ANALYSIS OF DIESEL ENGINE EXHAUST FOR NON-TARGET POLLUTANTS USING MULTIDIMENSIONAL GC-MS

Richard C. Striebich[1], Karin Straley[1], Brian Gullett[2], Sukh Sidhu[1]

[1]University of Dayton Research Institute, Dayton, OH 45469-0132
[2]U.S.Environmental Protection Agency, Research Triangle Park, NC 27711

Introduction

In recent years, endocrine disrupting chemicals (EDCs) have been linked to problems related to reproduction in wildlife and humans [1]. EDCs can be pharmaceuticals designed to be biologically active (e.g., oral contraceptives) [2], pesticides/herbicides, [3] or environmental contaminants such as polychlorinated biphenyls, nonylphenols or dioxins released into natural systems [4-6]. There has been significant investigation of *in vitro* and *in vivo* studies of the toxicology of EDCs, including the development of a comprehensive screening procedure to detect potential EDCs [7]. Despite these investigations, the extent to which EDCs can negatively impact human and animal health is a subject of debate [8]. Most of these EDC studies to date have focused on commercially available chemicals that are distributed in the environment. We are examining the possibility that combustion processes may be a significant source of EDCs in that combustion by-products are created which may have the same effect as known EDCs.

For the past two decades, numerous studies have been conducted to investigate the origin and formation mechanism of toxic combustion by-products. These studies have shown that known EDCs such as polychlorinated dibenzodioxins and furans (PCDD/Fs), alkyl phenols, phthalates, styrenes, polychlorinated biphenyls (PCBs), and polybrominated biphenyls (PBBs), are present in emissions from various combustion processes [9,10]. Along with these known EDCs, several hundred other chemicals are also present in combustion emissions. The complexity of combustion emissions has resulted in the identification of only a small percentage of the number of chemicals emitted, even though considerable effort has been expended to characterize emissions from some combustion sources [11]. We present here the results of efforts to more completely characterize combustion emissions using Multidimensional Gas Chromatography – Mass Spectrometry (MDGC-MS) analysis of emissions from an idling diesel engine.
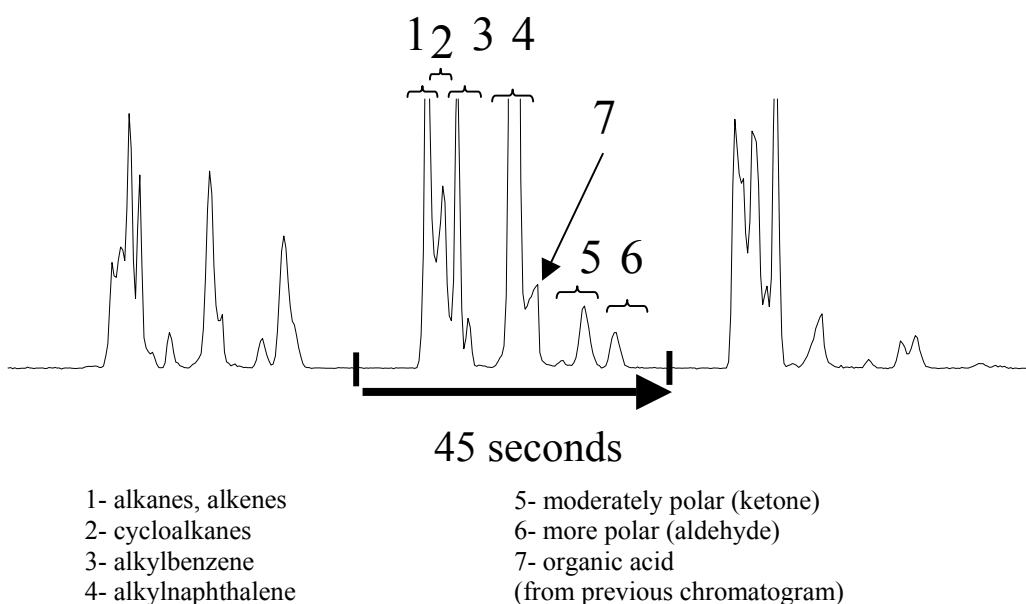
Methods and Materials

An idling diesel engine was operated and emissions were sampled using a filter arrangement and extracted using a Soxhlet apparatus [9] and concentrated. The sample was received for MDGC-MS testing and was not concentrated further. Analyses were performed using conventional GC-MS techniques (scanning mode) and using MDGC-MS. The theory and operation of the MDGC-MS system have been previously described [12]. The general conditions for operating both systems were kept as consistent as possible in order to compare high resolution GC-MS conducted in a traditional way to the dual column MDGC system. Emphasis in data analysis was placed on the more polar compounds which may include oxygen-containing compounds, oxy-PAHs, nitro-PAHs and other aromatics. Automated library searching was conducted for each sample. More than 1000 peaks were observed in the MDGC-MS analysis. Mass spectra for these peaks were searched against existing libraries. Excel spreadsheets were used to sort and classify the products detected.

Results and Discussion

MDGC-MS has, as its primary advantage, a way of separating by polarity those compounds which have similar vapor pressure characteristics and, therefore, would elute together on non-polar columns. In performing this separation, secondary chromatograms are created for each peak width (45 seconds) from the primary column. Therefore, multiple peak separations in the secondary chromatogram would be unseparated in conventional GC-MS as shown in the example in Figure 1.

Figure 1: Three 45-second chromatograms from the secondary column of the MDGC. From one single peak width of the primary chromatogram, more than 7 peaks can now be library-searched.

1- alkanes, alkenes	5- moderately polar (ketone)
2- cycloalkanes	6- more polar (aldehyde)
3- alkylbenzene	7- organic acid
4- alkylnaphthalene	(from previous chromatogram)

Polars from the idle diesel exhaust. Compounds that create toxic effects in screening tests are frequently found among the polar fractions of particular samples being tested. Since the MDGC-MS separates the secondary chromatogram by polarity, polar compounds of interest elute in distinct, definable regions. In the example of Figure 1, the peaks denoted by numbers 5, 6 and 7 are in the region of polar compound elution, typically oxygenates. It is interesting to note that this diesel exhaust sample contains so many components that one peak width from the primary column has (at least in this example) many different polarities of coeluting components in almost every compound class – alkanes, alkenes, cycloalkanes, aromatics, diaromatics, oxygenates and acids. Figure 2 shows a two-dimensional plot of alkanes, aromatics and polars, plotted by primary and secondary retention times. This figure exhibits the MDGC component separation into distinct ranges of polarity, which helps to classify and focus the search for compounds of moderate or high polarity. Compounds eluting before the arrival of alkanes (approximately 15-20 seconds) are actually components of the previous 45-second chromatogram. Thus, with a maximum retention time in the secondary column of 60 seconds, the polar and non-polar compounds may be plotted. The number of polar compounds in this sample was high in comparison to the alkanes. This observation indicates that the engine is efficient in oxidizing (at least to some extent) the great

majority of the compounds. The unburned n-alkanes in this sample are the highest in concentration; however, their toxicity is low and their identity is relatively unimportant. More time can therefore be spent in examination of the aromatic and polar regions.

Figure 2. Two dimensional plot of the idle diesel extract showing the compound class separated saturates (alkanes, alkenes), aromatics and polar components
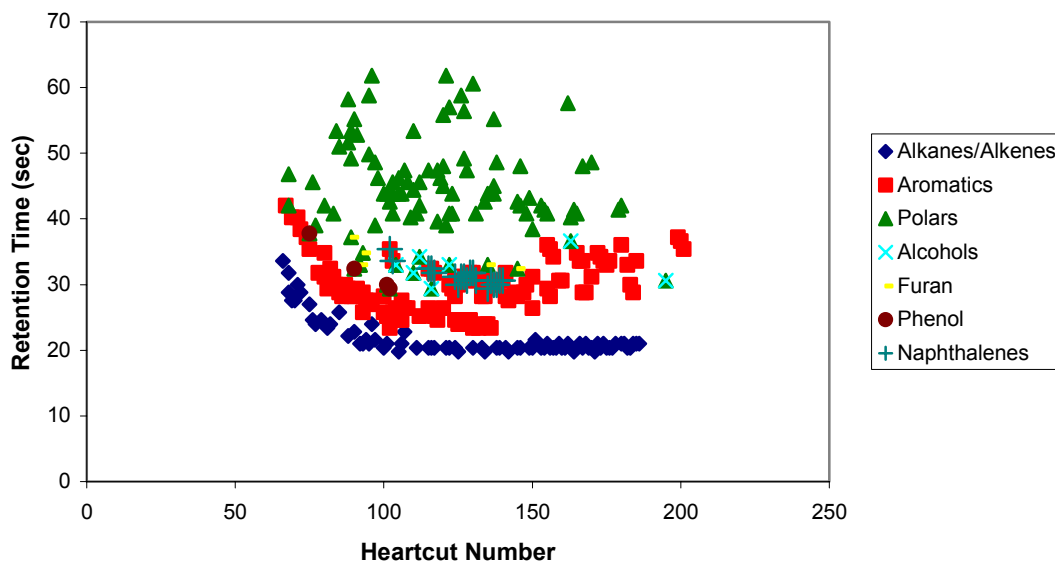
Polar compound identification by automated routines. Because of the enhanced separation provided by the secondary column, automated library search routines provide higher match quality results than conventional techniques. Especially with hydrocarbon matrices such as petroleum, high levels of n-alkanes typically dominate complex spectra in conventional GC-MS, making identification of trace oxygenates (which may have alkane branches in them) almost impossible. For this sample, the threshold for automatic integration was lowered, allowing over 1000 peaks to be integrated from this MDGC-MS chromatogram. Automated library searching was then conducted with background subtraction and the results were filtered such that only match qualities above 60 (out of 100) were retained. At this point, filtering the library search reports by character strings for various indications of compound class was performed: "phenol" for phenols, "ol" for alcohols, "oxy" or "one" for other oxygenates, etc. Using these techniques, the results of analysis of the oxygenates from the diesel idle exhaust are provided in Table 2.

Conclusions
It is possible to tentatively identify trace polar compounds in complex combustion matrices using MDGC-MS with automated library searching. Polar compounds elute in a defined portion of the secondary chromatogram and, due to better separation by MDGC-MS, library searching gives higher match qualities. Polars and oxygenates in diesel exhaust were easily separated from major hydrocarbon components. Work is continuing to identify unknown polars which may be EDCs.

Table 2: Polar components* tentatively identified in diesel exhaust by MDGC-MS.

polar classification	# identified with match quality > 60	Example compounds from this class	Match quality
ketones	40	Acenaphthenone	72
		Xanthone	83
		Anthrone	90
acids	12	Benzoic Acid	90
		Salicylic Acid	91
		Hexanedioic acid, dioctyl ester $$	64
hydroxy / alcohol	25	2-Hydroxy-3-methylbenzaldehyde	94
		o-Hydroxybiphenyl	86
		Benzaldehyde, 2-hydroxy-	96
phthalates	1	Bis(2-ethylhexyl) phthalate	83
phenols	9	Phenol	90
		Phenol, 2-nitro-	64
		Phenol, 4-ethyl-	83
aldehydes	30	Benzaldehyde	91
		Benzaldehyde, 4-ethyl-	68
		9-Anthracenecarboxaldehyde	72
alkyl-naphthalenes	51	Naphthalene, 1-methyl-	91
		1-Naphthalenol	90
		Naphthalene, 2,3,6-trimethyl-	97
nitrogen-containing	9	2-Nitro-1-naphthol $$ 1-Naphthalen	89
		Phenol, 3-nitro-	72
		Benzenamine, 4-methoxy-N-(2-pyridi	64

Number of compounds integrated: 1091
Number of identifications with Match Quality greater than 60: 483
* Polars identified include naphthalenes and decalins (decahydronaphthalene)

References
1. Colborn, T., Vom Saal, F. S., and Soto, A.M., *Environ. Health Perspect.*, **1993**, 101, 378.
2. R. Siegener and R.F. Chen, in *Analysis of Environmental Endrocrine Disruptors*, **2000**, ACS Symposium Series 747, 125-132.
3. Colborn, T*., Arctic Res. U S*, **1994**, 8, 220-223.
4. Routledge, E.J., Parker, J., Odum, J.,Ashby, J.,and Sumpter, J.P., *Toxicol. Appl. Pharmacol*., **1998**, 153, 12-19.
5. Steinmetz, R, Brown, N.G., Allen, D.L., Bigsby, R.M. and Ben-Jonathan, N., *Endocrinology,* **1997***,*138, 1780-1786.
6. Crews, D., Bergeron, J.M., McLachlan, J.A., *Environ. Health Perspect*., 1995, 103, 73.
7. Zacharewski, T., *Environ. Sci. Technol.*, **1997**, 31, 613.
8. Matthiessen, P.,*Ecotoxicology*, 2000, 9, 21-24.
9. Gullett, B.K., and Ryan J.V., *Environ. Sci. Technol*., **2002**, 36, 3036-3040.
10. Sidhu, S.S., Maqsud, L., and Dellinger, B., *Combustion and Flame*, **1995,** 100, 11.
11. Rogge, W.F., Hildemann, L.M., Mazurek, M.A., and Cass, G.R., ***Environ. Sci. Technol.,*** **1993**, 27, 636-661.
12. Striebich, R.C., Klosterman, J.R., Rubey, W.A., *Waste Management*, **2002**, 22, 413-420.