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The EPA National Fuels Surveillance Network. I. Trace Constituents in Gasoline and Commercial Gasoline Fuel Additives

by Robert H. Jungers,* Robert E. Lee, Jr.,* and Darryl J. von Lehmden*

A National Fuels Surveillance Network has been established to collect gasoline and other fuels through the 10 regional offices of the Environmental Protection Agency. Physical, chemical, and trace element analytical determinations are made on the collected fuel samples to detect components which may present an air pollution hazard or poison exhaust catalytic control devices.

A summary of trace elemental constituents in over 50 gasoline samples and 18 commercially marketed consumer purchased gasoline additives is presented. Quantities of Mn, Ni, Cr, Zn, Cu, Fe, Sb, B, Mg, Pb, and S were found in most regular and premium gasoline. Environmental implications of trace constituents in gasoline are discussed.

Introduction

The combustion of petroleum-based fuel in motor vehicles represents an important emission source of both particulate and gaseous pollutants to the environment. The potential health hazard associated with the combustion products from fuels and fuel additives was recognized in the Clean Air Act as amended in 1970, Section 211, which empowers the Environmental Protection Agency (EPA) to require manufacturers of fuels and fuel additives to register their products. As an integral part of this program, EPA established a National Fuels Surveillance Network (NFSN) in 1972 for the collection and analysis of fuels and fuel additives throughout the country.

* Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, North Carolina 27711.

In addition to providing data for validating information provided by fuel and fuel additive manufacturers, the NFSN should also serve as a source of information for a variety of other uses including: (a) the detection of constituents in motor vehicle fuel which could poison exhaust catalytic control systems used to meet statutory standards, (b) detection of toxic components in fuel, especially heavy metal contaminants introduced during transport and storage processes, (c) the development of accurate emission factors for assessing the contribution of trace metals and other fuel components to the atmosphere, (d) the enforcement of federal regulations on fuel additives such as the regulated limits on lead and phosphorus in gasoline and (e) the design of studies to identify emission constituents.

This is the first in a series of reports on the NFSN, and is limited to a description of the network operation, chemical analytical

methods used, and a summary of results of trace constituents in gasoline and commercially marketed consumer purchased gasoline additives.

Experimental

Operation of the National Fuels Surveillance Network

Fuel samples are generally collected by the ten EPA regional offices in accordance with specific requests from EPA's National Environmental Research Center (NERC) located in Research Triangle Park, North Carolina. NFSN was established in 1972, during which 200 gasoline samples were collected. It is anticipated that approximately 1000 samples will be collected annually thereafter and sent to the NERC for in-depth chemical and physical analysis. During the early phases of the network, the collection of gasoline and consumer purchased gasoline fuel additives was emphasized; however, proportionately larger quantities of other fuels will be collected in subsequent years to include aviation gasoline, jet fuel, diesel fuel, distillate and residual fuel oil, and motor oil samples.

Generally, fuel samples are collected at the last point in the distribution system, i.e., the retail outlet such as service stations and heating oil distributors, although selected samples from refineries and pipelines will also be collected. Samples are collected in a metal-jacketed 500 ml Wheaton hard-glass container with a Teflon-lined cap. The Wheaton bottle is cleaned by soaking 24 hr in 1:1 nitric acid, rinsing with distilled water, and soaking for an additional 24 hr in distilled water. This procedure has been found to remove detectable levels of trace metal contaminants from the container.

In sampling gasoline, at least 1 gal is discarded from the pump before filling the container completely, discarding the gasoline, refilling the container to the shoulder, capping tightly, and marking the level on the bottle. The collected sample is placed inside another metal can which is filled with an absorbant, sealed, labeled and sent to the NERC Fuels Laboratory by ground transportation in accordance with Title 49, Code of Federal Regulations (*1*). In the laboratory, the samples are ordinarily stored at room temperature in subdued light, although refrigeration is suggested for long term storage.

Chemical Analysis

Procedures outlined by the American Society for Testing and Materials (ASTM) are followed for gasoline, diesel fuel, distillate and residual fuel oil, crankcase oil and consumer purchased fuel additives to determine ash content (*2*), viscosity (*3*), thermal value (*4*), API gravity (*5*), and saturates, nonaromatic olefins, and aromatics (*6*). Ordinarily these determinations are made only on selected samples and are not part of the routine analysis carried out.

Sulfur is determined by combustion in an oxygen enriched atmosphere or by burning in an artificial atmosphere of 70% carbon dioxide and 30% oxygen (*7*); phosphorus in gasoline by ignition with zinc oxide, dissolution in sulfuric acid followed by spectrophotometric analysis with ammonium molybdate–hydrazine sulfate; and carbon, hydrogen, and nitrogen by pyrolysis at 975°C over platinized carbon with a Perkin-Elmer 240 elemental analyzer and a procedure in accordance with the manufacturer's instructions.

Lead in gasoline in the range of 0.01 to 0.10 g/gal is determined by atomic absorption spectrometer (*8*). The lead in the sample is extracted into methyl isobutyl ketone with a quaternary ammonium salt (tricapylmethylammonium chloride) after the organic lead has been converted to inorganic lead with iodine. The lead content of the sample is determined by atomic absorption flame spectrometry at 2833 Å by use of standards prepared from reagent grade lead chloride. By the use of this treatment,

all alkyl lead compounds give identical response.

Two multielement techniques that were intensively investigated for obtaining elemental data on gasoline and other fuels in the trace concentration (ppm-ppb) range were neutron activation analysis and spark source mass spectrometry. Studies to evaluate the accuracy and precision of these methods are reported elsewhere (*9*). Neutron activation analysis was limited for the analysis of gasoline because of the possible explosion of the volatile sample in the nuclear reactor and the masking effect of bromide which swamps the radioactive signal of elements having similar half-lives.

On the other hand, spark source mass spectrometry was applicable for the analysis of over 20 elements in gasoline including Be, Cd, As, V, Mn, Ni, Sb, Cr, Zn, Cu, Se, B, Ag, Al, Fe, Mg, Cl, P, Pb, and Ca. A gasoline sample is oxidized with bromine followed by freeze drying to remove the liquid and final drying to remove the odor of gasoline. The remaining residue, including the trace elements, is mixed with graphite until homogenous and is pressed into an electrode for analysis with an AEI MS 702R spark source mass spectrometer equipped with photograph plate output (*10*).

In the study reported here, over 40 gasoline samples were collected for tract element analysis, which included at least two regular grades in each of the following cities: Boston, New York, Philadelphia, Atlanta, Chicago, Kansas City, Denver, Dallas, San Francisco, and Seattle. In addition, a total of 6 no-lead or low-lead gasoline samples were collected in Seattle, Boston, Philadelphia, and Kansas City. Six oil companies were represented in the study, including Texaco, Mobil, Shell, American, Exxon, and Gulf.

Eighteen samples of commercially available consumer purchased gasoline additives were purchased at retail outlets in the Raleigh-Durham, North Carolina area and analyzed by neutron activation. The brands sampled included: STP Gas Treatment; Gumout, Fuel Mix Tune Up; Wynn's Engine Tune up; Wynn's Spitfire Gas Power Booster; K-Mart Gas Treatment; Zerex Gasoline Antifreeze; Prestone Carb Tune up; Dupont Gas Booster; and Max S-E-T Gas Booster.

Results and Discussion

Trace Elements in Gasoline

Table 1 presents a summary of the concentration range of trace constituents in 50 gasoline samples collected for the NFSN. Except for Pb and S, all determinations were made by spark source mass spectrometry (*10*). In premium grade gasoline measurable concentrations of Cd, As, V, Mn, Ni, Sb, Cr, Zn, Cu, B, Ca, Ag, Al, Fe, Mg, Cl, P as well as Pb and S were found. Measurable amounts of the same elements were also found in regular gade gasoline except for Cd, V, Ag, and Al. In low-lead gasoline, measurable amounts of Mn, Ni, Cr, Zn, Cu, Fe, Cl, Ca, Pb, and S were detected.

No association was apparent in the levels of trace constituents found in gasoline and the sampling location. It seems, therefore, that the elements detected were native to the crude oil before refining, were introduced as a fuel additive or as a contaminant of a fuel additive, or were extracted during the transfer and storage process, e.g., pipelines and service station tanks. In both imported and domestic crude oils, Se, As, Ni, S, and V are known (*11*) to be present; however, it is likely that the levels of these elements are reduced or even removed in the gasoline fractions during refining process. It should be noted that it is extremely difficult to carry out a "materials balance" on gasoline; i.e., follow the path of trace constituents from the crude through the refinery to the service station. On the other hand, B, Ca, Cu, Mn, Zn, P, Pb, Cl, and S are known (*12*) to be components in some organic fuel additives reported to EPA, although not all are necessarily associated with an individual fuel manufacturer. These organic fuel addi-

Table 1. Trace elements in gasoline. [a]

Element	Premium (22 samples)		Regular (22 samples)		Low lead (6 samples)	
	Range, μg/ml	Avg, μg/ml	Range, μg/ml	Avg, μg/ml	Range, μg/ml	Avg, μg/ml
Be	<0.001		<0.001		<0.001	
Cd	<0.001–0.03		<0.08		<0.04	
As	<0.001–0.002		<0.004–0.009		<0.1	
V	0.001–0.002		<0.007		<0.003	
Mn	0.002–0.03	0.013	0.001–0.011	0.006	<0.002–0.03	
Ni	0.003–1.5	0.086	0.001–0.07	0.02	0.03–2.00	0.12
Sb	<0.003–0.05		<0.007–0.5		<0.10	
Cr	<0.001–0.34		<0.003–0.03		<0.005–0.016	
Zn	0.004–2.00	0.16	0.010–2.00	0.06	0.20 –0.50	0.35
Cu	0.011–0.25	0.14	0.010–0.40	0.08	0.06 –0.20	0.13
Se	<0.06		<0.06		<0.04	
B	0.001–0.210	0.021	0.004–0.08	0.02	[b]	
Ag	<0.002–0.03		<0.54		<0.1	
Al	<0.001–0.02		<0.007		[b]	
Fe	0.07–6.00	1.07	0.07–3.80	0.91	0.3–13.0	6.7
Mg	<0.002–0.004		<0.002–0.01		[b]	
Cl	0.02–0.80	0.19	0.05–1.10		<0.007–0.90	
P	<0.001–0.30		<0.001–2.0		<0.02	
Pb [c]	238–763	600	190–750	494	132–135	134
S [d]	10–360	81	10–640	177	4–720	200
Ca	0.06–0.26	0.24	<0.06–3.0		<0.2–0.7	
Sn	<0.02–0.40		<0.01–0.2		<0.6	

[a] Determined by spark source mass spectrometry (*10*) except as noted; values designated as < represent concentrations at below detectable levels which can vary from sample to sample because of matrix effects.

[b] Sample data were lost during processing.

[c] 200 samples by atomic absorption spectrometry; ASTM D–3238 (*8*).

[d] 103 samples by ASTM D–1236 (*7*).

tives are compounds which are added to the fuel by the manufacturer.

It appears that a portion of the trace constituents found in gasoline is introduced in fuel additives or is extracted from the transport and storage system. Hydrocarbon-soluble metal compounds can form by reaction of phenols, mercaptans and other acidic materials in gasoline with metals in contact with the gasoline between the refinery and the automobile (*13*). Metals can degrade antioxidant additives such as phenylenediamines and hindered phenols which prevent gum formation. To reduce oxidative deterioration in gasoline, a metal deactivator such as *N*, *N'*-disalicylidene-1,2-propanediamine is used to chelate Cu and other metals. Although metal deactivators are effective suppressors of oxidative deterioration, the chelated metal contaminants will be combusted thereby acting as potential poisons of exhaust catalytic devices or the metals may be emitted into the air as pollutants. Indeed, most of these elements have been identified in auto exhaust (*14*).

Table 2 presents concentration ranges of lead and phosphorus for 197 premium, regular, and low-lead gasoline samples collected during 1972 in ten designated cities. Units of grams per gallon are used to facilitate comparison with federal standards. A review of this table shows that the lead concentration range in New York is well below 2.0 g Pb/gal as required by NYC regulations. The Federal standard for lead and phosphorus, as published in the Federal Register (*15*) defines lead-free gasoline as containing not more than 0.05 g/gal, and phosphorus-free as containing not more than 0.005 g/gal. This 91 minimum octane gasoline was made available after July 1, 1974 in a substantial percentage of gasoline retail stations to provide a fuel which can be used with exhaust catalytic system. Of further interest, the

Table 2. Concentration ranges of lead and phosphorus in gasoline samples collected during 1972 in ten EPA regions.

City (metropolitan)	Lead, g/gal[a]			Phosphorus, g/gal[a]		
	Premium	Regular	Low-Lead	Premium	Regular	Low-Lead
Boston	(9) 1.49–2.85	(5) 1.23–2.84	(11) 0.009–0.68	(9) <0.0001–0.006	(5) <0.0001–0.004	(11) <0.0001–0.004
New York	(9) 0.85–1.31	(11) 0.72–1.08	(5) 0.018–0.29	(9) <0.0001–0.0002	(11) <0.0001–0.0001	(5) <0.0001–0.006
Philadelphia	(8) 1.31–2.77	(9) 1.19–2.70	(8) 0.010–0.60	(8) <0.0001–0.0003	(9) <0.0001–0.0001	(8) <0.0001–0.006
Atlanta	(6) 1.78–2.58	(7) 0.90–2.36	(6) 0.016–0.48	(6) <0.0001–0.004	(7) <0.0001–0.0001	(6) <0.0001–0.010
Chicago	(11) 1.09–2.72	(7) 0.98–2.43	(7) 0.008–1.70	(11) <0.0001–0.0003	(7) all <0.0001	(7) <0.0001–0.007
Dallas	(5) 2.10–2.89	(5) 1.39–2.72	(5) 0.032–0.44	(5) <0.0001–0.0002	(5) <0.0001–0.0001	(5) <0.0001–0.0002
Kansas City	(5) 1.21–2.65	(5) 1.42–2.20	(5) 0.011–1.46	(5) <0.0001–0.0001	(5) all <0.0001	(5) <0.0001–0.006
Denver	(5) 1.84–2.72	(5) 1.14–1.94	(4) 0.022–1.20	(5) <0.0001–0.0001	(5) all <0.0001	(4) <0.0001–0.005
San Francisco	(9) 1.48–3.52	(5) 1.28–2.32	(6) 0.037–0.63	(9) all <0.0001	(5) all <0.0001	(6) <0.0001–0.0001
Seattle	(4) 1.80–2.65	(7) 1.62–3.40	(3) 0.020–0.50	(4) <0.0001–0.0001	(7) <0.0001–0.0001	(3) <0.0001–0.009

[a] Numbers in parentheses preceding concentration ranges represent the number of samples specified for that concentration range.

standard (*16*) specifies a decreasing amount of lead which will be allowed in all gasoline dispensed by either the refiner, distributor, or retailer. This decrease is January 1, 1975, 2.0 g Pb/gal; January 1, 1976, 1.7 g Pb/gal; January 1, 1977, 1.5 g Pb/gal; January 1, 1978, 1.25 g Pb/gal. In regions in which lead manufacturing is absent, the reduction in lead should result in a definite decrease in atmospheric lead.

Trace Constituents in Commercial Consumer Purchased Fuel Additives

Eighteen commercially marketed gasoline additives were analyzed by neutron activation analysis (*17*). Results summarized in Table 3 show that measurable levels of Hg, As, V, Mn, Sb, Cr, Zn, Co, Se, Sn, Ag, Al, Fe, and Sr were found. Additives of this type are multifunctional acting as antioxidants, metal deactivators, corrosion inhibitors, anti-icers, and carburetor and valve deposit detergents. Ordinarily, these additives are used to supplement the additives already present in fuel and may not necessarily be representative of additives blended at the refinery.

Table 3. Trace elements in consumer-purchased fuel additives. [a]

Element	Concentration range, μg/ml	Avg, μg/ml
Hg	<0.0002–0.002	
Cd	<0.02–0.20	
As	<0.001–0.23	
V	<0.001–0.031	
Mn	0.007–2.71	0.16
Ni	<0.013–<0.340	
Sb	<0.0005–0.0041	
Cr	<0.002–0.096	
Zn	0.032–38.0	8.8
Co	<0.0002–0.0360	
Se	<0.001–0.032	
Sn	<0.07–140	
Ag	<0.0003–0.0065	
Al	<0.01–2.30	
Fe	<0.03–560	
Sr	<0.033–37	
Br	<0.014–10	
Cl	0.5–18,200	1,334
Na	<0.01–99	
Ba	<0.02–4.2	
Ca	<17–1,900	
K	<0.7–63	

[a] 18 samples analyzed by neutron activation (*17*).

Examination of Table 3 reveals the presence of comparative high levels of Sn (up to 140 μg/ml) compared to concentrations found in gasoline shown in Table 1. Apparently, the predominant source of the Sn and possible other elements such as Fe in the fuel additives may have been the metal packaging container, especially from the soldered connection. Intensive use of commercially marketed additives can add to the environmental trace metal burden and increase the potential for poisoning exhaust catalytic control devices.

Environmental Implications

The presence of metallic elements in gasoline, especially those which have suspected biological toxicity such as Ce, As, V, Ni, and Cr is of concern to environmentalists because of the potential widespread dissemination of these constituents, most in the respirable range, at ground level (*18*). Several studies of the particle size of trace metal components in ambient air have shown that Pb, V, and Zn are associated with particles predominantly of a submicron aerodynamic size (*19,20*). Particles in this size range can remain suspended in air for long periods of time and can penetrate deep into the human respiratory system (*21*). Furthermore, many of the metals found in gasoline, notably Fe and Pb (*22*), can act as catalysts in the transformation of primary atmospheric pollutants to secondary pollutants, e.g., SO_2 to SO_4. Although gasoline combustion may not necessarily be the major source of these constituents, the fact that over 100 billion gallons are consumed annually indicates that gasoline combustion should be considered in estimates of environmental emissions of these metals.

Another environmental concern, mentioned earlier is the presence of constituents such as S, which may poison exhaust catalytic devices thereby reducing their effective operating life. Coupled with this concern is the distinct possibility that fine metal particles may be produced from the exhaust

catalysts themselves as recently reported by Balgord (*23*). There is also concern that S in gasoline may be emitted as sulfuric acid mist after oxidation by catalytic devices. It becomes important to characterize the trace constituents in the fuel in order to assess the amount of trace metals emitted by exhaust catalytic devices. The widespread use of consumer purchased gasoline additives which contain trace elements that can effect catalytic performance also presents a serious problem.

As more information becomes available through the National Fuels Surveillance Network, it may be necessary to institute some type of control at the refinery or distributor outlet to remove trace contaminants from fuel before it is combusted in the motor vehicle.

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