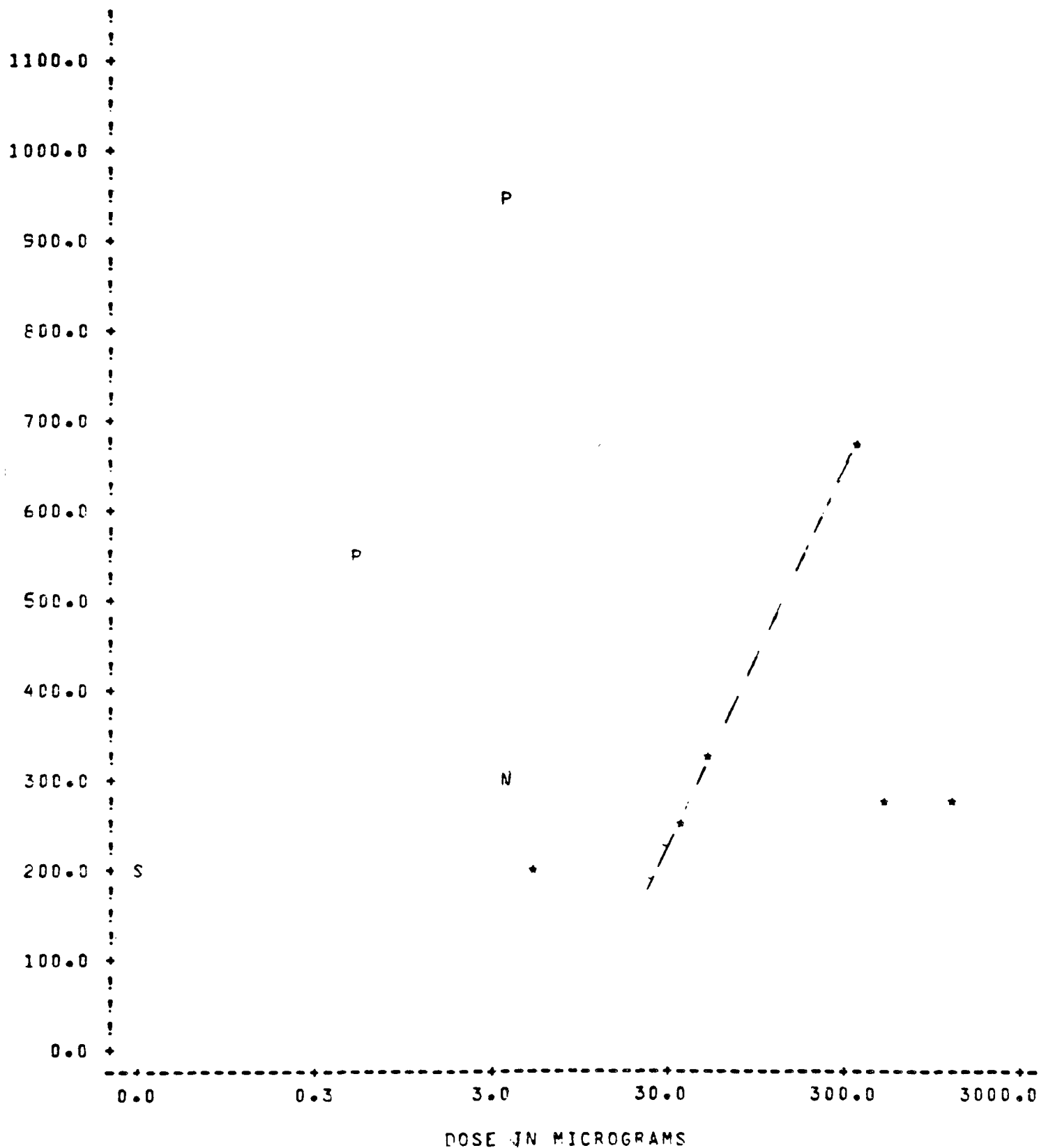
PLOT OF AVGCOUNT*DOSE SYMBOL IS VALUE OF SPIND



GRAPH A11. MUTAGENICITY OF 11007 - TA100 -S9

S=SOLVENT P=POSITIVE N=ANTHRAMINE W/O S9 *=TEST COMPOUND
 CONTRACT=2075 CHEMICAL=11007 STRAIN=100 DATE=012282 ACTIVATN=

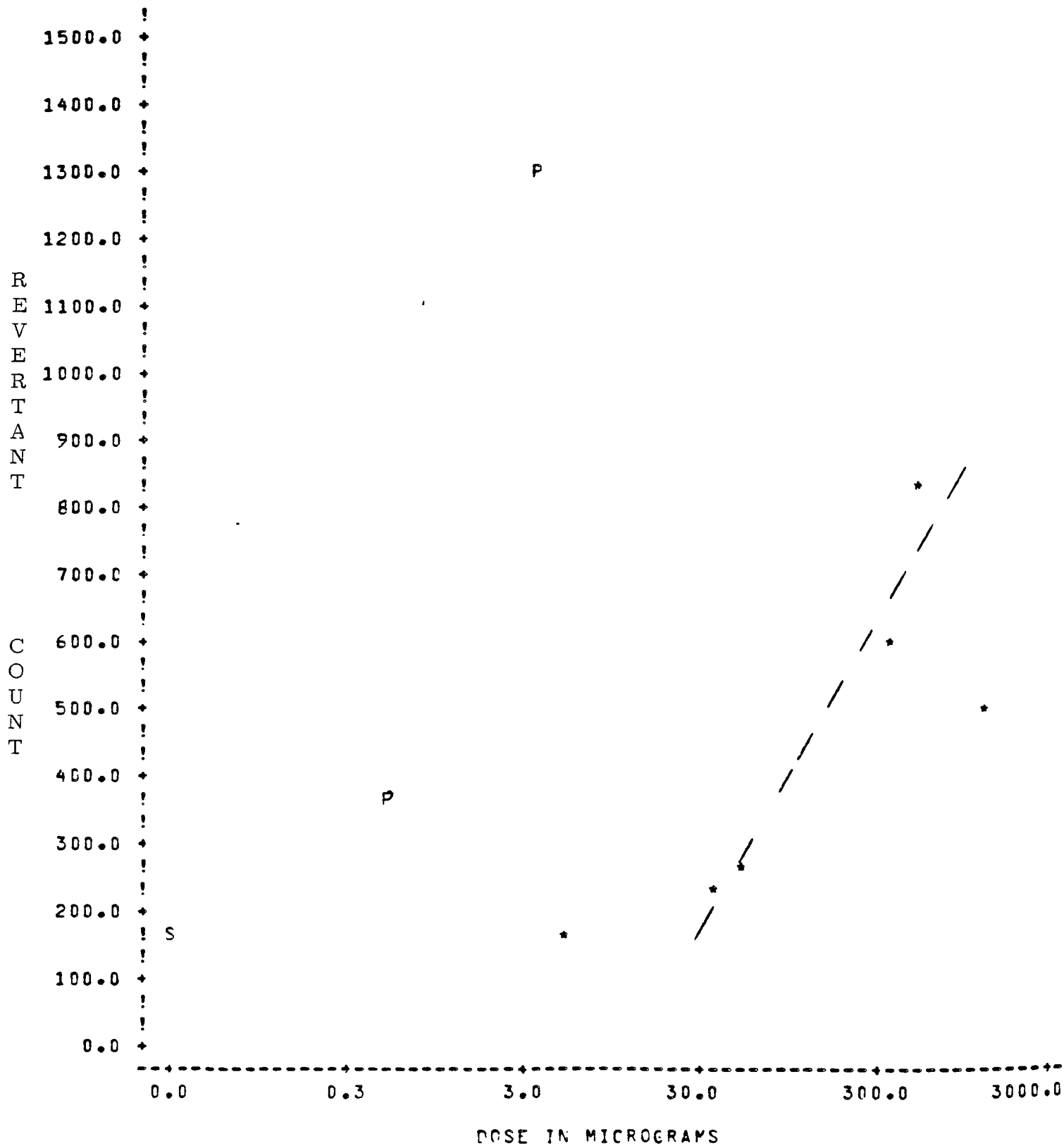
PLOT OF AVGCOUNT*DOSE SYMBOL IS VALUE OF SPIND



GRAPH A12. MUTAGENICITY OF 11007 - TA100 +S9

S=SOLVENT P=POSITIVE N=ANTHRAMINE W/O S9 *=TEST COMPOUND
 CONTRACT=2075 CHEMICAL=11007 STRAIN=100 DATE=012282 ACTIVATN=RLI002

PLOT OF AVGCOUNT*DOSE SYMBOL IS VALUE OF SPIND



APPENDIX B

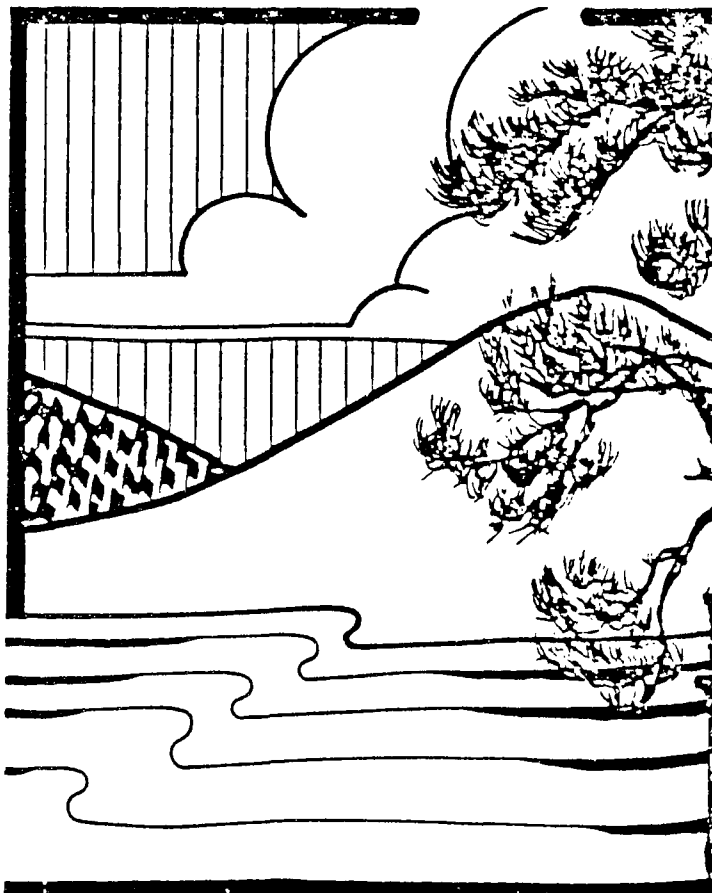
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RESULTS OF HEALTH AND ECOLOGICAL EFFECTS BIOASSAYS FOR THIRTY-TWO
RESIDENTIAL WOOD COMBUSTION RESIDUE SAMPLES

Robert Young,¹ Curt Hutchinson,² D.R. Jagannath,¹ David J. Brusick,¹ and Ray Merrill³

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This report presents the results of U.S. Environmental Protection Agency Level 1 environmental assessment bioassays on 32 Source Assessment Sampling System train samples collected from 12 separate residential wood-fired combustion source configurations (Auburn project). Three types of samples were supplied for testing from each combustion configuration, namely: (1) particulate catch extract, (2) combined organic module rinse and XAD-2 extract, and (3) combustion residue (bottom ash). The particulate catch extract was a composite sample consisting of (1) the front half wash residue, (2) the combined cyclone catch, and (3) the filter catch.

1. Ames Mutagenicity Assay

- a. The samples of combustion residue (bottom ash) that were evaluated did not show any mutagenic activity.
- b. Making very general comparisons between burning areas (fireplace and baffled and nonbaffled stoves), there is an apparent difference between the fireplace and the stoves. The mutagenicity of the filter particulate catch extract and of the XAD-2 extract of the fireplace samples was consistently lower than that of the same samples from the stoves. The significance of this is difficult to interpret without more information on the chemistry of these samples.
- c. No consistent difference between oak or pine and green or seasoned wood was observed in this study. Both produced roughly equivalent mutagenic effects.

2. Chinese Hamster Ovary Cell Clonal Toxicity Assay

The particulate catch and XAD-2 extracts consistently showed high levels of toxicity to Chinese hamster ovary cells in culture, regardless of burning area, wood type, or moisture content. These effects appeared to support the Salmonella results.

3. Rabbit Alveolar Macrophage Cytotoxicity Assay

This test was conducted on the bottom ash samples and produced results showing low toxicity to rabbit alveolar macrophages.

4. Freshwater Invertebrate Test

The acute toxicities of two combustion residues were determined in the ecological effects bioassay using the freshwater invertebrate Daphnia magna. Based on the defined LC₅₀ ranges, both samples tested against Daphnia magna were considered nontoxic.

MUTAGENICITY OF EMISSIONS FROM AN AIRTIGHT WOODSTOVE

Ann C. Austin, Robert E. Hall, Ray Merrill, and Joellen Lewtas

U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Woodstoves, now widely used for residential heating purposes, emit relatively high concentrations of particulate matter and organics. The objective of this study was to determine the mutagenicity of the organics extracted from the diluted particles emitted during wood combustion. The wood, seasoned pine and oak, was burned in a Johnson Energy Converter Model J-1000 airtight woodstove. The stove was operated with the following periods: a cold start up, a constant burn, a fuel addition, and a burndown. The emissions from each burning period were collected separately using a standard dilution tunnel sampling system, and the organics were removed by Soxhlet extraction with dichloromethane and prepared for bioassay in dimethylsulfoxide. The extracts were bioassayed in the Ames Salmonella typhimurium plate incorporation assay and were found to be mutagenic in Salmonella typhimurium TA98. Although there was some direct-acting activity, the addition of an S9 metabolic activation system increased the activity of each sample four- to twenty-one-fold. During the cold start up period for pine and the cold start up and fuel addition periods for oak, the organic emission rate (mg/m^3) was significantly greater than during the constant burn period. Similarly, the mutagenicity of the organics ($\text{rev}/\mu\text{g}$) during these respective periods was also greater. However, since the cold start up and fuel addition periods are relatively short compared to the total burn, the time averaged mutagenicity over the burn of all four periods closely resembles the mutagenicity of the constant burn period. The pine exhibited a higher particulate and organic emission rate than did the oak, and the organics emitted from the pine were somewhat more mutagenic. The mutagenicity of the organic emissions from woodstove and residential oil combustion were compared. Although the woodstove organics were two to five times less mutagenic than the oil, the woodstoves exhibited a much greater organic emission rate per joule of heat and the resultant mutagenicity of the woodstove emissions per joule of heat was greater than oil combustion.

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>				
1. REPORT NO. EPA-600/7-84-094		2.		3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Characterization of Emissions from the Combustion of Wood and Alternative Fuels in a Residential Woodstove			5. REPORT DATE September 1984	
7. AUTHOR(S) R. S. Truesdale, K. L. Mack, J. B. White, K. E. Leese, and J. G. Cleland			6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute P. O. Box 12194 Research Triangle Park, North Carolina 27709			8. PERFORMING ORGANIZATION REPORT NO. RTI/1914-39-01F	
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15. SUPPLEMENTARY NOTES IERL-RTP project officer is Michael C. Osborne, Mail Drop 65, 919/541-4113.				
16. ABSTRACT The report gives results of a comparison of emissions from the combustion of alternative fuels to those from wood in a residential woodstove, and of a study of the effects of woodstove operating parameters on combustion emissions. Overall, oak wood is the best fuel tested, considering both emissions and stove operation. Compressed wood logs with binders and bituminous coal produce the highest emissions of SO₂, particulate, and NO_x. Compressed wood logs without binders and treated lumber produce the highest PAH emissions. Important parameters affecting CO emission levels are fuel structure and, to a lesser degree, combustion air flow. SO₂ emission levels are related directly to fuel sulfur content. NO_x emissions are controlled by fuel nitrogen content and combustion air flow rate. Organic emissions are affected by fuel consumption rate, fuel structure, and the amount of air through the stove. Total discharge severities for PAHs measured during this study indicate that PAHs are the pollutants of highest concern in the flue gas effluent stream. PAH formation is affected by combustion air flow, firebox temperature, and fuel structure. Bioassay results indicate the presence of both mutagens and promutagens in the organic extracts of flue gas samples from both wood and coal combustion tests.				
17. KEY WORDS AND DOCUMENT ANALYSIS				
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group
Pollution Stoves		Pollution Control		13B 13A
Flue Gases Bioassay		Stationary Sources		21B 06A
Combustion Mutagens		Woodstoves		06E
Coal Aromatic Polycyclic				21D
Wood Hydrocarbons				11L 07C
Wood Products				
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