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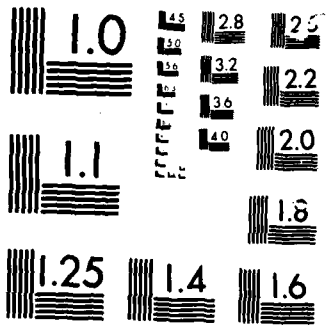

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INVESTIGATION OF THE EFFLUENTS PRODUCED DURING THE FUNCTIONING OF BLACK AND WHITE COLORED SMOKE DEVICES

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The qualitative quantitative analyses on the combustion effluents from black and white colored smoke devices have been completed. Techniques for qualitative identification of the structures from combustion effluents were basically similar to that described in the previous paper. Quantitative analyses were completed by obtaining the smoke settling curve at first. Only the amount of smoke collected within the range of the smoke settling curve plateau was used to calculate the quantities of each combustion product.

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SUMMARY

In a previous publication we reported the sampling techniques, sample preparation, methods of qualitative and quantitative analyses, and structure determination of the combustion effluents from green, yellow, red, and orange colored smoke devices. Recently we have completed the qualitative as well as quantitative analyses on the combustion effluents from black and white colored smoke devices.

Techniques for qualitative identification of the structures from combustion effluents were basically similar to that described in the previous paper. Quantitative analyses were completed by obtaining the smoke settling curve at first. Only the amount of smoke collected within the range of the smoke settling curve plateau was used to calculate the quantities of each combustion product.

Quantification for most of the combustion effluents was accomplished by comparing the areas of HPLC and GC spectra with that of the standard compounds which are commercially available. Others were estimated by total ion counts or single ion monitoring methods using a mass spectrometer with or without internal standards.

I. INTRODUCTION

There are many different types of pyrotechnic devices. These devices contain a wide variety of chemical compositions designed to emit flame, light, sound, heat, smoke, etc. The purpose of this work is to identify and quantify any environmentally hazardous emissions that may be generated during the functioning of colored smoke devices while they are undergoing surveillance testing or other required evaluations.

In previous studies of combustion effluents from colored smokes,[1-8] it was observed that significant amounts of environmentally hazardous materials were generated when the organic dyes used in the compositions were decomposed. The pyrolysis leads to the formation of polycyclic aromatic hydrocarbons (PAH's) and polycyclic organic materials (POM's), some of which are extremely toxic. This report gives the qualitative and quantitative results of the combustion products produced from burning black and white colored smoke devices.

II. EXPERIMENTAL

Smoke Devices and Composition

The typical black colored smoke contains approximately 63% hexachloroethylene (oxidizer and carbon source), 15% magnesium (fuel) and 22% anthracene (cooling and blacken agent). The white colored smoke contains 44% dye (beta chloroanthraquinone), 30% potassium chlorate (oxidizer), 19% sugar (fuel), 3% sodium bicarbonate (cooling agent), and 4% diatomaceous earth (binder).

Modified EPA Method 5 Sampling Train

The modified EPA Method 5 sampling train used was similar to the one described in the previous papers.[5-8] The diagrams of the sampling set-up are shown in Figure 1 and Figure 2.

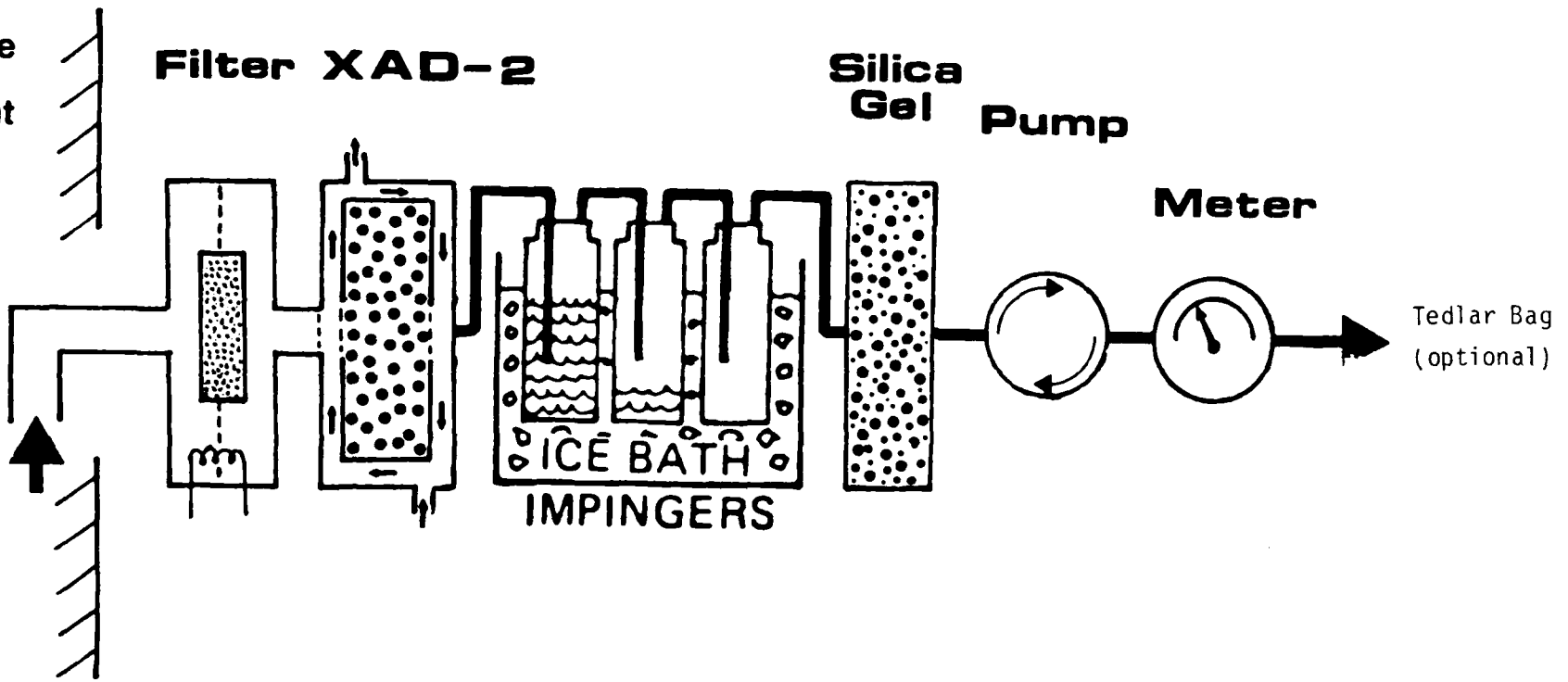

Figure 1. Modified EPA Method 5 Sampling Train

Analytical Procedures

In general, the qualitative analysis procedures were similar to those described in the previous reports.[5-8]. The solid phase samples (particulate) were collected on the 0.3 um thick glass fiber filter paper. The samples were then separated by TLC, HPLC, and analyzed by DuPont DP-102 GC/MS and Nicolet MHz 1000 NMR spectrometer.[9]

The solid phase collected on the glass fiber filter paper was analyzed by EDX (electron dispersive x-ray) analyzer. A tiny solid smoke particle was glued on a silver base plate and scanned by x-ray. Elements with different core electron binding energies would show at different energy positions (e.v.) on the spectrum.

The vapor phase samples (combustion products not absorbed by filter paper) collected in the XAD-2 trap (a styrene-divinylbenzene polymer) were extracted with pre-distilled methylene chloride. The concentrated extracts were analyzed by GC/MS using a 30 meters long glass capillary column, stationary phase - SE54, column head pressure - 30 psi, column end pressure - 0 psi, splitless injection, temperature programmed from 50° to 250°C at 3.5°C/min.

The gaseous phase of the combustion effluents collected in the Tedlar bag was injected directly onto a column (100/120 Carbosieve S, 7 ft x 1/8 in SS) in a Perkin Elmer Sigma 1 Gas Chromatograph with both TCD and FID detectors. Conditions: flow rate of 40 ml/min programmed at 25°C/min from 25°C to 175°C and held for four minutes.

Quantitative Sampling

Quantitative sampling of the black and white colored smoke combustion products was performed under various atmospheric conditions: hot and humid and cold and dry days. Since the settling rate of smoke particles was relatively fast at lower temperatures, on colder days the sampling was done in the first few minutes after a burn was completed. Since the experimentally determined smoke settling curve remained at plateau for about only 15 minutes at 50°F and slightly longer at higher temperature, a faster sampling flow rate (5 liters/minute) was used to assure more accurate collection of smoke effluents.

Quantitative Analysis

Quantification for most of the combustion effluents was accomplished by comparing the areas of HPLC, GC, and GC/MS[10] chromatograms with those of the standard compounds, which are commercially available. Others were estimated by total ion counts or selected ion monitoring methods using a mass spectrometer; or by computer compensation method using nuclear magnetic resonance spectrometer,[9] with or without internal and external standards. When peak area in GC/MS chromatogram was used to measure the quantities of vapor phase samples, a computer program called MC[11] was used to calculate the relative peak area. By comparing with standards, the absolute quantity of each component was obtained. A higher scanning rate (400 amu/sec) was always applied when the selected ion monitoring method of quantitative analysis was used. In general, the ion counts (or total ion counts) of the base peak, molecular ion peak (parent peak) or both were usually selected to compare with the standards.

The computer compensation method for quantification of some of the combustion effluents was accomplished by using the nuclear magnetic resonance spectrometer. The computer program was a great assist in determining trace components and separate overlapping components in multicomponent NMR spectra. Otherwise, an internal standard (CH_3NH_2) was used to quantify some of the combustion products when computer compensation method was not used.

III. RESULTS AND DISCUSSION

The qualitative and quantitative analyses of the combustion effluents produced from burning black and white colored smoke devices have been completed. Results of these studies, including all the combustion species observed and yields, are listed in Tables 1-2, respectively. The toxicity information of most combustion products can be obtained from the available literatures and will not be discussed in this paper. It should be noted that the true toxicity from those smoke products may vary due to the combination effects.

Quantitative Sampling and Smoke Settling Curve

Since the amount of smoke collected after burning the colored smoke directly affected the precision of quantitative analysis, smoke settling curves were established to optimize the flow rate and timing of sampling. In order to have the most accurate collection of smoke products, sampling had been done with the Modified EPA Methods System under various atmospheric conditions: hot and humid days and cold and dry days.

It is apparent that equilibrium is established quickly after a colored smoke completes its burn in that the best percentage recovery of material is obtained at that time. In the summer months, equilibrium of the various compounds will remain relatively constant for the first 20-30 minutes; however, in the winter time, the condensation of the dyes and their products occurs very rapidly. Therefore, we recommend that sampling be done in the first few minutes after a burn is complete in order to collect a more complete sample of the effluents.

TABLE 1. COMBUSTION PRODUCTS FROM BURNING BLACK COLORED SMOKE DEVICE

PROBABLE PRODUCT OR RESIDUE	STATE	Wt. % CONFINED	Toxicity Code
1H-indene	S	0.0050	U
9H-fluorene	S	0.0050	U
Anthracene	S	3.0137	UA1a,UA1e,UA3e,UD5e,pp
Carbon	S	20.0000	1A4a, 1A1a
Carbon Dioxide	G	0.1400	1A4a, 0A3d
Carbon Monoxide	G	0.1400	3B2d
Chlorine	G	0.0020	3A2a
Chlormethylbenzene	L	0.0320	3A2g, 2B3g
Dibenzofuran	S	0.0250	U
Dibenzofuran-9-one	S	0.0045	U
Dichlorobenzene	L	0.0630	2B2a,2B3a
Hexachloroethylene	S	5.0000	2D3e,2D2e,2D1e,2A3h,pp
Hydrogen Chloride	G	0.0030	3A2a,3A4a,3A1b,3B3h
Magnesium Chloride	S	70.3649	1B3g,2B2h
Naphthalene	S	0.0090	2B2h,2B1h,UD2e,pp
Perchlorocyclopropane	S	0.0125	U
Phenanthrene	S	0.0090	UD5e,2B3g,pp
Phenylacetylene	L	0.0100	1B3g
Styrene	L	0.0180	1B4a,1B1a,3B3a
Tetrachloroethene	L	1.0050	2A2a,2A4a,2A1a,UD5e,pp
Toluene	L	0.0200	1A1a,1A4a,1B3h,2B2a,pp
Trichloroacetic Acid	S	0.0180	1A1a,1A4a,1B3a,1A2a

TOXICITY RATING	EXPOSURE	ENTRY ROUTE	EFFECT
U - Unknown	ACUTE	1 - Skin	a - Irritant
0 - None	A - Local	2 - Inhalation	b - Caustic Burn
1 - Low	B - Systemic	3 - Ingestion	c - Blistering
2 - Moderate	CHRONIC	4 - Eye	d - Asphyxia
3 - High	C - Local	5 - Unknown	e - Possible Carcinogen
	D - Systemic		f - None
	NOT GIVEN		g - Unknown
	N		h - Poison
			i - Weakness

pp=Priority pollutant

TABLE 2. COMBUSTION PRODUCTS FROM BURNING
WHITE COLORED SMOKE DEVICE

PROBABLE PRODUCT OR RESIDUE	STATE	Wt. % CONFINED	Toxicity Code
1,2-dimethylbenzene	L	0.0450	3A2a,3A4a,3B3a
1-chloroanthraquinone	S	81.0000	2A4a,1A1a,3B3h
2-chloroanthraquinone	S	1.0000	U
Alkane Hydrocarbons		0.0770	U
Anthracene	S	0.0380	UA1a,UA1e,UA3e,UD5e,pp
Anthraquinone	S	0.0410	1D2a
Benzoic Acid	S	0.0330	2C1a,3D2a
Benzophenone	S	0.0080	2B3a
Biphenylene	S	0.0030	2A1a,2A2a,2B3h
Carbon Dioxide	G	0.1400	1A4a,0A3d
Carbon Monoxide	G	0.0500	3B2d
Chlorine	G	0.0001	3A2a
Diethylphthalate	L	0.0880	3B2a,pp
Hydrogen Chloride	G	0.0017	3A2a,3A4a,3A1b,3B3h
Insolubles (CH_2CL_2)	S	14.0000	U
Naphthalene	S	0.0080	2B2h,2B1h,UD2e,pp
Phenylacetylene	L	0.0110	1B3g
Potassium Chloride	S	2.0000	1B3h,1A4a
Styrene	L	0.0550	1B4a,1B1a,3B3a
Toluene	L	0.0300	1A1a,1A4a,1B3h,2B2a,pp
1-chloro-2,4-dimethylbenzene	L	0.0020	U

TOXICITY RATING	EXPOSURE	ENTRY ROUTE	EFFECT
U - Unknown	ACUTE	1 - Skin	a - Irritant
0 - None	A - Local	2 - Inhalation	b - Caustic Burn
1 - Low	B - Systemic	3 - Ingestion	c - Blistering
2 - Moderate	CHRONIC	4 - Eye	d - Asphyxia
3 - High	C - Local	5 - Unknown	e - Possible Carcinogen
	D - Systemic		f - None
	NOT GIVEN		g - Unknown
	N		h - Poison
pp=Priority pollutant			i - Weakness

Product Identification

The identification of the GC/MS peaks was based on careful comparison of the observed spectra with standards, published or computer stored spectra, and on fundamental interpretation. No standard reference compounds were synthesized in this laboratory for the structure determination.

The directed EDX (electron dispersive x-ray) analysis on the combustion effluents from the white colored smokes collected on the fiber glass filter paper indicated the presence of potassium, sodium, chloride and trace amount of aluminum, lead, silicon and iron. Although carbon may also be one of the products, it cannot be detected by EDX. The black smoke contains copper, lead, silicon, magnesium and chloride.

Vapor phases which could not be caught by the fiber glass filter paper were taken by the Amberlite XAD-2. The XAD-2 is a porous polymer adsorbent used to sample organic vapors in effluents from different kinds of combustion processes. Although a careful clean-up procedure was taken to wash the adsorbents before using, the polymer may still decompose in the presence of oxides of nitrogen which were also present in the combustion effluent streams.

Product Quantification

Assuming that both the detectors and recorders used for analysis yield linear signals, quantitative analyses of gases, liquids, and solids were achieved by total ion counts, selective ion counts, peak areas and peak height measurements techniques. However, to achieve accuracy and precision in quantification, strict adherence to chromatographic operational parameters is essential as well as awareness of error sources attributed to the chromatographic system as a whole. For example, ion count and peak measurements were performed by one or all of the three different ways depending on chromatographic conditions: (1) electronic digital integration where the input signal fed to a voltage-to-frequency converter which generated

an output pulse rate proportional to peak area or ion counts; (2) cutting and weighing the paper obtained for each identified peak; (3) using planimeter to trace the perimeter of each peak.

The precision of results obtained by these integration methods varied with concentration, as did the analysis time required to perform the integration. It should be noted that there was a clear progression both in data-handling time (decrease) and in precision (increase) as we proceeded from manual planimetry to the electronic digital integration technique. Some examples of quantification of combustion effluents were discussed in the Experimental Section.

Since the amount of effluents produced from colored smokes varied from sample to sample, the yields of combustion products have to be reported in terms of ug/g (weight of combustion product/per gram of effluent collected) in order to unify the results. The total yield of any specific combustion species can be calculated by multiplying ug/g and total weight of effluents collected for that specific burn. The advantages of using ug/g as unit of quantification data is that all burn results can be normalized regardless of whether the smoke devices have different explosive weight or the combustion is not or only partially completed.

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