SURVEY OF ULTRA-TRACE METALS IN GAS TURBINE FUELS

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Gas turbines are multi-fuel capable power generation systems. Because of their robust design, they can operate on low heating value gases, liquid fuels, natural gases and refinery gases. In a recent industry study, the environmental impact related to gas turbine operation on fuel oil was determined based on the available emissions data for metal emissions from gas turbines. Data collected by EPA reported the noted detectable trace metal emissions during oil operation. However, many of the tests were over fifteen years old, and fuel from the storage tanks at the facility may have been even older. Attempts to determine an accurate environmental assessment were hindered by the quality of the emissions data, and the paucity of fuel sample analytical results for distillate fuels..

Considering the great improvements in the US refining infrastructure, we concluded that any metals in a distillate fuel oil sample would probably be at the ultra-trace level, and would very likely be at the detection limits of the most analytical methods. Further, the concentrations of any hazardous metals (such as lead or mercury) would be extremely low, and the modeled emissions from using such a fuel would yield no measurable health impact. To address this question, we reviewed the existing literature on the subject, and found that no coordinated effort had attempted to identify the concentrations of trace hazardous metals, certainly not using some of the latest measurement methods (in this case ICP-MS).

The next step was to collect samples, and screen them for the presence of eight hazardous metals. Fuel samples (distillate) were collected from around the United States, taken from existing storage facilities, with fuel tanks assigned to a gas turbine power generation unit. Samples were taken to be representative of each Petroleum Administrative Defense Districts (PADD). The survey results revealed no measurable concentrations of Arsenic, Mercury or Lead in any fuel sample taken. No detectable levels of Chromium VI were reported. All samples were screened using Mass-Spec, with detection levels below 1 ppb. These results indicate that the distillate feedstocks available to the power generation industry are essentially free of toxic metals, and pose no health risk to the public when used in a gas turbine. The results also suggest that the petroleum distillate transmission and distribution system does not introduce cross contamination to the fuel supply.

Introduction

Non-combustible materials present in a fuel are typically released into the environment during the combustion process. With low-grade fuels, such as residual fuel oil or coal, metals, including toxic metals can be present in significant concentrations. Such is not the case for distillate fuels. Yet, there has been a widely held perspective that distillate fuels encumbered with potentially toxic metals.

The metals of most concern are those that exhibit a high degree of toxicity, or carcinogenicity, at very low concentrations. Mercury and lead are two key metals where there has been intense interest to reduce or eliminate their release into the environment. Removal of lead from gasoline, and switching to cleaner fuels has had a positive impact in reducing these emissions into the environment. In the twenty years since the removal of lead from gasoline was mandated there has been a steady decrease in lead emissions, and a steady increase in the quality of liquid fuels available for the power generation industry. As the results show here, the quality of distillate fuels is exceptional, and the metal contaminants found in liquid fuel oil are even lower than those mandated in drinking water.

Experimental

Samples from across the US were collected at storage facilities supplying fuel to power generation installations. Thirteen samples were collected and analyzed using ion mass spectrometry to identify the presence of specific metal toxins in the fuels

The toxic metals selected for this study were based on the needs for conducting an environmental health risk analysis related to gas turbine operation. In the risk analysis, emissions from a gas or fuel oil fired gas turbine were determined based on the mass emission rates of each toxic component. Both organic and inorganic emissions were used in the health risk analysis. For liquid fuel (No. 2 fuel oil) operation, the analysis assumed that any metal in the exhaust was due to the presence of metals in the fuel oil. In the initial phase of the study, the dominant metal of concern (based on results of emission tests on gas turbines) was chromium, since emission measurements of chromium yielded the highest emission factors. Yet with chromium, the dominant risk is the Cr-VI oxidation state. However, the existing emissions test data did not attempt to quantify the oxidation state of any metals reportedly detected in the exhaust.

Routine industrial fuel tests, with metal detection levels in the ppm range, report measurable concentrations of arsenic and lead. However, the metals are almost routinely reported at the detection limits of the apparatus, which was not sufficient for our needs. In the risk analysis, the presence of either arsenic or lead at the ppm level would calculate unacceptable risk levels. To address the accuracy of the earlier fuel tests, and to estimate health risks related to emissions from burning liquid fuels, the set of metals selected for a detailed ultra-trace survey was selected. Those metals in selected are shown in the following table.

1. Arsenic	5. Nickel
2. Cadmium	6. Manganese
3. Chromium	7. Selenium
4. Lead	8. Mercury

Metal Analysis from Fuel Samples Selected from Across United States
Samples collected from Gas Turbine Installations around the United States

All concentrations are reported in units of ppb (by weight)

	State or Region	Sample ID	PADD	Arsenic	Cadmium	Total Chromium	Chrome VI	Lead	Manganese	Nickel	Selenium	Mercury
1	California	30352	V	0	0	175	0	3.01	6.9	0	0	0
2	Colorado	30374	IV	0	0	203	0	1.89	6.73	0	0	0
3	Florida	30391	III	0	0	244.6	0	3.48	5.56	0	0	0
4	Wisconsin	30353	III	0	0	226.8	0	2.07	6.03	4.93	0	0
5	Florida	30354	III	0	0	238.2	0	5.29	5.76	12.33	0	0
6	Minnesota	30355	II	0	0	272.1	0	7.2	6.35	184.77	0	0
7	California-South	30405	V	0	0	175.8	0	18.79	10.07	15.05	0	0
8	NC	30423	III	0	0	259.16	0	2.3	6.61	28.95	0	0
9	Arkansas	30424	IV	0	0	202.49	0	46.18	10.95	28.2	0	0
10	Arkansas	30447	IV	0	0	403		61	0	0	0	0
11	Arizona	30494	IV	0	0	306		41	0	0	0	0
12	California-North	30522	V	0	0	165	0	0	0	0	0	0
13	Maine	30425	I	0	0	279.88	0	2.59	7.11	101.78	0	0
	Average			**0**	**0**	**242.4**		**15.0**	**5.5**	**28.9**	**0**	**0**
	SD			**0**	**0**	**65.05**		**20.59**	**3.53**	**54.51**	**0**	**0**
	Max			**0**	**0**	**403**		**61**	**10.95**	**184.77**	**0**	**0**
	Detection Limit, ppb			**0.9**	**0.1**	**0.07**		**0.08**	**0.1**	**0.2**	**5**	**0.2**

Table 1. Summary Of Distillate Oil ICP Results.

Analytical Method. Fuel characterization methods have been used extensively to quantify the presence of various components, including metals, in fuel oil. Historically, most of the test methods have cutoff their analysis at the 1 ppm (1,000 ppb) level, and usually this has been sufficient.

But to accurately determine the impact of burning liquid fuel, and the subsequent release of any metals into the environment, it has been necessary to push for a deeper and more thorough analysis using improved methods methods.

For this study, an Inductively Coupled Plasmas-Mass Spectrometer (Thermo-Elemental X7 ICP/MS) was used. It uses a high temperature plasma between 6000 K and 8000 K, connected to a high sensitivity mass spectrometer. The plasma is formed in an RF chamber, where the sample can be delivered as a solution, vapor, or even solid. The mass spectrometer is a quadrapole mass-spec designed to rapidly measure ions at each mass unit. Detection limits are species dependent, and range from parts-per-trillion (ppt) to parts-per-billion (ppb).

No. 2 Fuel Oil Analysis Results. The results of the survey show that No.2 Fuel Oil to be remarkably clean and of high quality. A detailed summary of the analytical results is shown in Table 1. the most prevalent compound in the fuel samples was chromium, although no Cr-VI was detected. The fuels were essentially free of arsenic, cadmium, selenium, and mercury. The concentration of arsenic permitted in drinking water is higher than the quantities reported in the fuel samples.

Comparison with Other Fuel Samples. As the name implies, residual fuel is the components of the petroleum feedstock that remain after distillation. Because of the nature of the distillation process (atmospheric or vacuum), most of the heavy metals would be expected to be found in the residual fuel oil. This appears to be the general rule that is easily demonstrated.

However, the mere presence of a metal, such as chromium, in the fuel, does not necessarily imply that it is in a toxic form in the turbine exhaust. For chromium, the oxidation state of concern is the +6. A 1998 survey of industrial boilers using heavy oil reported that the metal of critical concern was Nickel. In the case of Nickel, it is the presence of nickel-subsulfide (Ni_2S_3) that is the hazardous component. But it is not the nickel oxide of concern, NiO, but the nickel subsulfide (Ni_2S_3). However, nickel sub-sulfide is in a reduced state, a condition that should be difficult to maintain in intense industrial burner.

With the recent regulatory focus on a wide range of industries, there has been intense focus to determine what compounds represent any real, or potential hazard. A recent survey of residual fuels used in large boilers indicated that nickel was present in ranges from 30-40 ppm, significantly higher than the levels of nickel observed in the current fuel study)[1]. Stack test measurements revealed that there was no evidence of reduced nickel in the particulates, indicating that good combustion (and excess oxygen levels) are effective means of fully oxidizing all the compounds in the fuel. We would expect similar results from the nickel present in the No. 2 fuel oil samples noted in this study.

In a 1999 survey of crude oil samples, McGaw reported data on 18 metals trace metals in a wide range of crude oil samples[2]. A comparison of the average concentrations found in the McGaw reveals are markedly improved compared to the distillate samples from this study.

Table 2. Comparison Of Crude Samples With Distillate Results

Metal	As	Cr	Pb	Ni	Hg	Cd
Concentration in crude oil samples (McGaw 1999 study), ppb	60	270	32	19690	60	10
Concentrations in distillate fuel oil (this study). ppb	0	242	15	28	0	0

In a study on Iowa ground water quality, researchers used similar techniques as those selected here to identify any role between underground storage of fuels and possible aquifer contamination.[3] The Iowa ground water survey examined transportation fuels, which are even more tightly specified than the fuels used in gas turbines. The authors of that study also failed to identify the presence of any mercury in No. 2 diesel fuels taken from selected regional sources. The highest chromium reported in the study was only 31 ppb, although there was no attempt to identify the presence of any specific

oxidation states of the chromium. In essence, this earlier study from a relatively select group of sources further confirms the high quality, and lack of toxic metals, in the US distillate fuels base.

Conclusions

Gas turbine liquid fuel samples were characterized for the presence of eight trace hazardous metals. The study revealed that many of the metals of concerned (including mercury and arsenic) are not present at any level above the detection limits of the ICP-MS used. Chromium is not present in the +6 oxidation state, the oxidation state of most concern. Nickel is present at even lower concentrations, but there is no evidence that nickel could form the toxic sulfide compound during a combustion process that occurs with excess oxygen available. The source of lead is probably due to cross contamination from the small quantities of leaded fuels that are still used today (aviation gasoline is still marketed as a low lead fuel).

References

(1) *"Nickel Speciation of Flyash from Residual Oil-Fired Power Plants"*, Kevin Galbreath, University of North Dakota Energy & Environmental Research Center; presented at Air Quality IV, 22-24 Sep 2003, Arlington, Va.

(2) Magaw, RI, McMillen, SJ, Gala, WR., 1999. Risk evaluation of metals in crude oils: *Proc. 6th Int'l Petrol. Environmental Conf.* Nov. 16-18, Houston, TX, pp. 460-473.

(3) Rich Heathcote, Don Simmons, and Steven Hernholz, *Analysis of Motor-Vehicle Fuels for Metals by Inductively Coupled Plasma-Mass Spectrometry;* Hygenic Laboratory**,** Volume 39, No. 4, pp. 1-4, 2001, The University of Iowa.