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MOLECULAR FINGERPRINTING OF GASOLINE BY A MODIFIED EPA 8260 GAS CHROMATOGRAPHY-MASS SPECTROMETRY METHOD

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Automotive gasoline is a common petroleum product found at contaminated terrestrial sites. The need to recognize and distinguish different types of gasoline(s) that may be present at a contaminated site and the need to determine the relative proportion of inputs from different sources, are often critical components of environmental 'forensic' investigations. Historically, identification and differentiation of automotive gasolines (particularly when weathered) has been hampered by analytical limitations of existing methods, notably US EPA Method 8260. In this article, we describe a modified EPA Method 8260 that is suitable for environmental investigations involving gasoline (and other light petroleum products). In the modified EPA 8260 method, 109 analytes that can occur in automotive gasoline are quantified in nonaqueous liquid samples (NAPL), water, and soil matrices. The accuracy and precision of the method is demonstrated through comparative analysis using several NIST SRM gasoline standards and replicate analyses.

Keywords: Hydrocarbon analysis; Oxygenates; NAPL; Groundwater; Soil

INTRODUCTION

Automotive gasolines are complex fuels blended from a variety of intermediate refinery streams, each with different physical and chemical properties (Table I). Historic gasolines were blended primarily to achieve physical specifications for boiling range, vapor pressure, oxidation stability, and octane with the goal being suitable engine performance, namely cold/hot starts, acceleration, knock, resistance to vapor lock, etc. How these physical specifications were achieved was largely left up to the individual refiners. Consequently, historic gasoline compositions were quite variable in chemical composition in both a temporal and spatial sense.

Modern reformulated and oxygenated gasolines must now meet stricter physical and chemical specifications. The latter include restrictions on the content of olefins, sulfur, benzene, total aromatic hydrocarbons, and oxygen. These stricter specifications have

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TABLE I Inventory of common gasoline blending stocks used in the production of modern automotive gasolines

Blending stock	General characteristics			
	Octane	Chemistry	Boiling range	RVP
Oxygenates	high	ethers–alcohols	low	low
Reformates	high	high aromatics	full	low
Isomerates	high	high isoparaffins	low	high
Alkylates	high	paraffinic	full	low
Light cat gasoline	high	high olefins	full	mid
Heavy cat gasoline	high	high aromatics	high	low
Light uncrackate	mid	high isoparaffins	low	high
Light medium uncrackate	low	paraffinic	high	low
<i>n</i> -butane	high	paraffinic	very low	very high
C5s and C6s	low	paraffinic	low	high
Mixed C5s	mid	paraffinic	low	high

reduced the compositional variability that had existed within the gasoline pool, yet nonetheless, on a molecular level chemical differences between different ‘types’ of gasolines persist. Different types of gasoline will exhibit chemical differences that are not attributable to environmental weathering. These can include different gasoline grades (e.g., relative abundance of octane boosters), different refining characteristics (e.g., presence/absence of olefins), and/or different additives (e.g., lead alkyls, MTBE), etc.

Because releases of automotive gasolines from leaking underground storage tanks (UST) into the environment have been a persistent environmental problem, environmental ‘forensic’ investigations often attempt to recognize the presence/absence of particular gasoline ‘types’. Recognition of multiple types of gasoline in a study area provides evidence that multiple releases had occurred (while the opposite is not necessarily true). Sometimes this information, in combination with historical records, geology, and hydrogeology, can be used to assess the source(s) or age(s) of this contamination, two common objectives of forensic investigations. Regardless of the objective of an investigation, any defensible assessment of the type(s) of gasoline contamination at a given site requires, at its heart, detailed molecular characterization of the contamination.

Widely accepted analytical methods for the molecular characterization of contamination derived from automotive gasoline have relied upon high-resolution capillary gas chromatography. The standard method adopted by the compliance-driven US Environmental Protection Agency (EPA) for the characterization of volatile organic compounds in solid wastes, SW-846 Method 8260 (*Volatile Organic Compounds by Gas Chromatography-Mass Spectrometry*) [1], provides inadequate detail in the characterization of gasolines. For example, EPA Method 8260 includes only eight hydrocarbons among the target analytes, namely benzene, toluene, ethylbenzene, *m*-, *p*-, and *o*-xylene, styrene, and naphthalene. Similarly, EPA Method 8021 (*Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors*) [1] targets only the BTEX compounds (benzene, toluene, ethylbenzene and the sum of *o*-, *m*-, and *p*-xylenes). However, gasoline contains hundreds more hydrocarbons than these few aromatic compounds [2,3]. Alone, these few BTEX aromatic compounds are of limited use in forensic investigations requiring detailed fingerprinting of gasoline due to their ubiquity

in different types of gasoline. Thus, existing US EPA Methods are generally inadequate to provide the level of molecular characterization necessary in 'fingerprinting' gasolines in environmental matrices.

The American Society for Testing and Materials (ASTM) methods for the characterization of finished automotive gasolines are focused on physical properties (distillation, vapor pressure, oxidation stability, density, etc.), performance properties (research and motor octane, vapor-liquid ratio), or specific additives, compounds, elements, or compound classes (e.g., sulfur, lead, phosphorous, benzene, manganese, C₂-C₅ hydrocarbons, oxygenates, total olefins, total aromatics, etc.) [4]. While the presence/absence of specific compounds-additives can be useful in environmental forensic investigations [5], the ASTM methods, which are only applicable on liquid petroleum samples, generally are too focused on specific compounds (as might occur in fresh gasolines) to provide a comprehensive assessment of gasoline-derived contamination in environmental matrices.

Environmental forensic investigators previously have recognized the shortcomings of the existing EPA and ASTM methods in distinguishing gasoline types [6-8]. Thus, there has been the need to modify or develop new analytical methods that provide the degree of molecular detail necessary to address most forensic objectives. In this article, a modified EPA Method 8260 for the detailed molecular characterization of gasoline-derived contamination using purge-and-trap gas chromatography-mass spectrometry (PT-GC-MS) analysis is presented.

Data are presented to demonstrate the utility of the modified Method 8260 in establishing detailed molecular characteristics of gasoline-derived compounds in environmental matrices.

Developing an Appropriate Target Analyte List

The most obvious modification to the EPA Method 8260 that is necessary is a revision in the target analyte list. As noted above, gasoline contains only a handful of the target analytes listed under EPA Method 8260. Therefore, the development of a more comprehensive target analyte list that is based on the actual composition of gasoline was first necessary.

Gasoline contains hundreds of chemical compounds that include both hydrocarbons and nonhydrocarbons [9]. The hydrocarbons that are present in gasoline occur within five compound classes: *Paraffins*, *Isoparaffins*, *Aromatics*, *Naphthenes*, and *Olefins* – often referred to by the acronym 'PIANO'. The major nonhydrocarbon classes in gasolines can include oxygen-containing ethers (e.g., methyl-*tert*-butyl ether, *tert*-amyl-methyl ether, etc.) [10], alcohols (e.g., *tert*-butyl alcohol, methanol, ethanol, isopropyl alcohol) [10], sulfur- (e.g., mercaptans, thiophenes, disulfides, thiolanes, thlanes) [11-13], and nitrogen-containing moieties (e.g., pyrroles, indoles, anilines, etc.) [14].

Each of these compound classes can be of use to the forensic investigator so long as sufficient detail surrounding the individual chemicals within each compound class is obtained. However, as noted above, gasoline is an extremely complex mixture of hundreds of compounds; for example, Whittmore (1979) resolved and identified 361 individual compounds in gasoline using an analysis run time of just over 4 h [15]. While this degree of resolution and identification may be possible, it is not practical in most laboratory situations and probably not necessary for forensic applications of

these data. Therefore, the selection of which compounds are practically achievable and necessary for forensic investigations warrants consideration and, in our opinion, depends on several factors. Certainly, an important factor is that the target compounds collectively comprise a significant mass of most gasolines. Therefore, all of the major compounds that are normally present in gasolines should be included in an appropriate target analyte list. In developing our target analyte list some guidance on what was 'normally present' was obtained from a review of the fuel [2,3,15,16] and environmental forensic literature [17,18].

The relative abundance of a compound, however, was not the only prerequisite for selecting target analytes since some very minor compounds can reveal important diagnostic features concerning the nature of gasoline. For example, olefins are generally in low relative abundance in gasolines, but their presence indicates that a thermally- or catalytically-cracked blending stock was used in production of gasoline [19]. Similarly, most sulfur-containing compounds are also not abundant in most gasolines (generally < 0.03% sulfur) [20], yet their presence can be important in distinguishing gasoline refined from high-sulfur (sour) crude oil feedstocks and/or use of a fluid cat-cracked naphtha blending stock [11]. Finally, the relative proportions of various minor isoalkanes, not just the major isoalkane (2,2,4-trimethylpentane a.k.a. isooctane), can reveal differences in the nature of the alkylate blending stock used in the production of gasoline [9]. Therefore, some target analytes were included with the specific intention of recognizing peculiarities that may be inherited from refinery processes that may be useful in forensic investigations.

The selection of target compounds also considered the approximate boiling range, with the intention being to have representatives of the hydrocarbon compound classes spanning as wide a boiling range as possible. This was particularly important if the method would be used to study weathered gasoline samples, in which the most volatile compounds might be reduced or absent.

Because of their utility in distinguishing gasoline types [21], those gasoline additives that were amenable to study by the modified EPA 8260 Method were also considered as target analytes. These included the oxygenate additives (alcohols and ethers) used in oxygenated gasolines, lead scavengers (1,2-dichloroethane and 1,2-dibromoethane) [10], and methylcyclopentadienyl manganese tricarbonyl (MMT).

Finally, prerequisites to the target analytes included their availability as authentic standards and their ability to be quantitatively purged and recovered using the 8260 M method (described below). The availability of standards was necessary in order to both (1) confirm the identification of individual compounds in authentic samples via mass spectral and retention time matches and (2) develop response factors for each target analyte that could be used in the quantitative measurement in authentic samples. Some compounds, e.g., alkyl lead compounds, simply could not be purged effectively and therefore were not included among target analytes for this method.

Given the considerations and prerequisites discussed above, we developed a suite of 109 target analytes that is the basis of our modified 8260 M target analyte list for automotive gasolines and other light distillates (Table II). The target analyte list includes representatives from the five hydrocarbon compound classes (PIANO) as well as selected oxygen- and sulfur-containing analytes. The oxygenated compounds include five ethers that have been used in gasoline, as well as the alcohol TBA. Methanol, ethanol, and isopropyl alcohol were not included due to the difficulty of purging these compounds and other analytical constraints, particularly with water

TABLE II Target analytes and their associated mass spectral quantification ions and reporting limits (RL) currently used in the characterization of gasoline in environmental samples

Pk #	Compound name	Compound class	Quantification ion m/z	Confirmation ion m/z	Reporting limits		
					Product mg/kg	Soil µg/kg	Water µg/L
1	Isopentane	I	43	57	58	1.16	0.29
2	1-Pentene	O	42	52	145	2.89	0.72
3	2-Methyl-1-butene	O	55	42	45	0.91	0.23
4	<i>n</i> -C5 (pentane)	P	43	57	191	3.83	0.96
5	<i>trans</i> -2-Pentene	O	55	42	38	0.77	0.19
6	<i>cis</i> -2-Pentene	O	55	42	54	1.09	0.27
7	2,2-Dimethylbutane	I	57	71	193	3.86	0.97
8	<i>t</i> -Butanol	OX	59	41	1,965	39.30	9.83
9	Cyclopentane	N	42	55	151	3.02	0.75
10	Methyl- <i>tert</i> -butyl ether	OX	73	43	207	4.14	1.04
11	2-Methylpentane	I	43	71	67	1.34	0.33
12	3-Methylpentane	I	57	56	68	1.36	0.34
13	1-Hexene	O	56	41	250	5.00	1.25
14	<i>n</i> -C6 (hexane)	P	57	43	170	3.41	0.85
15	Di-isopropyl ether	OX	45	87	203	4.06	1.02
16	<i>trans</i> -2-Hexene	O	55	84	32	0.64	0.16
17	2-Methylpentene-2	O	69	41	135	2.70	0.67
18	<i>cis</i> -2-Hexene	O	55	84	133	2.66	0.67
19	Ethyl- <i>tert</i> -butyl ether	OX	59	87	208	4.16	1.04
20	2,2-Dimethylpentane	I	57	85	70	1.40	0.35
21	1,2-Dichloroethane	ADD	62	64	200	4.00	1.00
22	Methylcyclopentane	N	56	42	230	4.60	1.15
23	2,4-Dimethylpentane	I	43	57	137	2.74	0.69
24	Benzene	A	78	-	257	5.13	1.28
25	Thiophene	S	84	58	210	4.20	1.05
26	Cyclohexane	N	56	84	238	4.76	1.19
27	2-Methylhexane	I	43	85	127	2.54	0.63
28	2,3-Dimethylpentane	I	56	43	68	1.36	0.34
29	<i>Tert</i> -amyl-methyl ether	OX	73	43	200	4.00	1.00
30	3-Methylhexane	I	43	57	72	1.44	0.36
31	2-Methyl-1-hexene	O	56	41	155	3.09	0.77
32	2,2,4-Trimethylpentane	I	57	41	208	4.15	1.04
33	<i>trans</i> -3-Heptene	O	41	56	136	2.71	0.68
34	<i>n</i> -C7 (heptane)	P	43	57	202	4.04	1.01
35	<i>cis</i> -3-Heptene	O	41	56	138	2.76	0.69
36	<i>trans</i> -2-Heptene	O	55	56	138	2.76	0.69
37	<i>cis</i> -2-Heptene	O	56	41	218	4.35	1.09
38	Methylcyclohexane	N	83	55	238	4.75	1.19
39	2,4-Dimethylhexane	I	43	57	76	1.51	0.38
40	<i>ctc</i> -1,2,4-Trimethylcyclopentane	N	70	55	58	1.15	0.29
41	<i>ctc</i> -1,2,3-Trimethylcyclopentane	N	70	55	71	1.42	0.36
42	2,3,4-Trimethylpentane	I	43	71	216	4.31	1.08
43	Toluene	A	91	92	159	3.18	0.79
44	2,3,3-Trimethylpentane	I	43	71	218	4.36	1.09
45	2-Methylthiophene	S	97	98	203	4.06	1.01
46	2,3-Dimethylhexane	I	43	70	78	1.56	0.39
47	3-Methylthiophene	S	97	98	203	4.06	1.02
48	2-Methylheptane	I	43	57	202	4.04	1.01
49	1,2-Dibromoethane (EDB)	ADD	107	109	200	4.00	1.00
50	1-Octene	O	55	41	285	5.69	1.42
51	2,2-Dimethylheptane	I	57	56	213	4.27	1.07
52	<i>trans</i> -2-Octene	O	55	41	71	1.42	0.35
53	Isopropylcyclopentane	N	68	69	164	3.27	0.82
54	<i>cis</i> -2-Octene	O	55	41	145	2.89	0.72

(continued)

TABLE II Continued

Pk #	Compound name	Compound class	Quantification ion <i>m/z</i>	Confirmation ion <i>m/z</i>	Reporting limits		
					Product mg/kg	Soil µg/kg	Water µg/L
55	2,2,4-Trimethylhexane	I	57	56	215	4.30	1.07
56	2,4-Dimethylheptane	I	43	85	215	4.29	1.07
57	1,1,4-Trimethylcyclohexane	N	111	69	149	2.98	0.75
58	Ethylcyclohexane	N	83	55	200	4.01	1.00
59	2,6-Dimethylheptane	I	43	57	213	4.25	1.06
60	<i>n</i> -C8 (octane)	P	43	57	211	4.22	1.05
61	Ethylbenzene	A	91	106	238	4.77	1.19
62	2-Ethylthiophene	S	97	112	198	3.96	0.99
63	<i>ctt</i> -1,2,4-Trimethylcyclohexane	N	111	69	88	1.77	0.44
64	<i>m</i> -Xylene	A	91	106	78	1.55	0.39
65	<i>p</i> -Xylene	A	91	106	158	3.15	0.79
66	2,3-Dimethylheptane	I	43	41	75	1.50	0.37
67	4-Methyloctane	I	43	85	216	4.32	1.08
68	2-Methyloctane	I	43	57	147	2.93	0.73
69	<i>ctc</i> -1,2,4-Trimethylcyclohexane	N	69	111	48	0.97	0.24
70	1,1,2-Trimethylcyclohexane	N	69	111	97	1.94	0.48
71	<i>o</i> -Xylene	A	91	106	79	1.57	0.39
72	1-Nonene	O	56	41	283	5.65	1.41
73	<i>trans</i> -3-Nonene	O	55	41	73	1.45	0.36
74	<i>cis</i> -3-Nonene	O	55	41	145	2.90	0.73
75	<i>n</i> -C9 (nonane)	P	43	57	196	3.93	0.98
76	<i>trans</i> -2-Nonene	O	55	41	72	1.44	0.36
77	Isopropylbenzene	A	105	120	71	1.41	0.35
78	<i>cis</i> -2-Nonene	O	55	41	145	2.90	0.73
79	Isopropylcyclohexane	N	83	82	234	4.67	1.17
80	2,2-Dimethyloctane	I	57	56	158	3.16	0.79
81	<i>n</i> -Butylcyclopentane	N	69	55	150	3.01	0.75
82	3,3-Dimethyloctane	I	71	43	161	3.22	0.80
83	Propylbenzene	A	91	120	157	3.15	0.79
84	1-Methyl-3-ethylbenzene	A	105	120	77	1.53	0.38
85	1-Methyl-4-ethylbenzene	A	105	120	79	1.57	0.39
86	1,3,5-Trimethylbenzene	A	105	120	36	0.73	0.18
87	1-Methyl-2-ethylbenzene	A	105	120	78	1.56	0.39
88	3-Methylnonane	I	57	71	242	4.83	1.21
89	1,2,4-Trimethylbenzene	A	105	120	78	1.57	0.39
90	1-Decene	O	41	55	299	5.98	1.50
91	<i>sec</i> -Butylbenzene	A	105	134	76	1.53	0.38
92	<i>n</i> -C10 (decane)	P	43	57	215	4.31	1.08
93	1,2,3-Trimethylbenzene	A	105	120	215	4.29	1.07
94	Indane (indan)	A	117	118	231	4.63	1.16
95	1,3-Diethylbenzene	A	105	119	207	4.15	1.04
96	1,4-Diethylbenzene	A	105	119	172	3.45	0.86
97	1,3-Dimethyl-5-ethylbenzene	A	119	134	37	0.74	0.18
98	1,2-Diethylbenzene	A	105	119	38	0.75	0.19
99	1-Methyl-2- <i>n</i> -propylbenzene	A	105	134	83	1.67	0.42
100	1,2-Dimethyl-4-ethylbenzene	A	119	134	79	1.58	0.39
101	1,3-Dimethyl-2-ethylbenzene	A	119	134	38	0.76	0.19
102	<i>n</i> -C11 (undecane)	P	57	43	217	4.34	1.08
103	1,2,4,5-Tetramethylbenzene	A	119	134	15	0.31	0.08
104	1,2,3,5-Tetramethylbenzene	A	119	134	201	4.03	1.01
105	1,2,3,4-Tetramethylbenzene	A	119	134	200	4.01	1.00
106	<i>n</i> -Pentylbenzene	A	91	148	148	2.96	0.74
107	MMT	ADD	120	55	201	4.01	1.00
108	Benzothiophene	S	134	147	230	4.60	1.15
109	<i>n</i> -C12 (dodecane)	P	43	57	179	3.58	0.89

(continued)

TABLE II Continued

Internal Standards			
Benzene- <i>d</i> ₆	RIS	84	56
Toluene- <i>d</i> ₈	RIS	98	70
Ethylbenzene- <i>d</i> ₁₀	RIS	98	106
1,4-Difluorobenzene	RIS	114	
Chlorobenzene- <i>d</i> ₅	SIS	117	82
1,4-Dichlorobenzene- <i>d</i> ₄	SIS	150	152

Reporting Limit = (concentration of analyte in lowest calibration level)/normal sample weight; Normal Sample Weight Assumptions: product 0.1 mg; soil 5 g; water 20 mL.

TABLE III Quality control and data quality objectives used in the modified EPA 8250 method

<i>QC type-parameter</i>	<i>DQO targets</i>
Procedural blank	< 5 × Reporting limit
Surrogate control sample	50–130%
Laboratory control sample	50–130%
Sample triplicate	< 35 % Relative standard deviation
<i>Instrument calibrations</i>	
Initial (minimum of 5-point)	% RSD for each analyte < 25% each RF, average RF < 15%
Continuing calibration check (bracketing samples every 12 h)	RF for each analyte < 25% difference from average RF for 90% of analytes

matrices. Sulfur compounds include various C₀–C₁ thiophenes and benzothiophene. The utility of nitrogen-containing compounds has not been evaluated in forensic applications and therefore, no nitrogen moieties were included.

The 8260 M target analyte list that we have been utilizing (Table II) is not intended to be all inclusive or ‘fixed’. Analytes can be added or removed from the list if sufficient reason exists to do so. We envision this suite of target analytes is both useful and practically achievable, and therefore provides a good first step in the characterization of environmental samples impacted by volatile petroleum products.

Description of Modified EPA Method 8260

While the revised analyte list (Table II) is the primary modification to EPA Method 8260, other modifications to the EPA Method 8260 involving instrumentation (or software) are minimal (Table III). Analysis is performed on a Hewlett-Packard 5890 programmable gas chromatograph (GC) with flows controlled by an electronic pneumatic control (EPC) system. The detector used is a Hewlett-Packard 5972 Mass Selective Detector (MS). Sample introduction is accomplished using a Tekmar Precept II robotic autosampler and Tekmar 3100 liquid concentrator system (LCS). System control and data acquisition was performed by the integration of both Hewlett-Packard Enviroquant[®] software (Version 3.0) and Tekmar Teklink[®] software (Version 5.0). Data analysis and reduction is performed on the Hewlett-Packard Enviroquant[®] software.

The GC is configured using the capillary split/splitless injection port with a direct interface to the LCS for sample introduction. The injection port is capped with a Merlin Microseal[®] septa and housed a 2 mm splitless glass liner (Restek). The GC is

outfitted with a 50 m, RTX-1 PONA[®] 50 m, 0.32 i.d., 0.5 μ m film thickness fused silica capillary column (Restek) with a direct interface to the MS. The GC-MS conditions employed are as follows:

Initial column temperature:	35°C
Initial hold time:	15 min
Program rate 1:	2°C/min
Final temperature:	120°C
Hold time:	0 min
Program rate 2:	15°C/min
Final temperature:	220°C
Final hold time:	10 min
Injector temperature:	220°C
Column flow rate:	~1 mL/min (helium)
Detector temperature:	280°C
MS scan parameters:	Full Scan Mode; range 35–350 <i>m/z</i>

The autosampler and LCS units are directly interfaced to the injection port of the GC. The autosampler and LCS units are designed to strip the sample of volatile analytes by purging with a fine stream of helium. The volatiles and purge gas are then passed through a VOCARB 3000[®] (Carbopack B/Carboxen 1000 & 1001) sorbent trap within the LCS, which is designed to absorb a broad range of volatile compounds. The instrumental conditions for the LCS are as follows:

Purge temperature:	35°C
Purge time:	11 min
Purge flow:	40 mL/min
Desorb flow:	40 mL/min
Sample preheat:	3 min
Sample temperature:	40°C
Dry purge:	5 min
Desorb preheat:	245°C
Desorb time:	2 min
Desorb temperature:	250°C
Bake time:	10 min
Bake temperature:	285°C

Standard Preparation

Because of the complexity of gasolines, accurate quantitative analysis of environmental samples requires accurate identification of each target analyte. Toward this end, it is imperative to incorporate the use of certified, standard grade reference materials and calibration solutions in the modified 8260 method described. These chemical standards were assembled from various commercial vendors (i.e. Supelco and Restek). Preliminary analysis of standards was performed to test their purgability and to optimize chromatographic conditions to establish reproducible retention times based on the methods described above.

For the modified EPA Method 8260 analysis described in this paper a calibration solution containing all 109 of the target analytes (Table II) was prepared as a stock

solution in methanol, at a concentration of approximately 5 µg/mL. This stock solution was then serially diluted to generate a suite of (at least) 5 linear calibration solutions, with the desired range of analysis for each target analyte to be approximately 0.025–4.0 µg.

The use of a calibration solution that contains all of the target analytes is a significant modification from the EPA Method 8260, which requires only selected analytes in the calibration. A calibration solution containing all of the target analytes allowed for the development of compound-specific response factors using the most appropriate ion for each target compound.

Surrogate and recovery internal standard solutions necessary to monitor purging efficiency are prepared at a concentration of 400 µg/mL in methanol. Surrogate internal standard monitoring compounds included 1,4-difluorobenzene, chlorobenzene-*d*₅, and ethylbenzene-*d*₁₀, while recovery internal standards included benzene-*d*₆, toluene-*d*₈, and 1,4-dichlorobenzene-*d*₄. These internal standard compounds were chosen primarily since they span the full boiling range of the analysis and do not coelute with their non-deuterated analogs.

Authentic Sample Preservation and Preparation

Protocols for the handling and preparation of samples after they are received in the laboratory are critical to accurate and precise sample analysis. Protocols followed during sample collection in the field and during shipping are equally important, but sometimes beyond the control of the laboratory. At a minimum, samples for detailed analysis of gasoline constituents should be stored at < 4°C from the time of their collection. In addition, an effort to minimize any headspace in sample containers should be made in order to minimize potential losses due to evaporation.

Nonaqueous Phase Liquids and Neat Product Samples

Upon receipt at the laboratory, dispensed gasolines or nonaqueous phase liquid (NAPL) samples are stabilized in a methanol solution. These samples are prepared in an area free of solvent fumes by rapidly weighing approximately 20 mg of the product into a tared 10 mL volumetric flask containing HPLC Grade methanol. The resulting diluted extracts (at a concentration of approximately 2.0 mg/mL) are then transferred to, and stored in, 4 mL Teflon[®] lined screw capped vials with no measurable headspace, and further protected against losses with Teflon[®] tape. The samples are then stored at 4°C (±2°C) in a dark refrigeration unit free of solvent fumes with the extracts being analyzed within 40 days of stabilizing the sample.

In a sealed 40 mL VOA vial, exactly 20 mL of reagent water is spiked through a Teflon[®] septa with 50 µL of the sample–methanol extract. This vial is then placed onto the autosampler tray, with the instrument fortifying the sample with the necessary surrogate internal standard–recovery internal standard (RIS–SIS) solution. The analytical sequence is then initiated, with the automated purging, trapping, and desorbing of the sample onto the GC column being performed. Samples are then analyzed under the same conditions as the calibration standards.

Water Samples

From a 40 mL VOA vial containing the water sample (with < 1% headspace), exactly 20 mL of aqueous sample is removed from the vial by a 25 mL syringe, and transferred into a sealed 40 mL VOA vial. This vial is then placed onto the autosampler tray and fortified with the necessary RIS–SIS solution. The analytical sequence is then initiated, with the automated purging, trapping, and desorbing of the sample onto the GC column being performed. Samples are then analyzed under the same conditions as the calibration standards. This method is designed for water samples containing individual purgeable compounds at concentrations of approximately 25 µg/L or less.

Soil–Sediment Samples (High and Low Levels)

Due to the variability in concentration of contaminants in soil and sediment matrices, two preparation methods are employed. For samples where minimal gasoline contamination is expected (e.g., based upon the absence of odor), a ‘low-level’ method for samples is performed by purging a heated soil–reagent water slurry containing both the surrogate and internal standards. If the expected concentration for target analytes is less than 0.1 mg/kg (dry weight), a 5-g sample is prepared. If the expected concentrations are between 0.1 and 1 mg/kg (dry weight), a 1-g sample is prepared. A 40 mL VOA vial containing the appropriate amount of soil–sediment and a Teflon[®] coated magnetic stir bar is placed onto the autosampler tray. The autosampler then adds 10 mL of reagent water and RIS–SIS solution to the vial. The spiked soil–sediment sample is then preheated to 40°C and automatically stirred, forming an aqueous slurry. The analytical sequence is then initiated, with the automated stirring and purging, trapping, and desorbing of the sample onto the GC column being performed. The samples are then analyzed under the same conditions as the calibration standards.

If the concentration of a soil–sediment sample is expected to exceed 1 mg/kg (e.g., they exhibit an obvious gasoline odor), samples are prepared by the ‘high-level’ methodology. A 5 g aliquot of the sample is added to 10 mL HPLC grade methanol and then gently mixed, allowing the methanol to extract target analytes from the soil–sediment samples. A 50–100 µL aliquot (dependent on the expected level of contamination) is then removed from the methanol extract and added to a 40 mL VOA vial containing 10 mL of reagent water. This vial is then placed onto the autosampler tray, with the instrument fortifying the sample with the necessary surrogate RIS–SIS solution. The analytical sequence is then initiated, with the automated stirring and purging, trapping, and desorbing of the sample onto the GC column being performed. The samples are then analyzed under the same conditions as the calibration standards.

If during the course of the initial analyses, a sample has a target analyte at a concentration that exceeds the working range of the initial calibration, the sample must be reanalyzed at a more dilute concentration. If it has been determined that a sample has exceeded the calibration range and potentially saturated the transfer system, a reagent water blank must be analyzed to demonstrate that the system is free from interferences. If the reagent water blank analysis is not free of interferences, the system must be decontaminated utilizing either a bake-out procedure or through more detailed instrument maintenance. Sample analysis should not resume until a reagent water blank can be analyzed and shown to be free of interferences.

Determination of Absolute Concentrations and Response Factors

As noted above, the modified EPA Method 8260 method described herein employs a calibration solution containing all of the target analytes, allowing for the development of compound-specific response factors using the most appropriate ion for each target compound (Table I). Each level of the multilevel calibration contains target analytes and internal standards and surrogates. It should be noted that although each level of the calibration has a different concentration of each target analyte (used to generate an average response factor over the working analytical range), surrogates and internal standards contained in these levels are constant and equivalent to that amount spiked into authentic samples.

The calculation of an average response factor (RF) for each compound is as follows:

$$\text{RF} = (A_s \times C_{is}) / (A_{is} \times C_s)$$

where A_s is the area of the characteristic ion for the target analyte to be measured; A_{is} is the area of the characteristic ion for the appropriate recovery internal standard; C_{is} is the amount of the recovery internal standard added to the extract (ng); C_s is the amount of the target analyte to be measured.

Based on the average response factors generated from the initial calibration set, concentrations for the target compounds are calculated using:

$$C_e = [(A_s \times I_s) / (A_{is} \times \text{RF})] / V_s$$

where C_e is the sample extract concentration; A_s is the area of the characteristic ion for the target analyte; A_{is} is the area of the characteristic ion for the appropriate recovery internal standard; I_s is the amount of recovery internal standard added to the extract (ng); RF is the average response factor for the target compound from initial calibration; V_s is the sample size (volume (L), g dry, wet or oil weight).

Quality Control

The quality of volatile concentration data is an essential component of any environmental forensic investigation. No standard protocols exist and therefore different laboratories employ different degrees of quality control (QC) in the course of sample collection, analysis, and reporting of data. Fingerprinting data to be used in a given forensic investigation should be analyzed in exclusive analytical batches, and, to the extent possible, within the same analytical sequence. Replicate analyses (duplicates or triplicates) within each analytical batch are highly recommended as a means of demonstrating analytical precision.

Prior to the acquisition of authentic sample data, the GC-MS is tuned and calibrated. Tuning of the instrument involves both the GC-MS software's initial (standard) autotune followed by manual tuning with perfluorotributylamine (PFTBA) (see Table III for criteria). All subsequent analyses of standards and authentic samples employ the identical GC and MS parameters. As noted above, a minimum five-point calibration curve is used to demonstrate the linear response of compounds over the desired analytical range (approximately 0.025–4.0 μg) and to generate response factors for analytical purposes. The calculated relative percent difference (RPD) for target

compound in the calibration set is not to exceed $\pm 25\%$, with all compounds having an average RPD less than 15%.

A rigorous QC program, along with a predetermined set of data quality objectives (DQOs), accompanies the sample grouping (Table III). A continuing calibration verification standard, at concentration levels equal to the mid level of the original calibration curve, is analyzed at the beginning of approximately each 12-h period during which analyses are performed (approximately every 8 samples, using the above mentioned GC temperature program). Analysis of a continuing calibration verification standard must bracket all samples contained in the analytical batch, or every 12 h within a batch. Both the initial and final verification standard must meet all data quality criteria for continuing calibration standards (Table III). The bracketing of samples with calibration standards, which is a notable modification from standard purge and trap techniques (e.g., EPA Method 8260), ensures that data generated for all samples is consistent over the analytical range for all samples, with degradation or discrimination having no sample-to-sample influence.

Once the calibration verification standards meets the acceptance criteria, a set of QC samples are analyzed in order to ensure that all methodology meets the DQOs. A procedural blank (PB), prepared along with the authentic samples and carried through the analytical process, is purged and acquired to ensure that the purge and trap system is free from (cross-) contaminants. A laboratory control sample (LCS) is then prepared and analyzed. The LCS is a verification standard consisting of representative PIANO class compounds from a source independent of the initial calibration. The results of this sample analysis ensure that both the calibration and analytical methodology are acceptable. Further QC samples prepared and analyzed with each batch can include a sample duplicate or triplicate to monitor and ensure analytical precision.

Samples Analyzed in this Study

A small suite of samples was chosen for analysis in this study (Table IV). The samples included a calibration stock solution prepared in our laboratory that contained all of the target analytes (as described above). Authentic standards for those target analytes that were not included in the PIANO standard were purchased from various chemical suppliers and spiked into the PIANO standard to achieve the calibration stock solution containing all of the target analytes (Table II) at the desired concentration.

In addition, seven gasoline standard reference materials (SRMs) were purchased from the National Institute of Standards and Technology (NIST) for analysis and to

TABLE IV Inventory of National Institute of Standards and Technology (NIST) standard reference materials (SRM) analyzed in this study

<i>Standard sample description</i>	<i>Supplier</i>	<i>Catalog number</i>	<i>Battelle ID</i>
Reformulated gasoline	NIST	SRM 2297	990920-38
Reformulated gasoline	NIST	SRM 2296	990920-39
Reformulated gasoline	NIST	SRM 2295	990920-40
Reformulated gasoline	NIST	SRM 2294	990920-41
MTBE in gasoline	NIST	SRM 2292	990920-42
ETBE in gasoline	NIST	SRM 2290	990920-43
TAME in gasoline	NIST	SRM 2288	990920-44

comprehensively assess the accuracy of the modified EPA Method 8260 by comparing our laboratory generated data to NIST's certified and reference values (Table IV).

An aliquot of each diluted sample extract (50 μ L) was added to approximately 20 mL of HPLC Grade reagent water along with surrogate and recovery internal standards, purged and concentrated as described above. Samples were then introduced onto the GC, analyzed via GC-MS techniques described above, and acquired for further analysis. A selected NIST gasoline, SRM 2290, was prepared and analyzed six times in order to demonstrate precision of the method. In addition, the SRM 2290 was spiked into a soil (that had been prebaked at 400°C) at a concentration of 20 mg_{gasoline}/kg_{soil} that was subsequently prepared and analyzed as a soil sample (described above). Accompanying the analysis of all of these samples were QC samples that included procedural blanks and laboratory control samples (as per Table III).

RESULTS

Chromatography

Figure 1 shows the total ion current (TIC) obtained from the analysis of the calibration stock solution containing all 109 of the target analytes listed in Table II. (Peak identifications correspond to Table II.) Sufficiently good chromatographic separation, peak shape, and mass discrimination are evident across the entire boiling range of the analysis. Absolute separation of every analyte is not necessary given the ability of mass spectrometry to recognize coeluting compounds using unique quantification and confirmation ions (Table II). However, a certain degree of separation is necessary to distinguish between isomers sharing similar mass spectra and elution times. For example, the modified method described sufficiently resolves *m*- and *p*-xylenes (Peaks 64 and 65) allowing them to be quantified individually in spite of their similar mass spectral properties. Another notable feature of the chromatography is the good peak shape and lack of mass discrimination, i.e., the higher molecular weight compounds are purged and recovered at levels comparable to the lower molecular weight compounds (Fig. 1).

Accuracy of the Modified EPA Method 8260M

The accuracy of the modified EPA Method 8260 is demonstrated through the comparison of the published NIST SRM certified and reference values and the concentrations determined by the modified EPA 8260 method described herein. The comparative results for the 23 analytes included in both the NIST and modified EPA Method 8260 target analytes for the seven NIST SRMs studied are shown in Table V. (Note that NIST provided the total *m*- + *p*-xylene values only. Thus, the EPA Method 8260M data represent the sum of the individual isomers.)

The RPD between the NIST and modified EPA Method 8260M results are shown to be less than 15% for most compounds. Overall, the comparability of the data is remarkably good. The highest RPDs are evident in compounds present at low concentrations; e.g., in some SRMs thiophene was not detected by the modified method while NIST reported concentrations around 30 mg/kg (Table V). This disparity is not surprising given these low concentrations. In addition, the RPDs for 1,2,4,5-tetramethylbenzene

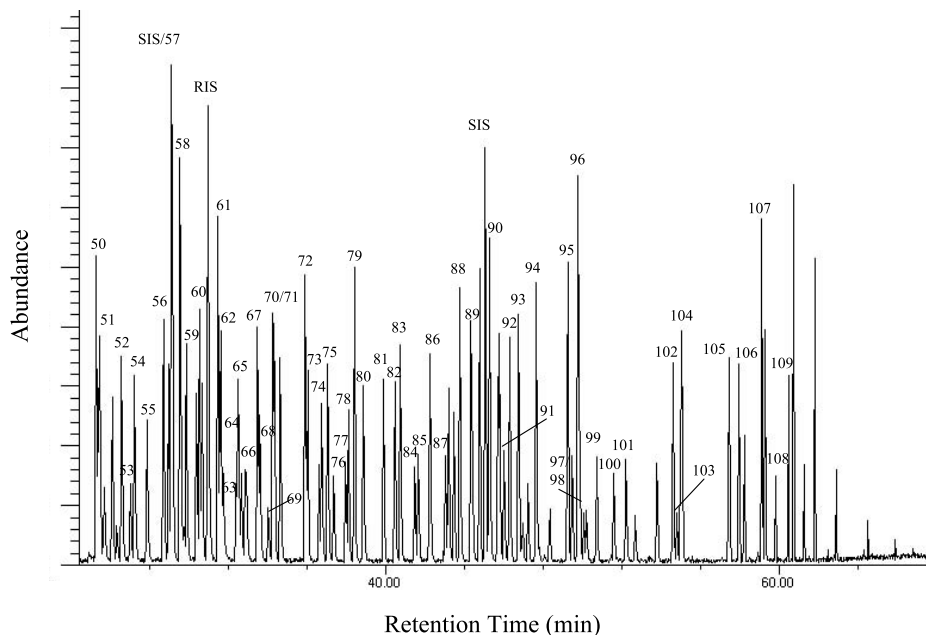
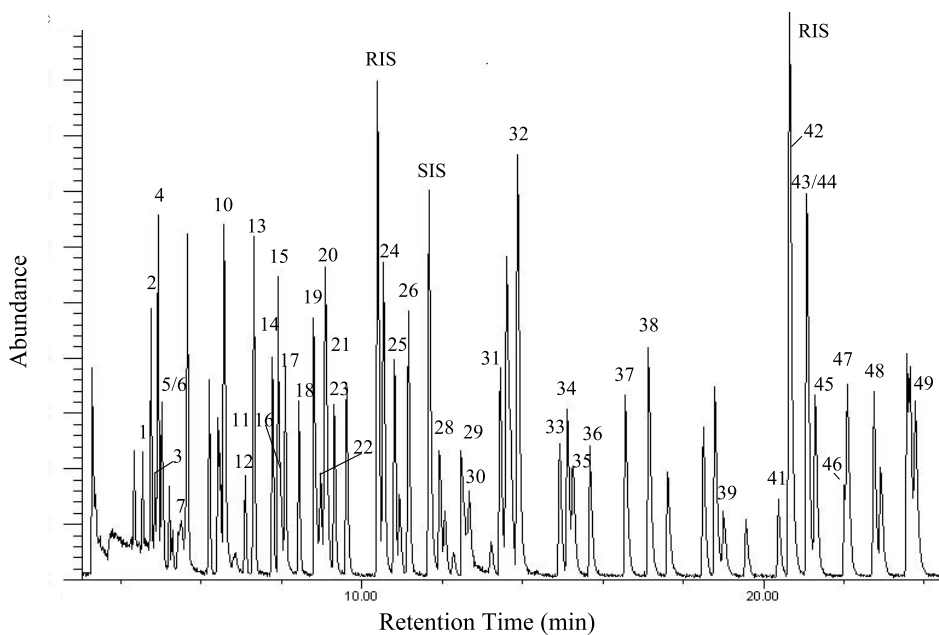


FIGURE 1 Total ion chromatogram of the calibration standard used in the modified EPA Method 8260 characterization of gasolines. Peak numbers correspond to the 109 analytes listed in Table II. RIS and SIS compounds are internal standards.

MOLECULAR FINGERPRINTING

TABLE V Comparison of certified concentrations reported for seven NIST SRM gasolines and measured concentrations using the modified EPA Method 8260 described herein. Bold values highlight relative percent differences (RPDs) that exceeded 20%.

Peak/ compound	Compound name	TAME in gasoline (SRM 2288)		ETBE in gasoline (SRM 2290)		MTBE in gasoline (SRM 2292)		Reformulated gasoline (SRM 2294)		Reformulated gasoline (SRM 2295)		Reformulated gasoline (SRM 2296)		Reformulated gasoline (SRM 2297)		
		NIST	RPD	NIST	RPD	NIST	RPD	NIST	RPD	NIST	RPD	NIST	RPD	NIST	RPD	NIST
2	1-Pentene	1228	1137	1242	6621	7700	8	6186	7400	9	6572	7500	7	5661	7800	16
4	<i>n</i> -C5 (Pentane)	21 041	20 565	22 647	25 939	37 300	18	25 261	35 700	17	25 368	36 300	18	22 631	37 600	25
10	MTBE	ND	ND	106 323	109 600	2	87 827	109 700	11	143 248	145 400	1	56	ND	ND	ND
14	<i>n</i> -C6 (Hexane)	14 157	15 893	19 288	34 259	38 700	6	34 732	37 000	3	28 054	37 700	15	30 888	39 100	12
19	ETBE	410	111 007	127 800	7	ND	ND	ND	ND	ND	104 619	130 200	11	ND	ND	ND
23	2,4-Dimethylpentane	6417	6710	7693	72 152	82 600	7	84 560	79 000	3	65 948	80 500	10	73 441	83 400	6
24	Benzene	15 803	13 428	15 034	10 374	10 300	0	9 719	9900	1	8884	10 100	6	10 010	10 400	2
25	Thiophene	ND	ND	ND	ND	30	100	290	260	5	ND	31	100	210	310	19
26	Cyclohexane	1575	1483	1706	90 035	92 500	1	91 339	88 400	2	87 667	90 100	1	87 255	93 400	3
29	TAME	96 452	127 800	14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
32	2,2,4-Trimethylpentane	19 686	18 991	21 326	76 720	123 400	23	113 623	118 000	2	81 867	120 200	19	115 285	124 500	4
34	<i>n</i> -C7 (Heptane)	5734	6274	7637	81 888	81 300	0	75 949	77 700	1	55 642	79 200	17	71 782	82 000	7
43	Toluene	49 560	47 413	52 868	84 898	82 900	1	73 682	78 900	3	73 356	80 200	4	88 564	82 700	3
47	3-Methylthiophene	ND	ND	ND	33	36	5	314	300	2	27	69	43	269	260	2
60	<i>n</i> -C8 (Octane)	3800	4000	5218	87 391	83 500	2	75 225	79 800	3	59 084	81 300	16	75 687	84 300	5
61	Ethylbenzene	24 330	22 934	26 366	21 383	20 500	2	19 732	19 600	0	17 873	19 900	5	19 886	20 700	2
64-65	<i>m</i> -+ <i>p</i> -xylene	19 924	19 196	66 848	48 124	61 400	12	63 965	58 700	4	59 228	59 800	0	77 691	62 000	11
71	<i>o</i> -Xylene	19 924	22 089	22 089	21 756	20 700	2	20 485	19 700	2	18 340	20 100	5	20 025	20 800	2
86	1,3,5-Trimethylbenzene	7105	6542	7945	21 795	20 700	3	19 257	19 700	1	17 327	20 100	7	21 969	20 800	3
89	1,2,4-Trimethylbenzene	20 576	19 113	23 143	21 593	21 000	1	19 751	20 100	1	17 117	20 500	9	19 438	21 200	4
92	<i>n</i> -C10 (Decane)	542	530	728	52 426	43 300	10	42 820	41 400	2	26 784	42 100	22	45 613	43 700	2
103	1,2,4,5-Tetramethylbenzene	635	583	732	4129	10 100	42	3512	9600	46	3108	9800	52	3681	10 200	47
108	Benzothiophene	28	43	58	79	70	6	418	440	3	49	36	16	261	440	26

TAME – *tert*-amyl-methyl ether; ETBE – ethyl-*tert*-butyl ether; MTBE – methyl-*tert*-butyl ether; ND – not detected above RL; RPD – relative percent difference.

were high (42–52%; Table V). We believe this disparity is, at least in part, due to the presence of additional C₄-benzene isomers in the NIST SRMs that we resolved and quantified separately in the modified EPA Method 8260 analysis. Notably, the average RPD values for the ether oxygenates and for the BTEX compounds in all SRMs was 8 and 7%, respectively. These low values clearly indicate that modified EPA Method 8260 analysis is very accurate for the target compounds examined in this study.

Precision of the Modified EPA Method 8260M

The NIST gasoline SRM 2290 was prepared and analyzed six times in order to demonstrate precision of the sample preparation and the modified EPA Method 8260. The percent relative standard deviation (%RSD) for each analyte was determined using the formula:

$$\%RSD = (\sigma/m) \times 100$$

where σ is the standard deviation of concentrations in six replicates; m is the mean concentration in six replicates.

Figure 2 shows that the %RSD tends to increase with decreasing concentration among the target analytes detected. The %RSD is generally less than 3% for analytes that are present at concentrations greater than 10 000 mg/kg. For this NIST standard, these include the three most abundant analytes, ETBE (Compound 19), toluene (Compound 43) and *m*-xylene (Compound 64). Pentane (Compound 4) was the only abundant analyte (22 000 mg/kg) that was measured at more than 3 %RSD, but this analyte still demonstrated excellent precision (6 %RSD). The %RSD was between 1 and 10% for all remaining analytes that are present in concentrations above 100 mg/kg. Such low %RSD demonstrates the remarkable precision that can be achieved in the analysis of gasoline using the modified EPA Method 8260 described herein. This level of precision, of course, can be critical in forensic analyses requiring the detailed comparison among similar samples. Notably, only one compound, benzothiophene (Compound 107), exhibits a %RSD exceeding the typical DQO for this analysis (35 %RSD; Table III). This resulted from a single (spurious though confirmed) detection of benzothiophene in one of the six replicates. If this had been a real set of replicates obtained within a batch of authentic field samples, benzothiophene would be necessarily excluded in the data analysis of samples.

As described above, product (gasoline) samples are prepared by spiking an aliquot into reagent water prior to purging. Thus, the precision demonstrated for the NIST 2290 gasoline shown in Fig. 2 is directly comparable to the precision obtainable for aqueous field samples by this method.

Recovery of Gasoline from Soil

The appropriateness of the modified EPA Method 8260 for soil matrices was also considered since the ability to purge the target analytes from soil is often necessary in environmental forensic investigations. Figure 3 shows the %RSD calculated for all 109 analytes (Table II) for six soil replicates that were spiked with NIST gasoline SRM 2290 at 20 mg/kg and analyzed by the modified method. As was observed

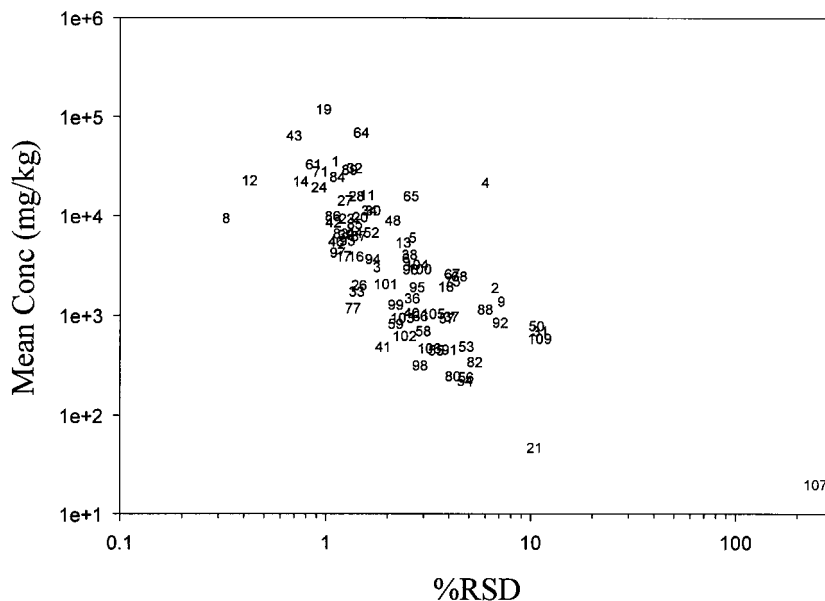


FIGURE 2 Cross plot of percent relative standard deviation (%RSD) versus mean concentration for analytes detected in six replicates of NIST gasoline standard (SRM 2290). Peak numbers correspond to the 109 analytes listed in Table II.

above, the %RSD tends to increase with decreasing concentration (Fig. 3). The %RSD was generally less than 20% for most analytes present in concentrations greater than 10 $\mu\text{g}/\text{kg}$ (dry). Notably, ETBE (Compound 19) was readily purged from the soil (as it had been from water; Fig. 2). The %RSD values are generally higher than were obtained for the product (or aqueous) sample replicates (compare Figs 3 and 4). This probably results for the reduced efficiency in the purging of soil, as compared to water samples. However, only one analyte, *trans*-2-octene (Compound 53) had a %RSD that exceeded the typical DQO for replicate analyses (35 %RSD; Table III).

If the average concentrations for the target analytes for the six replicates of NIST 2290 gasoline (Fig. 2) and for the six replicates for the soil spiked with NIST 2290 (Fig. 3) are normalized to their respective totals and compared, it is apparent that there is virtually no difference in the 'fingerprint' obtained (Fig. 4). Only two compounds, toluene and ethylbenzene (Compounds 43 and 64, respectively), were 'under-recovered' from the gasoline-spiked soils (as compared to the gasoline itself) by more than 0.5%. These compounds may be absorbed to organic carbon in soils, thereby slightly reducing their 'purgability'. Only one compound, ETBE (Compound 19), was slightly 'over-recovered' (2.5%) from the soil as compared to the gasoline itself. This is probably an artefact of the manner by which gasoline samples are prepared for analysis, i.e., spiking an aliquot of the gasoline into reagent water (see above). This may permit a small percentage of the highly soluble oxygenate compounds (e.g., ETBE, etc.) to enter and remain in aqueous solution during purging. However, this effect appears minimal (Fig. 4) but explains, at least in part, why the oxygenate compounds (ETBE, TAME, MTBE) were generally determined to be at slightly lower concentrations in the NIST gasoline standards that were analyzed by the modified EPA 8260

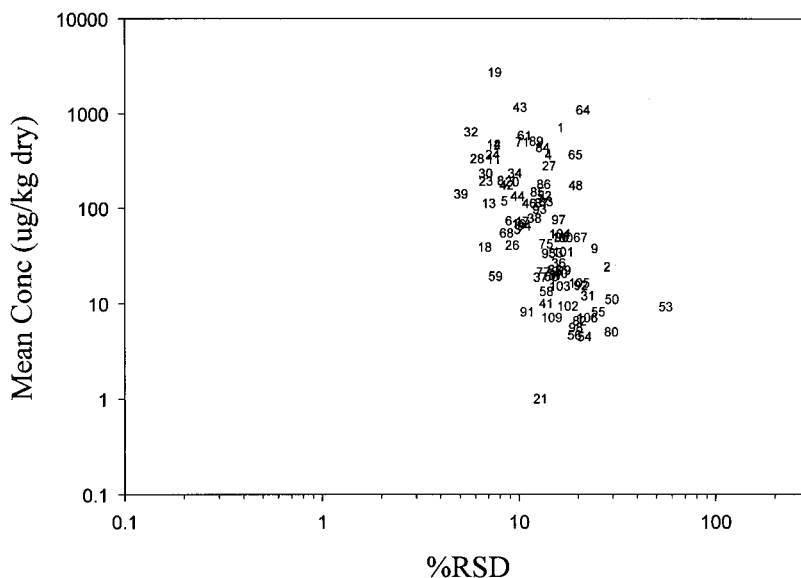


FIGURE 3 Cross plot of percent relative standard deviation (%RSD) *versus* mean concentration for analytes detected in six replicates of NIST gasoline standard (SRM 2290) spiked into soil at 20 mg/kg. Peak numbers correspond to the 109 analytes listed in Table II.

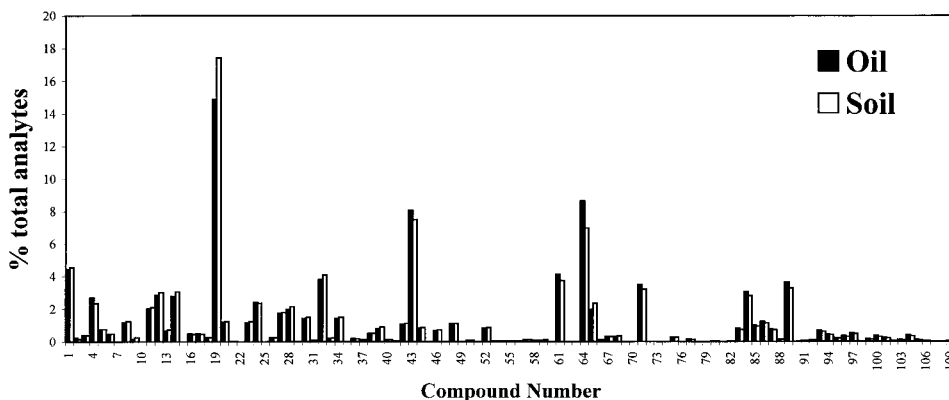


FIGURE 4 Histograms showing the mean normalized concentrations of analytes in NIST gasoline standard (SRM 2290) measured in neat gasolines (oil) and in spiked soils (soil). Compound numbers correspond to the 109 analytes listed in Table II.

method compared to the NIST-reported values (1–14%; Table V). The overall minimal effects that the type of matrix (product *versus* soil) has on the ‘fingerprint’ obtained (Fig. 4) should not significantly influence any comparisons between product (NAPL) and soil sample fingerprints, but should be acknowledged. Of course, the ‘fingerprints’ of authentic product and soil samples from the environment will be affected much more by the degree of weathering they have experienced (as compared to the minor effects of matrix on the purgability of selected compounds).

CONCLUSIONS

A method for the quantification of volatile compounds that are normally found in automotive gasoline and light petroleum distillates is described for environmental matrices including nonaqueous phase liquids, water, and soil–sediments. The method is a modification of US EPA Method 8260, with the principal modification being the development of a target analytes list that is appropriate for ‘fingerprinting’ automotive gasoline. In the modified method described, 109 analytes that can occur in automotive gasolines are quantified, thereby providing a significant degree of molecular detail about the nature of gasoline(s) in environmental samples. These compounds include numerous hydrocarbons within the five hydrocarbon classes that occur in gasolines (paraffins, isoparaffins, aromatics, naphthenes, and olefins), the so-called PIANO compounds. In addition, various sulfur- and oxygen-containing compounds are included along with selected additives (e.g., 1,2-dichloro- and 1,2-dibromo-ethanes and MMT). This detail allows for the molecular ‘fingerprinting’ of environmental samples impacted with gasoline(s) and other light petroleum products, as is required in many environmental forensic investigations.

Consistent with EPA Method 8260, the modified method’s hardware consists of an automated purge-and-trap (PT) system linked to a conventional gas chromatograph, mass spectrometer (GC-MS) and data system. NAPL water samples, and soil–sediment samples can be prepared and analyzed. The accuracy of the modified EPA 8260 method is demonstrated by analysis of seven gasoline SRMs obtained from NIST. The precision of the method is demonstrated by analysis of six replicates, prepared as both NAPL samples and as spiked soil samples.

This method can provide the sufficient molecular detail that is necessary to distinguish different types of automotive gasolines in environmental samples. This quantitative approach to gasoline fingerprinting is advantageous over qualitative fingerprinting due to the ability to analyze the results using numerical or statistical methods.

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