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Organic products of incomplete combustion of colored bags and inks

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Abstract

The goal of this study was to identify and trace the possible sources of organics emitted during the laboratory incineration of colored paper bags. An infrared incinerator was used to separately burn segments of colored paper bags and each ink component of the bags at a temperature of 300°C. Chemical analyses were performed to characterize the Products of Incomplete Combustion (PICs) emitted during the combustion process. A gas chromatograph/mass spectrometer (GC/MS) was used to identify organic groups ranging from alkanes to aromatics and polycyclic compounds. PICs identified and traced to their sources include: benzaldehyde, ethenylbenzene, furfural, naphthalene, and phenol. © 1998 Elsevier Science B.V.

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1. Introduction

The inadequate disposal of both municipal and industrial wastes has caused environmental deterioration, such as, the pollution of ground and surface waters and the contamination of soils. Approximately 250 million waste containers are disposed of each year, of which, about 30% or 75 million of these containers are estimated to be 50-lb bags [1]. The primary options for the disposal of 50-lb waste bags are recycling, which is not practical for paper bags; landfills, which imply transportation and long term storage; and open burning at the point of use. Open burning is the most used option

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because it is least costly to the user. In the United States, there are currently 126 Waste-to-Energy plants and 26 incinerators processing 31 million and 1.6 million tons of wastes per year, respectively [2].

Combustion process is recognized as one of the most effective technologies for organic waste destruction [3]. During the destruction process, free radical formations result in new intermediate compounds. These radicals contribute to the PICs identified during combustion.

During the combustion process, formation of free radicals results in the production of new intermediate compounds and Products of Incomplete Combustion (PICs). These free radicals are identified as molecular fragments which normally have a very short lifetime and are generally characterized by possessing an unpaired electron [4]. These radicals also contribute to the PICs identified during combustion. PICs can be either partial thermal decomposition products of the original compound, partial thermal decomposition of the original compound and/or new mixtures that have the same chemical identity as the original components [5]. PIC formations have been associated with the conditions of the incinerator and with the element and molecular chemical composition of waste feed [6]. These conditions may include: combustion temperature, residence time, waste chemistry, fuel/air ratio, and turbulence. PICs have been identified in waste material burned under a wide range of conditions, [7] and have been confirmed in laboratory tests [8]. For example, three types of PIC formation mechanisms were identified in the decomposition of 1,2-dichlorobenzene: unburnt parent compounds, combustion byproducts which include compounds of high molecular weights and carbon dioxide, and carbon monoxide [9]. These PICs exhibit characteristics of an uncontrolled and incomplete combustion process.

The US Environmental Protection Agency (USEPA) requires testing of industrial boilers and incinerators to identify their emissions. PICs identified from industrial boiler and incinerator tests include: chloroform, tetrachloroethylene, and benzene [10]. Current USEPA criteria pollutants include: particulate matter, lead, carbon monoxide, sulfur dioxide, nitrogen oxides, and volatile organic compounds. Furthermore, depending on the source, other pollutants monitored may include: cadmium, mercury, dioxin, furans, and acid gases (HCl, H₂SO₄, and HF).

This paper presents the results of a laboratory scale study to determine the organic PICs emitted when unused colored paper bags (designed for pesticide storage and transportation) and their ink components were combusted. Although the actual composition of inks used by manufacturers are trade secrets, a typical ink structure of each color burned was used to explain the results of the study. PICs identified in this study include: benzaldehyde, ethenylbenzene, furfural, naphthalene, and phenol.

1.1. Experimental and analytical procedures

Fig. 1 shows a schematic of a laboratory scale Shirco Thermogravimetric Analyzer (TGA) used for this study. The TGA consisted of a furnace (incinerator) 6 in. × 8 in. in size that is insulated with a heavy ceramic fiber blanket. The incinerator was heated with four silicon carbide infrared heating elements that heat samples of up to 500 g (1.1 lb) to a temperature as high as 1000°C (1832°F). A sample was suspended inside the furnace

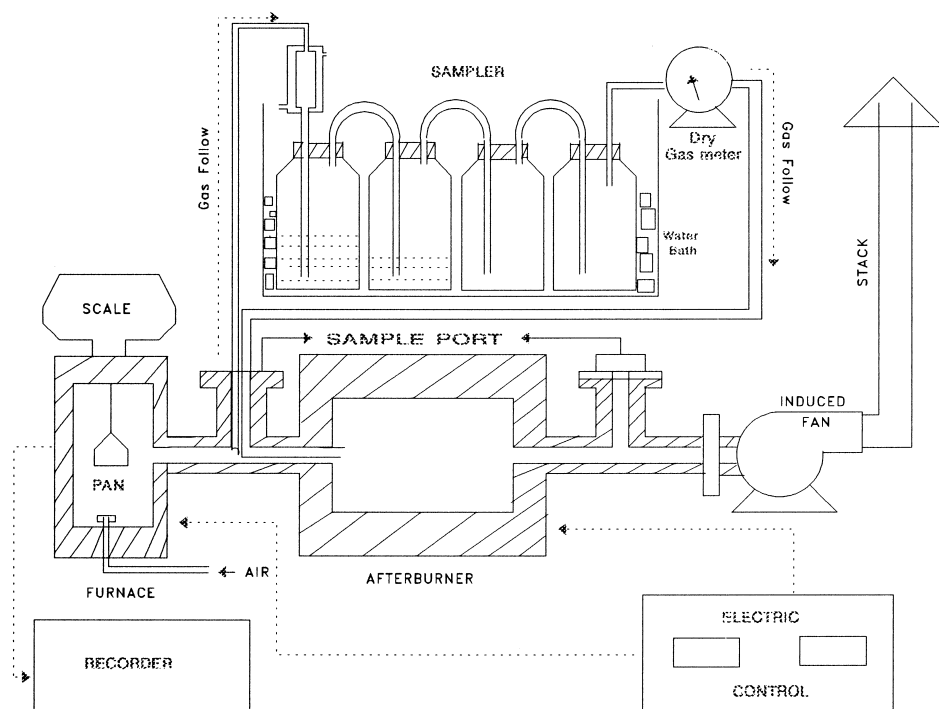


Fig. 1. Shirco laboratory TGA incinerator.

in a pan connected to an electronic balance mounted in an enclosure on top of the furnace. The bottom of the sample pan was made of metal mesh belting. This allowed the diffusion of hot air into and through a burning sample. A temperature profiler controlled the rate of temperature increase to a preset maximum temperature during a burn. While the sample was burned inside the furnace, the emitted gas samples produced were drawn through the sampling duct into the sampling train for the analyses of volatile and semi-volatile gases. A separate temperature profiler control insures that any residuals created in the incinerator and after sample gases were heated to 1000°C in the afterburner for a high degree of efficiency before the hot gases were drawn by the exhaust fan via the building stack into the atmosphere.

1.2. Materials

All solvents used for the study were of optimum grade recommended for pesticide analysis. XAD-2 resin (a styrene–divinylbenzene polymer) was used as a sorbent for the gases produced. The unused 50-lb pesticide bags and the inks used on the bags were supplied by a major agricultural company. The unused bags had 4-ply of kraft paper layers with multi color coating on the outside. The outer layer of the bag consisted of six colors: green, red, white, yellow, black, and blue.

1.3. Sample preparation

One hundred grams of resin were preconditioned by sequential 24 h extraction with methanol, acetone, and twice with methylene chloride. Once the resin was organic free, it was dried while passing pure nitrogen through the resin beds. The conditioned resin was then transferred into colored wide mouth glass containers, sealed, and stored in a cool dark place.

Twenty grams of various parts of the unused colored bags were strategically cut to include a visually representative sample of the bag, and rolled for burning to determine emissions. Twenty-five grams of each colored ink was weighed and stored in a glass crucible for burn analyses to determine emissions.

Modifications were made to Part 3, Chapter 10 of SW-846, 'Standard Operating Procedures of Modified Method 5 (MM-5) and Source Assessment Sampling System Operations Manual' [11]. The detailed modifications and step by step procedures were described in the 'Laboratory Evaluation of PIC Formation During the Burning of Agricultural Insecticide Bags' [12]. The first and second impingers of the MM-5 Train contained deionized distilled water. The third impinger was left empty, and the fourth impinger was filled with 250 g of silica gel.

1.4. Experimental procedure

Each 20 g sample of unused pesticide bag cuts was suspended by a hook from a scale on top of the incinerator. The reading on the scale was taken and the profiler was programmed to burn the sample at 300°C. The emission gases produced were isokinetically drawn through a heated quartz probe via a heated glass fiber particle filter at a temperature above 120°C until the gases reached a condenser mounted on top of the first impinger bottle of the MM-5 sampling train. The temperature of the drawn sample gases was dropped below 20°C by the cool condenser in the MM-5 water bath. The condensate flowed through 25 g of a preconditioned resin bed located below the condenser and collected in the first impinger bottle. The cooled sample gases continued through the preconditioned resin bed and the gases were scrubbed by the resin while contaminants were adsorbed onto the resin. The sample gases continued through two more impinger bottles in the sampling unit and continued to the silica gel where the gases were dried before going through the dry gas meter. Each sample was burned for 30 min. The oven temperature was programmed at a rate of 60°C/min. After 10 min into each run, the oven attained the preset temperature which was maintained until the end of each run. Two sets of gas samples (resin adsorbed and liquid condensate) were collected from each sample burned.

The temperature profiler was programmed to heat the incinerator and the sample pan without a sample to 1000°C for 1 h after each sample burn. This decontaminated the sampling system for other burns. After the system cooled, the glasswares and the quartz probe were washed, dried, and then baked in an oven at 450°C overnight for reuse.

1.5. Analytical procedures

Two analytical extracting techniques were used to isolate the possible organics from the liquid condensate and the resin adsorbed samples. The condensate samples were

extracted with methylene chloride using a liquid–liquid extraction method and the resin adsorbed samples were extracted with methylene chloride using the continuous Soxhlet extraction method.

1.6. Liquid–liquid extraction

The liquid condensate samples were extracted with methylene chloride forming liquid–liquid base/neutral and acid fractions. After separation, samples for the GC/MS were concentrated to 1 ml using the Kuderna Danish concentrator apparatus.

1.7. Soxhlet extraction

The USEPA Method 3540, which outlines the use of methylene chloride as an extracting solvent was used to extract the possible organics. The Soxhlet extraction process was done for 24 h. After the Soxhlet extraction process was completed, the liquid extracts were allowed to cool and were separated into base/neutral and acid fractions. After separation, each sample for the GC/MS was concentrated to 1 ml using the Kuderna Danish concentrator apparatus.

1.8. Instrumentation

The instrument used to analyze the samples was a Hewlett-Packard (HP) gas chromatograph (GC) model 5890 interfaced to a mass spectrometer (MS) model 5971A and driven by a model 7957-B data system of the same company. The mode of ionization was electron impact (EI) with a beam of 70 eV produced by a fine filament inside the ionization chamber of the mass spectrometer. The GC column was an HP-1 (Cross linked methyl silicone gum) 30 m \times 0.53 mm \times 2.65 μ m film thickness fused-silica capillary column (US patent No. 4293415). The oven temperature was programmed from 70°C to 300°C at 20°C/min. Ultra pure helium was used as the carrier gas at a flow rate of 30 ml/min. A 2 μ l sample was injected from a gas-tight syringe and the splitless injection mode was used.

2. Results and discussion

Over twenty-six PICs were tentatively identified when the bag samples were burned at a temperature of 300°C. Four identification procedures were used to select and identify compounds. The identified compounds were compared to library spectra and in some cases with actual sample spectra. Steps used for identification are enumerated below.

(1) The mass spectrum (MS) for each PIC detected was matched with the mass spectra in the National Institutes of Standards and Technology (NIST) library database (NBS49K). The compounds with the best matched spectra were indiscriminately selected.

(2) The second part of the procedure was based on an assumption about the tentative spectra identification of step 1. For example, the chemistry judgement was used to

estimate both the physical and chemical properties of both the tentative and found matches.

(3) Another essential assumption was that the mass fragments which appeared in the spectrum could be explained by a gain or loss of atoms or groups of atoms.

(4) Detected peaks with an intensity of less than 1% relative to the most abundant were not recorded but were considered signals due to frequency distortions in the instrument.

3. Unused bag test burns

Twenty grams sample of an unused colored bag was burned to provide a baseline for the emissions. Listed below are the GC/MS results of compounds identified from gases of an unused bag burned at 300°C. The mass spectra of the NIST library data base was compared with the spectra from the sample. Eleven known compounds from the NIST library matched the sample spectra of the emitted gases. Identified matched samples are given below.

(a) 2-Furancarboxaldehyde (mw 96) was identified at a retention time of 3:09 min. This compound with a molecular ion at a mass to charge ratio of 96 (m/z 96) showed a loss of hydrogen (H) to (m/z 95), a loss of C_2H to (m/z 71); another loss of CHO (m/z 67) and another fragment ion peak at (m/z 57). Sample spectra: 96-95-71-67-57; Library spectra: 96-95-67.

(b) Ethenylbenzene (mw 104) was identified at a retention time of 3:37 min into the GC/MS run. The compound (m/z 104) showed a loss of a hydrogen (H) to 103, a loss of C_2H to (m/z 78); and $C_4H_3^+$ (51). Sample spectra: 104-103-78-77-51; Library spectra: 104-103-78-51.

(c) (2-Furanyl)-1-ethanone (mw 110) was detected at a retention time of 3:96 min. (2-Furanyl)-1-ethanone (m/z 110) exhibited a fragment at (m/z 95), and a loss of CH_3CO to m/z 67. Sample spectra: 110-95-67; Library spectra: 110-95-67.

(d) Benzaldehyde (mw 106) was identified at a retention time of 4:45 min into the GC/MS run. Benzaldehyde (m/z 106) lost H to (m/z 105); $C=O$ to (m/z 77), and finally, a fragment ion at (m/z 51) ($C_4H_3^+$). Sample spectra: 106-105-77-51; Library spectra: 106-105-77-51.

(e) 5-Methyl-2-furancarboxaldehyde (mw 110) was identified at a retention time of 4:62 min and exhibited a loss of a hydrogen atom to (m/z 109); a loss of CHO to (m/z 81), and finally, a loss of C_2H_4 to m/z 53. Sample spectra: 110-109-81-53; Library spectra: 110-109-81-53.

(f) Phenol (mw 94) was identified at a retention time of 5:24 min into the GC/MS run. The compound lost $C=O$ to (m/z 66), hydrogen to (m/z 65), and finally a fragment ion at (m/z 55). Sample spectra: 94-66-65-55; Library spectra: 94-66-65.

(g) 2-Methoxyphenol and 4-Methoxyphenol are basically the same compound except for the position of the OCH_3 (ortho or para). A peak was detected at a retention time of 5:56 min in the GC/MS run with a base peak at (m/z 109). The database library indicated two compounds: 2-methoxyphenol with a base peak at (m/z 124) and 4-methoxyphenol with a base peak at (m/z 109) as a possible match. The detected

compound (mw 124) showed a base peak at (m/z 109) and exhibited a loss of CH_3 to (m/z 109); a loss of CO to (m/z 81), and finally another loss of C_2H_2 to (m/z 55) and a fragment ion at (m/z 53). Sample spectra: 124-109-81-55-53; Library spectra: 124-109-81-53.

(h) 3-Methylphenol (mw 108) was detected at a retention time of 5:98 min into the GC/MS run. 3-Methylphenol eluted late as compared to other compounds with a higher molecular weight. 3-Methylphenol exhibited a loss of H to (m/z 107), a loss of COH to (m/z 79), and other fragments including (m/z 69), (m/z 57), and (m/z 55). Sample spectra: 108-107-97-79-69-57-55; Library spectra: 108-107-90-79-77-53-51.

(i) Naphthalene (mw 128) was identified at a retention time of 6:13 min into the GC/MS run. Naphthalene (m/z 128) showed a loss of C_2H_2 to (m/z 102); a loss of C_2H_3 to (m/z 75) and a fragment ion at (m/z 51). Sample spectra: 128-102-75-51; Library spectra: 128-102-75-51.

(j) 2-Methoxy-4-methylphenol (mw 138) was detected at 6:49 min into the GC/MS run. The compound exhibited a loss of CH_3 to m/z 123, a loss of C=O to (m/z 95); a loss of HOH to (m/z 77), and other fragments including: (m/z 67), (m/z 57), and (m/z 55). Sample spectra: 138-123-95-77-67-57-55; Library spectra: 138-123-95-77-67.

(k) A peak (mw 152) with a retention time of 7:12 min was found in the resin extract. The mass spectrum of the compound shows (m/z 152) with a loss of CH_3 to (m/z 137); a loss of $\text{C}_3\text{H}_4\text{O}$ to (m/z 83); a loss of CH_2 to (m/z 69), and another loss of CH_2 to (m/z 55). The library match suggested one of following compounds:

- 4-Ethyl-2-methoxyphenol 152-137-121-77;
- 2,3-Dihydroxyacetophenone 152-137-83-55;
- 2,4-Dihydroxyacetophenone 152-137-83-55.

Sample spectra: 152-137-83-69-57-55.

4. Green ink test burns

Twenty grams sample of green ink was burned at 300°C in the laboratory incinerator. Fig. 2 shows the structure of a typical green ink and the PIC fragments identified in the emissions of gas produced during incineration. Compounds identified had retention times ranging from 3:09 min to 7:12 min into the GC/MS run. Organic compounds detected from the green ink burned at 300°C and identified by the GC/MS are given below.

(a) 2-Furancarboxaldehyde (mw 96) was identified at a retention time of 3:09 min. The mass spectrum showed a molecular ion at (m/z 96) with a loss of a hydrogen (H) to (m/z 95), a loss of C_2H to (m/z 71); another loss of CHO to (m/z 67) and an additional fragment peak at (m/z 57). Sample spectra: 96-95-67-57; Library spectra: 96-95-67.

(b) Ethenylbenzene (mw 104) was identified at a retention time of 3:37 min into the GC/MS run. The mass spectrum showed a loss of a hydrogen (H) to (m/z 103), a loss of C_2H to (m/z 78); and another loss of C_2H_2 to (m/z 51). Sample spectra: 104-103-78-51; Library spectra: 104-103-78-51.

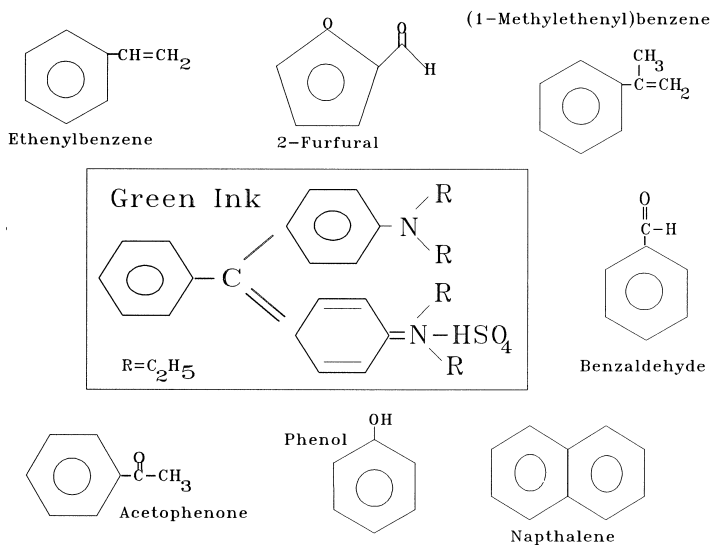


Fig. 2. Green ink with PIC fragments.

(c) (1-Methylethenyl)benzene (mw 118) was identified at a retention time of 4:43 min into the GC/MS run. (1-Methylethenyl)benzene (m/z 118) exhibited the loss of a hydrogen (H) to (m/z 117), a loss of CH₂ to (m/z 103), another loss of C₂H₂ to (m/z 78), and a fragment ion at (m/z 51). Sample spectra: 118-117-103-78-51; Library spectra: 118-117-103-78-51.

(d) Benzaldehyde (mw 106) was identified at a retention time of 4:45 min into the GC/MS run. Benzaldehyde (m/z 106) lost H to (m/z 105); C=O to (m/z 77), and finally, a fragment ion at (m/z 51). Sample spectra: 106-105-77-51; Library spectra: 106-105-77-51.

(e) Phenol (mw 94) was identified at a retention time of 5:24 min into the GC/MS run. The compound lost C=O to (m/z 66), a hydrogen atom to (m/z 65), and finally a fragment ion at (m/z 55). Sample spectra: 94-66-65-55; Library spectra: 94-66-65.

(f) Acetophenone (1-Phenylethanone) with a molecular weight of 120 was detected at a retention time of 5:49 min into the run. The compound (m/z 120) lost CH₃ to (m/z 105), a loss of C=O to (m/z 77), CH₂ to (m/z 63), and a fragment ion at (m/z 51). Sample spectra: 120-105-77-63-51; Library spectra: 120-105-77-63-51.

(g) Naphthalene (mw 128) was identified at a retention time of 6:13 min into the GC/MS run. Naphthalene (m/z 128) showed a loss of C₂H₂ to (m/z 102); a loss of C₂H₃ to (m/z 75) and a fragment ion at (m/z 51). Sample spectra: 128-102-75-51; Library spectra: 128-102-75-51.

(h) 4-Ethyl-2-methoxyphenol, 2,3-Dihydroxyacetophenone, or 2,4-Dihydroxyacetophenone each with a molecular weight of 152 were tentatively identified as possible matches for a compound at a retention time of 7.12 min. The compound (m/z 152) exhibited a loss of CH₃ to (m/z 137); a loss of C₃H₂O to (m/z 83); a loss of

CH_2 to (m/z 69), and another loss of CH_2 to (m/z 55). The library spectra match for these compounds include:

- 4-Ethyl-2-methoxyphenol 152-137-121-77;
- 2,3-Dihydroxyacetophenone 152-137-83-55;
- 2,4-Dihydroxyacetophenone 152-137-83-55.

Sample spectra: 152-137-83-69-57-55

5. Red ink test burns

The two red inks that were used in the bags are calcium and barium red. The main chemical structures of both inks resemble one another except for their anion group. Both inks were azo compounds, characterized by two nitrogen ions joined together by a double bond. One end of the azo linkage was attached to a phenyl substituted ring and the other end was attached to a substituted naphthalene group. Twenty grams sample of each red ink was burned at 300°C separately to test their emissions. Fig. 3 shows the structure of calcium red ink and the PIC fragments identified in the emissions of gas produced during incineration.

Organic compounds tentatively identified from both barium red ink and calcium red ink are the same, which was expected. Eight compounds were detected; six of these were identified by the library match, and two peaks were unmatched with the library database. Compounds detected from the red inks are given below.

(a) Ethenylbenzene (mw 104) was identified at a retention time of 3:37 min into the GC/MS run. The mass spectrum showed a loss of a hydrogen (H) 103, a loss of C_2H to

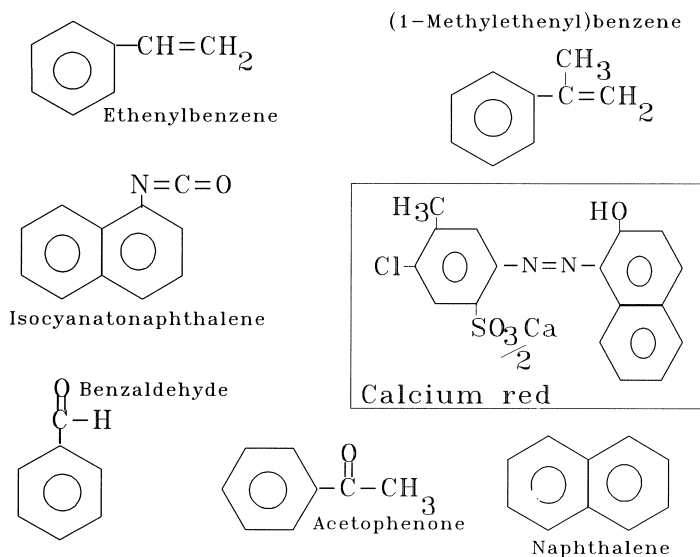


Fig. 3. Red ink with PIC fragments.

m/z 78; a loss of a hydrogen (H) to (m/z 77) and another loss of C_2H_2 to (m/z 51). Sample spectra: 104-103-78-77-57-51; Library spectra: 104-103-78-51.

(b) (1-Methylethenyl)benzene (mw 118) was identified at a retention time of 4:43 min into the GC/MS run. (1-Methylethenyl)benzene (m/z 118) exhibited a loss of a hydrogen (H) to (m/z 117), a loss of CH_2 to (m/z 103), another loss of C_2H_2 to (m/z 78), and a fragment ion at (m/z 51). Sample spectra: 118-117-103-78-51; Library spectra: 118-117-103-78-51.

(c) Benzaldehyde (mw 106) was identified at a retention time of 4:45 min into the GC/MS run. Benzaldehyde (m/z 106) lost H to (m/z 105); C=O to (m/z 77), and finally a fragment ion at (m/z 51) ($C_4H_3^+$). Sample spectra: 106-105-77-51; Library spectra: 106-105-77-51.

(d) Acetophenone (1-Phenylethanone) with a molecular weight of 120 was detected at a retention time of 5:49 min into the run. The compound (m/z 120) lost CH_3 to (m/z 105), C=O to (m/z 77), CH_2 to (m/z 63), and a fragment ion at (m/z 51). Sample spectra: 120-105-77-63-51; Library spectra: 120-105-77-63-51.

(e) Naphthalene (mw 128) was identified at a retention time of 6:13 min into the GC/MS run. Naphthalene (m/z 128) shows a loss of C_2H_2 to (m/z 102); a loss of C_2H_3 to (m/z 75) and a fragment ion (m/z 51). Sample spectra: 128-102-75-57; Library spectra: 128-102-75-57.

(f) Isocyanatonaphthalene (mw 169) was identified as a possible compound at a retention time of 8.80 min into the GC/MS run. The compound (m/z 169) exhibited a loss of CH_3 to (m/z 154), a loss of CH to (m/z 141), a fragment at (m/z 111), loss of N to (m/z 97) and (m/z 83), and a loss of C_2H_4 to (m/z 55). Sample spectra: 169-141-114-113-88; Library spectra: 169-141-114-85-71.

(g) An unknown peak (mw 183) was observed at a retention time of 9:36 min into the GC/MS run. The compound (m/z 183) shows an ion loss to (m/z 169), a loss of a CH_3 fragment to (m/z 154), a loss to (m/z 114), another loss to (m/z 69) and a fragment ion at (m/z 55). Sample spectra: 183-169-154-114-69-55; Library spectra: No match.

(h) Another unknown peak (mw 197) was observed at a retention time of 9:85 min into the GC/MS run. The compound (m/z 197) shows a hydrogen loss to (m/z 196), a loss to (m/z 169), another loss (m/z 114), and a fragment ion at (m/z 55). Sample spectra: 197-196-169-114-97-57; Library spectra: No match.

6. Aquaflex white ink test burns

Twenty grams sample of Aquaflex white ink was burned at 300°C in the laboratory. Fig. 4 shows the structure of Aquaflex white ink fragments identified in the emissions of gas produced during incineration. Compounds identified had retention times ranging from 2.40 min to 8.80 min. Six compounds were detected with two at a lower retention time of less than 3 min. Compounds detected are given below.

(a) At 2.40 min into the GC/MS run, an unidentified peak (mw 73) was detected. The compound (m/z 73) exhibited a loss to (m/z 69), a loss of C to (m/z 57),

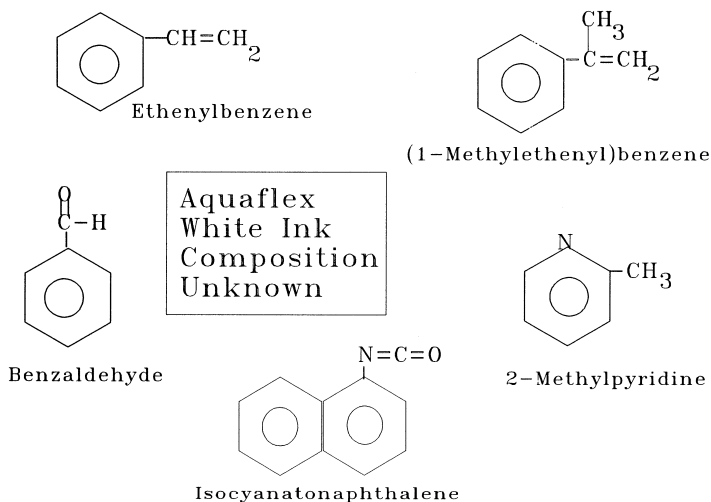


Fig. 4. Aquaflex white ink fragments.

fragments at (m/z 55) and (m/z 51). Sample spectra: 73-69-57-55-51; Library spectra: No match.

(b) 2-Methylpyridine (mw 93) was identified at a retention time of 2.96 min into the GC/MS run. This compound (m/z 93) showed a loss of hydrogen to (m/z 92), a loss of C_2 to (m/z 69), a fragment at (m/z 66), and a loss of C to (m/z 57). Sample spectra: 93-92-83-69-66-57; Library spectra: 93-92-78-66-51.

(c) Ethenylbenzene (mw 104) was identified at a retention time of 3:37 min into the GC/MS run. The mass spectrum showed a loss of a hydrogen (H) to m/z 103, a loss of C_2H to m/z 78; a loss of a hydrogen (H) to (m/z 77), a fragment at (m/z 57), and another loss of C_2H_2 to (m/z 51). Sample spectra: 104-103-78-77-57-51; Library spectra: 104-103-78-77-51.

(d) (1-Methylethenyl)benzene (mw 118) was identified at a retention time of 4:43 min into the GC/MS run. (1-Methylethenyl)benzene (m/z 118) exhibited a loss of a hydrogen (H) to (m/z 117), a loss of CH_2 to (m/z 103), another loss of C_2H_2 to (m/z 78), and a fragment ion at (m/z 51). Sample spectra: 118-117-103-78-51; Library spectra: 118-117-103-78-51.

(e) Benzaldehyde (mw 106) was identified at a retention time of 4:45 min into the GC/MS run. Benzaldehyde (m/z 106) lost hydrogen to (m/z 105), $C=O$ to (m/z 77), and finally a fragment ion at (m/z 51) ($C_4H_3^+$). Sample spectra: 106-105-77-51; Library spectra: 106-105-77-51.

(f) Isocyanatonaphthalene (mw 169) was identified as a possible compound at a retention time of 8.80 min into the GC/MS run. The compound (m/z 169) exhibited a loss of CH_3 to (m/z 154), a loss of CH to (m/z 141), a fragment at (m/z 111), a loss of N to (m/z 97) and (m/z 83), and a loss of C_2H_4 to (m/z 55). Sample spectra: 169-154-141-111-97-83-55; Library spectra: 169-141-114-85-71.

7. Black ink test burns

Twenty grams sample of black ink was burned to test for the emission of PICs produced during combustion. Fig. 5 shows the structure of black ink fragments identified in the emission of gas produced during incineration. Six compounds were identified by the GC/MS analyses. Compounds identified had retention times ranging from 2.94 min to 9:36 min. These tentative compounds are given below.

(a) 2-Methylpyridine (mw 93) was identified at a retention time of 2.96 min into the GC/MS run. This compound (m/z 93) showed a loss of hydrogen to (m/z 92), a loss of C_2 to (m/z 69), a fragment at (m/z 66), and a loss of C to (m/z 57). Sample spectra: 93-92-69-66-65-57-51; Library spectra: 93-92-78-66-51.

(b) Benzaldehyde (mw 106) was identified at a retention time of 4:45 min into the GC/MS run. Benzaldehyde (m/z 106) lost hydrogen to (m/z 105), $C=O$ to (m/z 77), and finally a fragment ion (m/z 51) at ($C_4H_3^+$). Sample spectra: 106-105-77-51; Library spectra: 106-105-77-51.

(c) Acetophenone (1-Phenylethanone) with a molecular weight of 120 was detected at a retention time of 5:49 min into the run. The compound (m/z 120) lost CH_3 to (m/z 105), $C=O$ to (m/z 77), CH_2 to (m/z 63), and a fragment ion at (m/z 51). Sample spectra: 120-105-77-63-51; Library spectra: 120-105-77-63-51.

(d) Isocyanatonaphthalene (mw 169) was identified as a possible compound at a retention time of 8.80 min into the GC/MS run. The compound (m/z 169) exhibited loss of CH_3 to (m/z 154), a loss of CH to (m/z 141), a fragment at (m/z 111), a loss of N to (m/z 97) and (m/z 83), and a loss of C_2H_4 to (m/z 55). Sample spectra: 169-141-111-97-83-55; Library spectra: 169-141-114-85-71.

(e) An unknown peak (mw 183) was observed at a retention time of 9:36 min into the GC/MS run. The compound (m/z 183) showed an ion loss to (m/z 169), a loss of a

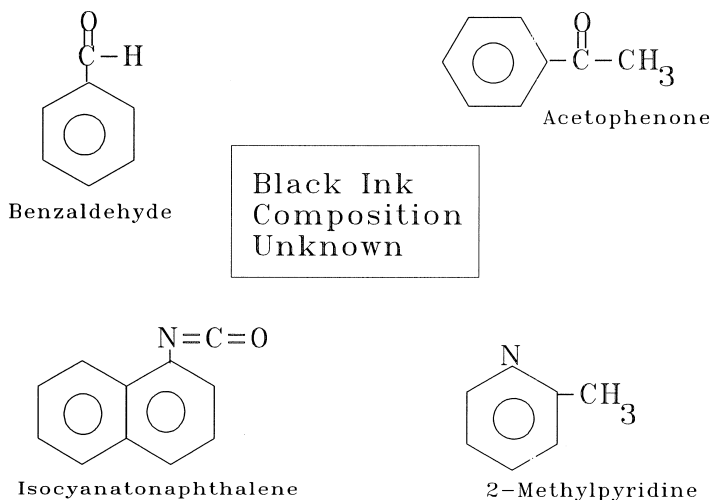


Fig. 5. Black ink fragments.

CH_3 fragment to (m/z 154), a loss to (m/z 114), another loss to (m/z 69) and a fragment ion at (m/z 55). Sample spectra: 183-169-154-114-69-55; Library spectra: No match.

8. Yellow ink test burns

Twenty grams sample of GS Yellow ink was burned at 300°C in the laboratory incinerator to test for the emission of PICs produced during combustion. Fig. 6 shows the structure of GS Yellow ink (Amido Yellow) and the PIC fragments identified in the emissions of gas produced during incineration. Compounds identified had retention times ranging from 2:96 min to 5:49 min into the GC/MS analyses run. Organic compounds detected and identified from the yellow ink burned are given below.

(a) 2-Methylpyridine (mw 93) was tentatively identified at a retention time of 2.96 min into the GC/MS run. This compound (m/z 93) showed a loss of hydrogen to (m/z 92), a loss of C_2 to (m/z 69), a fragment at (m/z 66), and a loss of C to (m/z 57). Sample spectra: 93-92-83-69-66-57; Library spectra: 93-92-78-66-51.

(b) Ethenylbenzene (mw 104) was identified at a retention time of 3:37 min into the GC/MS run. The mass spectrum showed a loss of a hydrogen (H) to m/z 103, a loss of C_2H to m/z 78; a loss of a hydrogen (H) to (m/z 77), a fragment at (m/z 57), and another loss of C_2H_2 to (m/z 51). Sample spectra: 104-103-78-77-57-51; Library spectra: 104-103-78-77-51.

(c) (1-Methylethenyl)benzene (mw 118) was identified at a retention time of 4:43 min into the GC/MS run. (1-Methylethenyl)benzene (m/z 118) exhibited a loss of a hydrogen (H) to (m/z 117), a loss of CH_2 to (m/z 103), another loss of C_2H_2 to (m/z

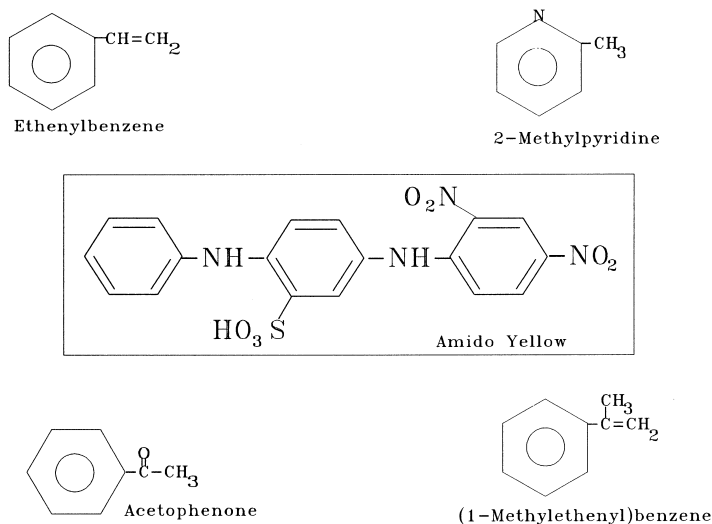


Fig. 6. Yellow ink with PIC fragments.

78), and a fragment ion at (m/z 51). Sample spectra: 118-117-103-78-51; Library spectra: 118-117-103-78-51.

(d) Acetophenone (1-Phenylethanone) with a molecular weight of 120 was detected at a retention time of 5:49 min into the run. The compound (m/z 120) lost CH_3 to (m/z 105), $\text{C}=\text{O}$ to (m/z 77), CH_2 to (m/z 63), and a fragment ion at (m/z 51). Sample spectra: 120-105-77-63-51; Library spectra: 120-105-77-63-51.

9. Blue ink test burns

Twenty grams sample of blue ink was burned at 300°C in the laboratory to test for the emission of PICs produced during combustion. Fig. 7 shows the structure of Alkaline blue ink and the PIC fragments identified in the emission of gas produced during incineration. Compounds identified had retention times ranging from 2.96 min into the GC/MS run to 8.80 min. Four compounds detected are given below.

(a) 2-Methylpyridine (mw 93) was identified at a retention time of 2.96 min into the GC/MS run. This compound (m/z 93) showed a loss of hydrogen to (m/z 92), a loss of C_2 to (m/z 69), a fragment at (m/z 66), and a loss of C to (m/z 57). Sample spectra: 93-92-83-69-66-57; Library spectra: 93-92-78-66-51.

(b) Ethenylbenzene (mw 104) was identified at a retention time of 3:37 min into the GC/MS run. The mass spectrum showed a loss of a hydrogen (H) to (m/z 103), a loss of C_2H to (m/z 78); a loss of a hydrogen (H) to (m/z 77), and another loss of C_2H_2 to (m/z 51). Sample spectra: 104-103-78-77-53-51; Library spectra: 104-103-78-77-51.

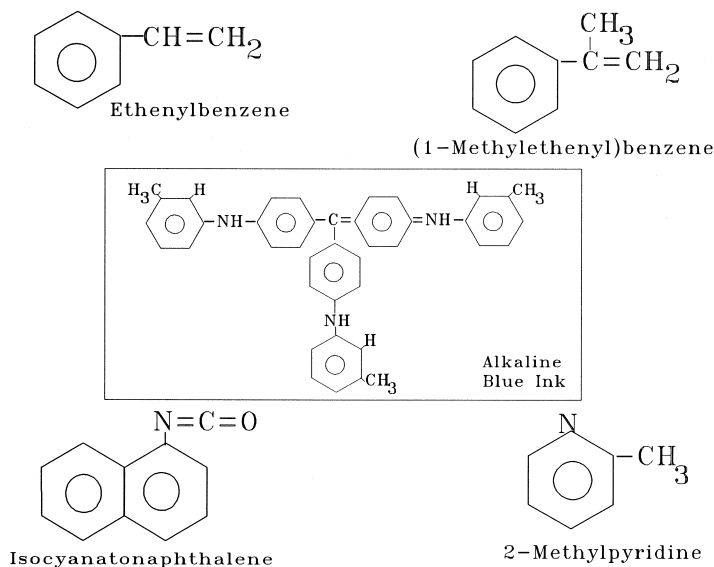


Fig. 7. Blue ink with PIC fragments.

(c) (1-Methylethenyl)benzene (mw 118) was identified at a retention time of 4:43 min into the GC/MS run. (1-Methylethenyl)benzene (m/z 118) exhibited a loss of a hydrogen (H) to (m/z 117), a loss of CH_2 to (m/z 103), another loss of C_2H_2 to (m/z 78), and a fragment ion at (m/z 51). Sample spectra: 118-117-103-78-51; Library spectra: 118-117-103-78-51.

(d) Isocyanatonaphthalene (mw 169) was identified as a possible compound at a retention time of 8.80 min into the GC/MS run. The compound (m/z 169) exhibited a loss of CH_3 to (m/z 154), a loss of CH to (m/z 141), a fragment at (m/z 111), a loss of N to (m/z 97) and (m/z 83), and a loss of C_2H_4 to (m/z 55). Sample spectra: 169-154-141-111-97-83-55; Library spectra: 169-141-114-85-71.

10. Summary

Twelve compounds were identified using the four step identification procedure setup earlier in the study. Table 1 shows a summary of compounds identified, confirmed with actual samples, and traced to their sources of origin during the incineration of unused bags burned at 300°C in the laboratory.

Observations resulting from the study showed that: (a) the same compounds were identified in both the resin and the liquid sample extracts; (b) most compounds found in the bag burns were also identified in the ink burns; (c) some compounds identified from bag burns were not identified from the inks. In the same way, compounds were identified in the ink burns but not the bag burns. This could be due to the relative size of the parent compound being too small in the bag burn experiments.

Specific observations suggested that: (a) green ink was the only source of the 2-furancarboxaldehyde and phenol identified in the bag burns; (b) green and red inks each contributed to the naphthalene identified in the emissions of the bag burns; (c) all inks, except for the black inks, produced ethenylbenzene that contributed to the ethenylbenzene identified in the emissions of the bag burns; (d) all inks tested, except for the yellow and blue inks, contributed to the benzaldehyde identified in the emissions of the bag burns.

A typical temperature profile for waste to energy facility ranges between 420°C to 2012°C and open burning from ambient temperature to 1200°C. Lot of wastes (trash) including colored papers and ink coated materials are burnt in municipal incinerators and waste to energy facilities. In case of a blackout or emergency shutdown in municipal incineration or in open burning situation, there may exist stagnant and cold zone areas

Table 1

Compounds	Colored bags	Green ink	Red ink	White ink	Black ink	Yellow ink	Blue ink
2-Furan-carboxaldehyde	✓	✓					
Ethenylbenzene (Styrene)	✓	✓	✓	✓		✓	✓
Benzaldehyde	✓	✓	✓	✓	✓		
Phenol	✓	✓					
Naphthalene	✓	✓	✓				

where the temperature drops below 300°C. Under these conditions, there is a possibility that PICs similar to the ones identified in this study may be formed.

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