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Accuracy of Trace Element Determinations in Alternate Fuels

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ABSTRACT

A renewed interest in characterization of fuels and alternate fuel sources has arisen in this country. Much of the research being conducted is directed toward developing usable fuels from other sources, such as coal and shale, as well as through the use of lower quality petroleum fuel.

NASA-Lewis Research Center (LeRC) is very active in the fuels work, especially with respect to current programs in aeronautics, ground transportation, and ground power. An important aspect of LeRC's fuels characterization is the measurement of trace levels of metals.

A primary concern in trace analysis is that the precision in the measurements between laboratories and between analytical techniques has been poor, especially for concentrations below 10 ppm. Good analytical measurements on any system at trace levels require experience and extreme care during sample preparation, therefore, with a system as complex as a fuel, the difficulties indicated by the available data are not unexpected.

A review of the techniques used at LeRC in trace metals analysis will be presented, including the results of Atomic Absorption Spectrometry (AAS) and DC Arc Emission Spectrometry (dc arc) of blank levels and recovery experiments for several metals.

The design of an Interlaboratory Study being conducted by LeRC will be presented. Several factors are under investigation, including: laboratory, analytical technique, fuel type, concentration, and ashing additive. It is hoped that conclusions drawn from the statistical analysis will help direct our research efforts toward those areas most responsible for the poor interlaboratory analytical results.

INTRODUCTION

Due to the continuing decline of available petroleum resources a great effort has been launched in this country to develop alternate fuel sources. To eliminate our foreign dependency on petroleum crude is certainly a major factor, however, there are several economic reasons as well. The U.S. possesses a considerable amount of oil shale and coal. Both have proven to be viable sources of liquid hydrocarbon fuel (Refs. 1 and 2). Although development of alternate fuel sources is essential if we are to meet our future demands, the continued use of petroleum derived fuels is also desirable. However, because refining fuels to the specifications required for good turbine engine performance and durability is a costly operation, much work is being conducted in materials research and engine design to develop components which can provide high efficiency yet withstand the use of fuels with broader ranges of properties than are presently specified.

The measurement of metals in fuels is one important area of NASA Lewis Research Center's fuels characterization programs. In order to provide accurate data for in-house research projects and to help develop the technology, studies have been started to improve the sensitivity, precision, and accuracy of trace metal analysis in fuels. Some metals have been shown to cause engine component failure at concentration ranges of a few parts-per-million (ppm or 10^{-6}) and below. Appendix A contains information concerning the known detrimental effects of trace metals in fuels. A discussion of the chemical forms and distribution of the metals in fuels is presented in Appendix B.

There has been much work published concerning the determination of trace metals in fuels, and repeatedly the precision among laboratories has been poor, especially for concentrations below 10 ppm, in spite of good precision within a laboratory (Refs. 3 to 5). Laboratories considered to be experienced in fuels analysis have reported results which disagree up to several orders of magnitude for a given sample. For an example, consider the data given in Table I. In an attempt to provide a trace element standard for use in petroleum analysis, the National Bureau of Standards (NBS) and the Environmental Protection Agency (EPA) distributed a residual fuel oil for analysis to 50 laboratories (Ref. 4). The table lists actual results for only a few of the elements under consideration and some of the laboratories. The ranges, however, were established from the values given for all laboratories. The difference in reported results for a given element covers as much as four orders of magnitude. Results for Ni and V varied over one order of magnitude and resulted in NBS certification at 36±4 ppm and 320±15 ppm, respectively (NBS SRM 1634). Interlaboratory precision and accuracy must be achieved to allow meaningful communication between the researcher, the refiner, and the end user.

EXPERIMENTAL

Apparatus

Sample containers. - All volumetric glassware was cleaned using hot 1:1 aqueous nitric acid.

Polyethylene containers, used for storage of the prepared fuel sample, were cleaned by leaching with 1:1 aqueous hydrochloric acid for 1 week, with 1:1 aqueous nitric acid for 1 week, and stored, after filling with deionized water, until use (Ref. 6).

High purity silica crucibles (Vycor brand, Corning Glass Works, Corning, NY) used during fuel preparation, were cleaned by fuming in sulfuric acid or aqua regia ($3HCl:1\ HNO_3$).

Clean air facility. - This laboratory has constructed a clean area which combines the principles of vertical laminar air flow through high-efficiency particulate air (HEPA) filters and positive-pressure principles. The HEPA filters will remove all particles larger than 0.3 microns. The clean area, shown in Fig. 1, has a working area of 32 ft^2. Curtains were placed around the filtered area to help maintain positive pressure conditions. The clean air is forced directly in front of a fume hood so that all make-up air used by the hood has been filtered. A chamber constructed entirely of chemically resistant polymethyl methacrylate was placed inside the fume hood so that the samples are in an area free from potentially corrosive material that could cause contamination.

Instrumentation. - An Instrumentation Laboratory Model No. 153 Absorption Spectrometer and an argon stabilized direct-current arc emission spectrometer (NASA LeRC) were used for all trace metal measurements.

Reagents and Standards

The reagents used during sample preparation included nitric (HNO_3), hydrochloric (HCl), and sulfuric acids (H_2SO_4). All were high-purity materials (Ultrex grade) obtained from J. T. Baker Chemical Co., Phillipsburg, NJ.

Aqueous inorganic standards were used for instrument calibration. Single element solutions prepared from the metal of interest were used for all atomic absorption spectrometric measurements, while a multielement solution was used for all dc arc measurements.

The Conostan reference material, designated C-21 (Continental Oil Co., Ponca City, OK), was used throughout this study to represent a fuel with known metal concentrations.

Fuel Samples

Although this discussion of analysis of trace metals in fuels could apply to any of the liquid fuels, derived from petroleum, shale oil or coal, the examples to be presented are limited to the following:

(1) Experimental Referee Broadened - Specification Fuel (ERBS)
A petroleum derived aviation turbine fuel blend prepared by the addition of 65 percent kerosine and 35 percent hydrotreated catalytic gas oil. The ERBS fuel is a research fuel blended to represent a possible future jet fuel (Ref. 7).

(2) Residual Fuel Oil (RFO)
The highest boiling fraction of a crude petroleum.

(3) Paraho Shale Oil
A shale derived fuel, where Paraho refers to the particular process used to recover the crude oil (Refs. 1 and 8).

(4) Solvent Refined Coal II (SRC II)
A fuel derived from coal using a solvent extraction process (Ref. 2).

Fuel Preparation Scheme

The sample size used varied with the expected concentration levels of the elements to be measured. A multielement analysis of RFO required ashing of approximately 3 g of sample, whereas, the ERBS fuel required a minimum of 25 g. The samples were weighed directly into a clean, dry crucible. One milliliter (ml) of the desired ashing additive (H_2SO_4 or HNO_3) was introduced into the crucibles using an Eppindorff pipet. A separate crucible, containing no fuel, was treated identically to the samples and served as the blank for the ashing steps. The dry ashing procedure involved the evaporation of the sample's volatile materials, including those produced by thermal cracking or partial oxidation. This was performed on a hot plate placed inside the chamber in the clean air facility. An infrared lamp, positioned outside the chamber was used to provide a more even heating of the fuel. A rapid heating rate may result in sample loss, either by spraying or bumping. Heating continued until all sample fuming had ceased and a solid, charred mass was obtained. This process required as long as two weeks depending on the type of fuel. The ashing process was completed in a quartz-lined muffle furnace at a temperature of 450° C.

Measurement Procedures

Once the fuel sample had been ashed the preparation procedure varied slightly, depending on the measurement technique used. The ash was dissolved using 1 to 2 ml concentrated HCl and 0.2 ml concentrated HNO_3. In some instances mild heating was required to complete dissolution. This solution was quantitatively transferred to a polyethylene container and diluted to an appropriate level for AAS measurement using an acetylene-air flame. The wavelength of the absorbing lines used for the measurements and the type of flame used are presented in Table II. The slit, hollow-cathode lamp current, and photomultiplier tube voltage used were those suggested by the manufacturer. Sample preparation for dc arc measurements involved mixing the ash with 0.1 ml concentrated HCl (with mild heating), 0.1 ml concentrated HNO_3, and 0.1ml H_2O. A fraction of or the total sample was quantitatively doped onto a high-purity carbon electrode for measurement (Ref. 9). The wavelength of the atomic emission lines used for the analysis are shown in Table III.

RESULTS AND DISCUSSION

Accuracy of Trace Metal Measurements

The accuracy required for an analytical measurement is determined by the intended use of the data. Often an internal laboratory consistency, or precision, is adequate if the immediate analytical problem can be monitored by observing changes in concentration levels. However, if the highest degree of accuracy possible is required, excellent reproducibility alone is meaningless. For example, obtaining accurate results is essential for measuring emission of toxic elements during fuel combustion, so that maximum allowable levels can be established and reliable testing can be performed. A predicting capability of the metals which cause corrosion has been made possible using a computer program for calculating complex equilibrium compositions of corrosion products following fuel combustion. Accurate input of reactants was manadatory in developing the theoretical combustion model (Ref. 10).

The results of an interlaboratory study conducted by LeRC are shown in Fig. 2. The bar graph depicts the ranges of results for 7 elements in a light, middle, and heavy fraction of an SRC II fuel. The samples were distributed to 3 laboratories for analysis by Instrumental Neutron Activation Analysis (INAA), Inductively Coupled Plasma Emission Spectroscopy (ICP), and Spark Source Mass Spectrometry (SSMS). Analysis by DC Arc Emission Spectrometry and Atomic Absorption Spectrometry was performed at LeRC. The results showed poor interlaboratory precision, ranging up to 5 orders of magnitude, for the light and middle fractions containing the lowest metal concentrations. Discouraging results of interlaboratory exercises, such as this, clearly demonstrates the errors involved with many analytical procedures at the ppm level.

A particular problem for the analyst is the lack of available SRMs with a certified trace content in a specific fuel matrix (Ref. 11). Table IV contains a list of those standards available. NBS SRM 1634, a residual fuel oil, has very few certified elements and the typical levels are higher than the concentrations of interest in our work. The Conostan reference materials, metal sulfonates in an hydrocarbon base oil, are useful, but there are no standards which possess the metal in the proportions typically found in fuels. Development of new SRMs possessing a distribution of metals more representative of a fuel matrix are required.

Dry Ashing Procedure

An ideal approach to fuels analysis would involve direct measurement of the element in an intact sample (INAA, X-Ray Fluorescence), however, the organic matrix, suspended particulates, as well as other metals present may seriously affect the behavior of the trace constituent. Also, because the concentration levels are typically less than 10 ppm the analytical technique requires preconcentration before analysis. The preparation techniques that are most commonly used for trace metal measurements in fuels include: extraction, wet oxidation, dry oxidation, and low temperature plasma ashing (Refs. 12 to 17)

A dry ashing procedure has been adopted by the author because it has proved to be the most practical and effective method of concentrating the fuel sample for multi-element analysis. Since few reagents are required in this procedure there is a reduced possibility of contamination from reagents.

The dry ashing technique is susceptible to elemental losses by volatilization and crucible retention. Volatilization losses may occur if the element to be determined is present in a volatile form or can react with some constituent of the sample to produce a volatile species (Ref. 18). During the fuel preparation procedure the temperature is no greater than 450° C, high enough to completely ash the organic constituents, yet in a temperature range where volatilization can be minimized. Retention losses may occur if there is a reaction between the sample and the crucible which forms a product insoluble in the reagents used to dissolve the sample ash. Two mechanisms leading to retention of trace elements in the crucible have been proposed:

(1) The formation of silicate glasses by reaction of the metal oxides with the silica crucibles.
(2) The reduction of the oxide to a metal and subsequent diffusion into the crucible (Ref. 19).

Two crucible types have been used in the analysis of fuels. Platinum crucibles were tried initially, however, on continued use sharp increases in the levels of the blanks were observed. It was concluded that the crucibles were demonstrating "memory effects," that is, the elements trapped in the crucible from previous ashings were being slowly released during later analyses at various and inconsistent rates. Due to the difficulties encountered with platinum crucibles high purity silica crucibles are now routinely used.

The dry ashing procedure may be made more efficient if performed with the addition of an ashing aid (Refs. 18 and 20). It may serve to accelerate decomposition of the organic material, improve the recovery by preventing volatilization of an element, or prevent retention of elements due to reaction between the sample and the crucible material. Ashing aids were used during the fuel preparation process. Sulfuric acid was the additive most commonly used in this work because of its ability to convert potentially volatile compounds into the higher-boiling sulfates. It was also particularly useful for oxidative ashing of fuels due to its ability to destroy metal-porphyrin complexes, which are highly volatile forms of some metals in fuels.

Table V contains typical metal concentrations (ppm) measured, in ERBS, RFO, SRC II, and Paraho Oil Shale fuel samples. These samples were prepared using the ashing procedure presented and all results were obtained using the dc arc emission spectrograph. The values reported as "less than" (<) indicate that the level of the element was lower than the detection limit of the instrument, therefore, this number was the highest concentration possible.

Blank Level Study

Earlier work, in this laboratory, indicated that the blank levels were hampering the ability to measure the metal content of the fuels at very low concentrations. Improvement in the fuels preparation procedure (high purity silica crucibles and acids and the use of a clean air facility) substantially reduced the blanks, thus allowing effective measurements in fuel samples at lower concentrations. The lower limit of detection for an element is seldom restricted by the sensitivity of the technique, but rather, determined by the variability of the blank. Since the blank plays such an important role in analysis of trace levels, a study was designed to observe blank flunctuations during fuel preparation procedures. The Conostan C-21 standard was chosen to represent a fuel. Changes in the blank levels were observed before and after ashing of the fuel matrix. New silica crucible were used so the history of each crucible was known, which allowed for a more accurate determination of the effect of the reaction vessel on the blank levels. Two crucible cleaning procedures were also compared; sulfuric acid fuming versus aqua regia fuming between each blank and fuel ashing step. The blanks were prepared following the exact procedure that would be used for a fuel sample. Measurements were made for 12 elements using AAS and 20 elements using the dc arc.

The blank adsorption values, measured by AAS at the optimum wavelength of each element, represented the apparent blank that would be subtracted from the fuel sample absorption. The intensity of absorption for each element was measured relative to deionized water and the apparent concentration was calculated by comparison to an inorganic standard. The blank value can be attributed to the signal produced from all blank components. Figure 3 is a plot of the blank level versus the number of uses of the crucible for six elements: Cd, Cr, Fe, Mg, Ni, and Zn. Adjacent graphs show the blank levels found in crucibles U and V, cleaned using sulfuric acid, and the levels measured in crucibles X and Y, cleaned using aqua regia.

The blank level measurements by dc arc were adjusted by a separate reagent blank. Due to its greater sensitivity, these levels are a better representation of the magnitude of elemental contamination obtained through the ashing procedure. Table VI lists the weights of the 20 elements measured in the blank. Crucible W was cleaned using sulfuric acid and crucible Z using aqua regia. Columns 2 and 3 present the values for each element in a blank using a new crucible while columns 4 and 5 list the blank levels after one ashing of the fuel.

The trace metal results reported for the blank study are only preliminary in nature. Measurements by both methods do not indicate that one cleaning procedure is better than the other for most of the elements studied. However, the levels of Al, B, and Si, all known components of the silica crucibles, increased following one ashing of a fuel sample. This was true using either crucible cleaning method but was much more pronounced in the aqua regia cleaned crucible. Additional measurements will be required to determine the extent of contamination due to the crucible and that which may result from the release of other previously trapped elements.

Trace Metal Recovery Study

Between each blank measurement made in the blank study a known amount of Conostan C-21 standard was ashed. The desired elements were measured in these samples to determine the recovery of trace metals. Table VII lists the AAS and dc arc percent recoveries for 6 elements. The blank corrections were made by subtracting the level of the previous blank measured in the same crucible.

The standard deviation of the measurements from 6 different fuel ashings are presented for the AAS results, however, the average percent recovery of each element using the dc arc was based on two ashings, therefore, only the range is reported. The average percent recoveries of trace metals are not extremely good, however, in view of the interlaboratory results, previously presented, which in some cases ranged over 5 orders of magnitude, these results appear to be very acceptable, particularly considering measurement of microgram quantities. The error introduced from the recoveries are trivial when compared to the total errors in the fuels analysis. However, it should be noted that in the recovery studies described above, the metals are present as sulfonates, a desirable form of the metal when using a dry ashing preparation scheme. Additional methods to demonstrate accuracy in trace metal measurements of actual fuel samples are required.

Experimental Design of a Fuels Interlaboratory Study

Several sources of error exist in trace metal analysis of liquid fuels, which may include procedures in the sampling technique, sample preparation, and the actual measurement stage. Each of these areas will require careful evaluation (Refs. 21 to 23). Although many investigators have planned or participated in interlaboratory studies of fuels, few have used a design planned to address specific questions concerning these sources of errors in the analysis. By use of a statistical design the effects of many important factors can be studied in one experiment as well as the interrelationship between these factors. In all such experiments one seeks to obtain the maximum amount of reliable information at the minimum cost to the experiimenter.

The dependent variable is the value determined in the experiment. The levels of the different factors are varied in a predetermined manner and how these changes effect the dependent variable is measured. The dependent variable in this experiment is the concentration (ppm) of the element. The factors chosen in this study and their levels are listed in Table VIII.

The study was conducted using commercial services, rather than a cooperative effort among laboratories for three reasons:

(1) To enable this laboratory to specify the fuel preparation procedure to be used.
(2) To assure obtaining all results for the planned statistical analysis of the effects, in a minimum time period.
(3) To test the reliability of the typical commerical laboratory.

All equipment and reagents necessary for the fuels analysis were specified so as to minimize additional variability due to an unknown preparation. Silica crucibles and high purity acids, were required. The temperature for ashing was established at 450° C. The use of a clean air facility was requested however, because they are not in widespread use, it was not always possible. The laboratories were not informed that they were participating in an interlaboratory study to guarantee that the samples would not be given additional care over a routine sample.

The experiment was designed to focus specifically on a dry ashing scheme. To determine the necessity of an ashing aid in the analysis three preparations were used. Each laboratory was to use AAS and one multielement technique. AAS analysis was limited to 8 of the 20 elements because of the cost factor involved when using a single element method. The fuels were chosen to provide samples with a varied fuel matrix, as well as, the particular fuels that would be important for the work conducted at LeRC. Residual fuel oil was used to provide a fuel with a relatively high metal content. A fuel blend was included to act as a control fuel to obtain a measure of the reliability of the laboratories' results. Each fuel type was distributed at a high and low metal concentration to test whether varying concentrations of an element in a given matrix affected the result obtained.

The statistical analysis of the data will be performed using the Analysis of Variance (Refs. 24 and 25). In this form of statistical analysis, the souces of variation are partitioned into their individual components (variation between levels of a particular factor or a variation caused by the interaction of changing levels of 2 or more factors). The expected relationship of these variance components can be derived, based on the experimental design model, and these expressions indicate the appropriate comparison to be made to measure the effects of each factor and their interactions.

The results are still being reported so no statistical analysis has begun. However, those results reported are showing considerable variation. Even with a rigidly specified preparation scheme, the results are still ranging up to 4 orders of magnitude.

CONCLUDING REMARKS

NASA-Lewis Research Center is seeking sub-ppm abilities in trace metal analysis in fuels. Instruments are capable of the required sensitivity, it is our lack of understanding of the complex systems of real samples and effective preparation techniques which are limiting our ability to obtain precision and accuracy.

Presently, we have focused solely on a dry ashing preparation scheme and have been working to reduce the blank size and variability. Additional studies will be required to more fully characterize this preparation procedure, with respect to volatilization, ashing aid effectiveness, and methods of measuring accuracy in trace metal determinations.

APPENDIX A

ADVERSE EFFECTS OF METALS IN FUELS

Although, most metals in the fuels are present of trace levels, some elements have been shown to adversly effect fuel processes on fuel using systems. Four major areas of concern exist:

(1) Detrimental effects on turbine blades
(2) Jet fuel thermal stability
(3) Effects on catalysts used in refining processes
(4) Air pollution.

The efficiency of turbines, both aeronautical and terrestial, may be reduced due to effects of trace metals and particulates in the fuels used. Refinery fuel treatments, such as filtration, use of fuel additives, and water-washing are used to upgrade the quality of the fuel by reducing the metal concentration to minimum levels. The typical upper limits allowed by refiners on the concentration of those metals, which may lead to high-temperature corrosion, are Na plus K, 150 ppm; Ca, 10 ppm; Pb, 1 ppm; and V, 0.5 ppm (Ref. 26). These metals form sulfates with S, which may melt on the turbine blades, at the high temperature obtained during operation, and dissolve the protective oxide coating leaving the metal surfaces open to oxidation, by elements such as Ca, P, and Mg. Turbine performance may also be reduced during the formation of ash deposits, which on build-up may partially, or totally, block the gas path (Refs. 27 to 29). Continued research in this area may lead to the recognition of other elements which may contribute to turbine component corrosion.

A major problem, particularly to the aeronautics field, is jet fuel thermal oxidative stability. Fuel thermal stability studies are concerned with the effects of fuel derived sediments and deposits resulting from chemical reactions when exposed to high temperatures. Thermal stability is dependent on the fuel's chemical composition as well as the environment to which it is exposed. Very thin, polymer deposits can block valves throughout the system. In places where fuel residence time is long, deposits can become very thick, flake off, and block down-stream passages (Refs. 30 and 31). One investigation of a fuel, which had caused deposition problems, showed the fuel to contain trace levels of Cu and Pb. Further tests showed that by addition of as little as 0.1 ppm of copper napthenate, oxidation reactions were substantially accelerated (Ref. 32). In a study using JP-7, a military kerosine fuel, the metal levels required to produce a significant change in the fuel's thermal stability were 0.015 ppm Cu, 0.025 ppm Fe, 0.1 ppm Zn, and 0.1-0.25 ppm Pb (Ref. 33). However, it was noted that there was some difficulty defining the concentration levels due to the interpretation of the deposits and in maintaining the metal in solution.

Several metallic elements, such as As, Cu, Fe, Ni, Ti, and V have been shown to alter the effects of catalysts used during the processing of petroleum and syncrudes (Ref. 27). They act either to change the selectivity of the catalyst or to poison it.

Determination of trace metals that pose environmental hazards has been of great concern. Environmental monitoring agencies have placed tighter restrictions on pollution control. This has initiated much effort toward achieving accurate determinations of such elements as As, Cd, Hg, Ni, Pb, Se, V, and S which are released during fuel combustion (Ref. 34).

APPENDIX B

BACKGROUND

Crude oil shows considerable variation in composition depending on the age, geological, and geographical location. The principal constituents of petroleum are hydrocarbons, including alkanes, cycloalkanes, alkenes, aromatics, and mixed hydrocarbons. Small quantities of non-hydrocarbon constituents are also present in all crude oils. These are heterocyclic compounds, which contain sulfur, oxygen, and nitrogen, and a variety of metallic elements (Ref. 1). Liquid fuels derived from coal and oil shale also possess much compositional variation, however, typically at different levels. For example, fuels from oil shale show a higher nitrogen content, while fuels from coals possess a higher percentage of aromatic compounds.

These crudes derived from (petroleum, shale, and coal) undergo a number of refining processes as well as separation by distillation to yield various fractions. The trace element compositions of a fuel reflects the fuel source and the particular refining processes it has undergone. The chemical form of the metals may be as metalloporphyrin chelates, transition metal complexes of tetradentate mixed ligands, organometallic complexes, carboxylic acid salts, or as inorganic particulates (Ref. 35). These metals may be native to the crude, introduced during storage or transport, or intentionally present as an additive to improve a particular fuel property. During fractionation of the crude into useable fuel products, most of the metals are concentrated in the residual oil, therefore, the element concentrations of distillate oil tend to be very low (Ref. 36). Table V demonstrates the difference in metal concentration between two petroleum derived fuels, ERBS, a light distillate fraction, and RFO, the heaviest fraction.

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TABLE I. - NBS-EPA INTERLABORATORY COMPARISON FOR ELEMENTS IN FUEL OIL, SRM 1634

Instrumental Technique[a]	Concentration Reported, ppm					Concentration Range, ppm[b]
Cadmium						
AAS	0.22	0.26	0.24	0.27	0.24	0.019-<10.0
OES[c]	7.0	7.0	6.0	7.0	6.0	
Chromium						
AAS	0.67	0.72	0.75	0.75	0.72	0.031-12
INAA	0.0724	0.0902	0.0900	0.0913	0.0998	
	0.0940	0.0945	0.1053	0.0960		
Nickel						
AAS	40.0	40.0	37.5	38.0	37.5	5.0-74.0
AAS	14.3	13.3	13.1	13.1	5.0	
SSMS[d]	5.0	5.0	10.0	10.0	5.0	
INAA	38.22	35.30	37.34	38.22	35.22	
	36.90	37.94	39.60	37.82		
Lead						
AAS	3.51	3.67	3.47	3.64	3.64	0.08-<40.0
OES	0.10	0.10	0.08	0.12	0.45	
Other	20.0	17.0	17.0	21.0	18.0	
Vanadium						
AAS	243.0	250.0	254.0	262.0	264.0	22.1-700
AAS	434.0	449.0	440.0	442.0	456.0	
XRF[e]	299.0	301.0	298.0	293.0	298.0	
INAA	332.6	312.0	301.6	304.1	295.3	
		333.8	321.8	292.5		

[a] Each technique listed was performed at different laboratories.
[b] Range was determined from results reported by all laboratories.
[c] Optical Emission Spectroscopy.
[d] Spark Source Mass Spectrometry.
[e] X-Ray Fluorescence Spectrometry.

TABLE II. - WAVELENGTH AND FLAME CHARACTER USED FOR AAS MEASUREMENTS

Element	Wavelength, nm	Flame* Characteristic
Cd	228.8	Rich
Cr	357.9	Lean
Fe	248.3	Lean
Mg	285.2	Stoichiometric-Rich
Ni	232.0	Stoichiometric
Zn	213.9	Rich

*An air-acetylene flame was used for all elements.

TABLE III. - WAVELENGTHS OF THE EMISSION LINES USED IN D.C. ARC MEASUREMENTS

Element	Wavelength, nm	Element	Wavelength, nm
Al	394.4	Mo	386.4
B	249.8	Na	589.0
Ba	389.2	Ni	356.6
Ca	396.8	P	255.3
Cd	346.6	Pb	283.3
Cr	425.4	Si	288.2
Cu	324.8	Sn	317.5
Fe	372.0	Ti	334.9
Mg	279.6	V	310.2
Mn	257.6	Zn	213.9

TABLE IV. - AVAILABLE STANDARDS FOR ANALYSIS OF FUELS

<table>
<tr><th colspan="4">Standard Reference Material 1634
Residual Fuel Oil</th><th colspan="2">General Materials GM-5
Residual Fuel Oil</th></tr>
<tr><th>Element</th><th>NBS Certified Concentration, ppm</th><th>Element</th><th>Suggested Concentration</th><th>Element</th><th>Concentration, ppm</th></tr>
<tr><td>Fe</td><td>13.5±1.0</td><td>As</td><td>0.0095</td><td></td><td></td></tr>
<tr><td>Ni</td><td>36±4</td><td>Be</td><td><0.01</td><td>Ni</td><td>93.0±1.2</td></tr>
<tr><td>Pb</td><td>0.041±0.005</td><td>Cd</td><td><0.01</td><td></td><td></td></tr>
<tr><td>S</td><td>2.14±0.02(%)</td><td>Cr</td><td>0.09</td><td>V</td><td>79.0±1.2</td></tr>
<tr><td>V</td><td>320± 15</td><td>Hg</td><td>0.0023</td><td></td><td></td></tr>
<tr><td>Zn</td><td>0.23±0.05</td><td>Mn</td><td>0.12</td><td></td><td></td></tr>
<tr><th colspan="6">Conostan Metallorganic Standards</th></tr>
<tr><td colspan="2">Single Element Standards (5000 ppm)</td><td></td><td colspan="3">Ag Al B Ba Be Bi Ca Cd Co Cr Cu Fe
K La Li Mg Mn Mo Na Ni P Pb Sb Si
Sn Ti V Y Zn</td></tr>
<tr><td colspan="2">Blended Standards (900, 500, 300, 100, 50, 30, and 10 ppm)</td><td>C-12</td><td colspan="3">Ag Al Cr Cu Fe Mg Ni Pb Si
Sn Ti</td></tr>
<tr><td colspan="2"></td><td>C-21</td><td colspan="3">C-12 elements + B Ba Ca Cd Mn Mo P V Zn</td></tr>
</table>

TABLE V. - TYPICAL TRACE METAL LEVELS IN VARIOUS FUELS
DC ARC EMISSION

Element	ERBS[a] Fuel	Residual Fuel Oil	Solvent Refined Coal (II)[b]	Paraho[c] Shale
Al	0.0005	7.4	0.2	4.2
B	0.0006	1.6	0.4	<20
Ba	NA[d]	3.4	<0.08	<0.01
Ca	0.001	15.6	0.04	39
Cd	<0.0004	<0.4	<0.004	NA
Co	NA	0.9	<0.0001	0.3
Cr	<0.0001	0.6	2.8	0.04
Cu	0.01	1.6	0.02	0.1
Fe	0.002	18.4	9.3	23.8
Mg	0.0002	4.5	0.1	44.6
Mn	<0.0003	0.4	0.2	0.4
Mo	0.001	<0.06	<0.004	0.08
Na	0.003	41.1	0.4	5.6
Ni	0.002	12.3	0.09	0.8
Pb	0.08	0.4	<0.2	<1
Si	0.02	13.6	0.3	10.3
Sn	0.001	<0.08	<0.02	<1
Sr	NA	0.2	0.0007	0.2
Ti	<0.0003	0.5	0.2	0.5
V	0.0008	4.9	0.7	0.7
Zn	0.001	8.2	<0.2	2

All results are reported in ppm.

[a] Refer to reference 7.
[b] A middle distillate fuel fraction.
[c] Refer to reference 8.
[d] NA - Element was not analyzed.

TABLE VI. - METAL CONCENTRATION LEVELS OF FUEL BLANKS
MEASURED BY DC ARC EMISSION SPECTROMETRY

Element	New Crucibles		Crucibles After 1 Fuel Ashing	
	W	Z	W[a]	Z[b]
Al	0.07	0.03	0.4	1.0
B	<0.03	<0.03	3.2	51.2
Ba	<0.03	<0.03	<0.03	<0.03
Ca	0.01	<0.003	0.04	0.04
Cd	<0.06	<0.06	<0.06	<0.06
Cr	0.001	0.004	0.002	0.007
Cu	0.006	<0.002	<0.002	<0.002
Fe	0.08	0.05	0.01	0.03
Mg	0.03	0.004	0.004	0.003
Mn	<0.0008	<0.0008	<0.0008	<0.0008
Mo	<0.002	<0.002	<0.002	<0.002
Na	<0.25	<0.20	<0.20	<0.20
Ni	0.07	<0.003	<0.003	<0.003
P	<1.3	<1.3	<1.3	<1.3
Pb	<0.03	<0.03	<0.03	<0.03
Si	2.0	1.4	0.6	2.1
Sn	<0.03	<0.03	<0.03	<0.03
Ti	<0.01	<0.01	<0.001	<0.001
V	<0.003	<0.003	<0.003	<0.003
Zn	0.1	<0.03	<0.03	<0.03

All results reported in micrograms (ug, 10^{-3}g)

[a] Blank was prepared following ashing of a 24.9 μg sample of Conostan C-21 reference material.

[b] Blank was prepared following ashing of a 31.7 μg sample of C-21.

TABLE VII - PERCENT RECOVERY OF METALS BY ATOMIC ABSORPTION SPECTROMETRY AND DC ARC EMISSION SPECTROMETRY

Element	Average Percent Recovery			
	H_2SO_4 Cleaned Crucibles		Aqua Regia Cleaned Crucibles	
	AAS (± Std. Dev.)	DC ARC (Range)	AAS (± Std. Dev.)	DC ARC (Range)
Cr	86.0±7.8	91.4 (25.1)	87.9+4.8	99.3 (22.6)
Cu	96.2±5.7	73.9 (20.8)	98.6±5.9	75.1 (17.8)
Fe	96.0±13.2	75.8 (21.9)	93.5±13.9	81.8 (21.6)
Mg	107.2±4.8	93.9 (21.6)	103.3±8.0	102.6 (51.5)
Mn	103.0±2.2	89.1 (5.6)	104.9±2.6	98.7 (23.0)
Na	99.7±11.6	79.8	97.0±6.4	69.8
Pb	98.7±12.4	71.2 (9.3)	100.4±11.3	73.4 (17.3)
Zn	100.4±3.3	70.4 (1.2)	101.4±3.2	83.8 (9.4)

TABLE VIII. - EXPERIMENTAL DESIGN FACTORS USED IN INTERLABORATORY STUDY OF TRACE METALS IN FUELS

Factor	Level	
Laboratory	Commercial (4) Academic (1) Government (1)	
Analytical Technique	AAS DC Arc DC Plasma INAA SSMS	
Fuel	ERBS SRC (II) RFO SRC (II) + RFO Blend	
Concentration	High	Low
	ERBS + C-21	ERBS
	SRC (II) + C-21	SRC (II)
	RFO	RFO + Xylene
	35% SRC (II) + 65% RFO	72% SRC (II) + 28% RFO
Ashing Additive	None H_2SO_4 HNO_3	
Element	Multielement Technique - Al, Ba, B, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Sr, Ti, V, Zn Single Element Technique - Al, Cr, Fe, Mg, Mn, Na, Ni, Zn	

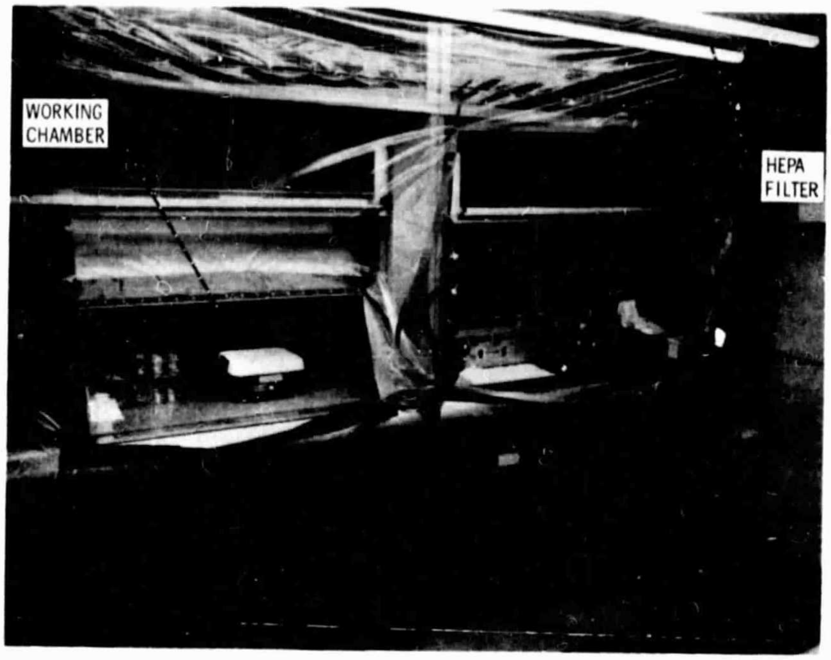

Figure 1. - Clean air facility.

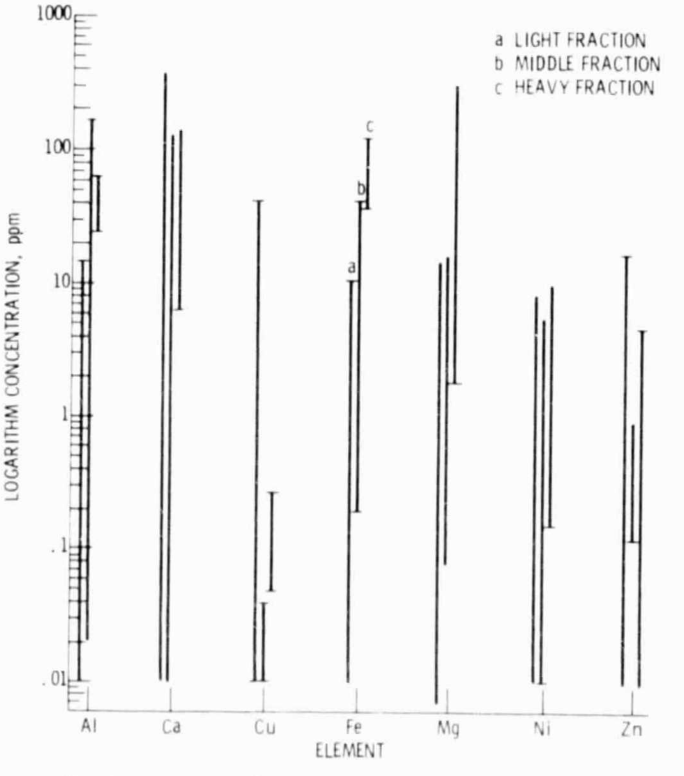

Figure 2. - Bar graph of elemental concentration ranges reported in NASA's interlaboratory study of Solvent Refined Coal (II).

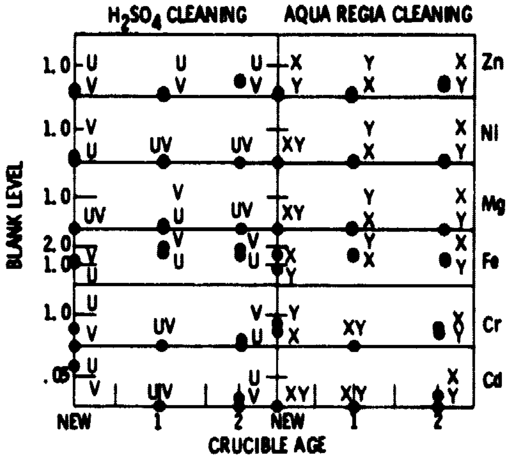

Figure 3. - Trace metal levels of the blanks measured by Atomic Absorption Spectrometry.