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Experimental Design of an Interlaboratory Study for Trace Metal Analysis of Liquid Fluids

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Summary

The accurate determination of trace metals in fuels is an important requirement in much of the research into and development of alternative fuels for aerospace applications. Recognizing the detrimental effects of certain metals on fuel performance and fuel systems at the part-per-million and in some cases part-per-billion levels requires improved accuracy in determining these low-concentration elements. Accurate analyses are also required to ensure interchangeability of analysis results between vendor, researcher, and end user for purposes of quality control.

The metal concentration levels of the fuels of particular interest to projects at the NASA Lewis Research Center are typically less than 10 parts per million. Previous interlaboratory studies have demonstrated the inability of different laboratories to agree on the results of metal analysis, particularly at low concentration levels, yet typically good precisions are reported within a laboratory.

An interlaboratory study was designed to gain statistical information about the sources of variation in the reported concentrations. Five participant laboratories were used on a fee basis and were not informed of the purpose of the analyses. This laboratory served as the sixth participant in the study. The effects of laboratory, analytical technique, concentration level, and ashing additive were studied in four fuel types for 20 elements of interest. The prescribed sample preparation schemes (variations of dry ashing) were used by all of the laboratories. The analytical data were statistically evaluated by using a computer program for the analysis-of-variance technique.

Independent analyses evaluating the magnitude and variability of the blank have provided information concerning possible sources of error. Metal recovery studies have supplied additional information concerning the merits of the preparation procedure used for the interlaboratory study. The results of these studies are valuable for indicating directions for further studies aimed at achieving improved interlaboratory results for trace elements in specification and alternative fuels.

Introduction

Accuracy in reporting the concentration of metals at trace levels in fuels is becoming increasingly important. In the past, analytical characterization of metallic element concentration levels in fuels focused primarily on determining those elements above trace levels or on detecting significant variations in levels, as for wear metals in oil. However, the detrimental effects of certain metals on fuel performance and fuel systems at the part-per-million (ppm, or 10^{-6}) and in some cases the part-per-billion (ppb, or 10^{-9}) levels necessitate improved accuracy in determining these low-concentration elements (refs. 1 to 3). Reliable measurements at these levels are also important in determining the extent of various refining treatments required to provide a fuel with the desired specifications.

Many trace metal studies reported in the literature have demonstrated good precision within a laboratory; however, in interlaboratory comparisons of trace metal measurements in fuels the agreement has been poor (refs. 4 and 5). The largest ranges are typically reported for low-metal-concentration fuels. Since the major research interests at Lewis are in those fuels at the low metal concentration levels, this laboratory began studies in an effort to identify the sources of error.

Of prime consideration when measuring any component at trace levels is the variability of the elemental contamination, commonly referred to as the blank (refs. 6 and 7). When attempting to measure analyte concentrations in the sub-ppm range, even slight blank variability may become the limiting factor in the precision of the measurements. Because of the important role the blank plays in trace level analyses and because the effects of the blank could not be readily incorporated into the interlaboratory study, the results of a study conducted within the Lewis laboratory to assess the error limits caused by elemental contamination are also presented.

A series of measurements of the recoveries of several elements were performed to learn how closely known levels of trace metals, following a dry-ashing preparation of the sample, could be determined.

In an effort to identify the sources of variation between laboratories in determining metal levels in a fuel matrix, an interlaboratory study was conducted. This study incorporated a series of statistically designed factorial plans in which four independent factors initially suspected to be contributors to the variation in results were varied at different levels for each of the 20 elements analyzed. The use of statistical designs and the analysis of the data collected allowed for efficient testing of the effects of changing the level of a given factor, or factors, on the measured variable.

Identifying the sources of variation would be useful in directing efforts to gain control of the methods to be followed in order to measure trace metals in fuels more accurately and improve the precision between laboratories for interchangeability of analytical results.

Experimental Procedure

Blank and Recovery Studies

Apparatus and reagents. – High-purity silica (Vycor brand, Corning Glass Works) and platinum crucibles were used as the dry-ashing vessels. Vycor crucibles were cleaned by fuming in high-purity sulfuric acid (H_2SO_4) (Ultrex grade, J.T.Baker Chemical Co.). Platinum crucibles were cleaned by a three-step process consisting of an acid fusion with potassium hydrogen sulfate (Fisher Scientific Co., certified ACS), a basic fusion with sodium carbonate (Fisher Scientific Co., certified reagent), and by fuming in H_2SO_4.

A study was conducted in this laboratory to observe blank fluctuations after sample preparation by using a dry-ashing method for 19 elements. Sulfuric acid was used as the ashing additive throughout these studies. Alternating blanks and samples were prepared in a given crucible according to the experimental parameters shown in table 1. The sample ashed before each blank preparation was a known quantity of Conostan C-21 reference material (Continental Oil Co). The ashing procedure was performed either in the typical laboratory atmosphere or in a clean-air facility. Both silica and platinum crucibles were used as ashing vessels. Thus the blank levels could be studied as functions of air environment, crucible material, and prior history of the crucible.

Since known quantities of the hydrocarbon standard were ashed in this blank study, this experiment was also used to determine the recovery of metals by the dry-ashing procedure (ref. 5). The sample ash for instrumental measurement was dissolved by using high-purity hydrochloric (HCl) and nitric (HNO_3) acids (Ultrex grade, J.T. Baker Chemical Co.).

The clean-air facility, a curtain type of vertical laminar-airflow unit with high-efficiency particulate air (HEPA) filters, was used throughout the preparation procedure for all work, unless otherwise noted.

Instrumentation. – Blank and metal recovery measurements were made with a direct-current arc emission spectrometer (dc arc) (ref. 8). Additional recovery measurements were made with an atomic absorption spectrometer (AAS) (Instrumentation Laboratory Model 153 and Perkin Elmer Model 5000). Multielement standards were used in all dc arc measurements. Single-element standards prepared from the metal or inorganic salt were used for the AAS recovery studies.

Experimental Design of Interlaboratory Study

Factors. – Four factors were considered in this study. Those factors and their levels chosen are presented in table 2.

Fuel samples, selection, and preparation. – The eight fuel samples distributed to each laboratory are shown in table 3. Three fuel types were used to prepare the samples analyzed. The experimental referee broadened-specification fuel (ERBS) (Sun Tech Division of Sun Oil Co.) is a petroleum-derived research aviation fuel considered to be "clean"; that is, any metals present would be in the low-ppb range (ref. 9). Residual fuel oil (RFO) (Sun Tech Division of Sun Oil Co.) is the highest-boiling-point fraction of petroleum crude oil and therefore contains a relatively high fraction of the total metals in crude. The middle distillate fraction of a coal-derived fuel, solvent-refined coal (II)[1] (SRC) (Pittsburgh and Midway Coal Co., Division of Gulf Oil Corp.), was included as the third fuel type. The expected concentration levels of the metals in this fuel would lie between those for ERBS and RFO. These particular fuels were chosen because they are of interest to the research programs conducted at this laboratory, as well as being fuels with varying levels of metals.

Since the concentration level was suspected as an important factor in the analysis, each fuel type was altered, either by dilution or by addition of a known amount of C-21, Conostan reference material, as is indicated in table 3. The concentration levels were chosen to obtain samples, of a given fuel type, containing metals close to blank levels and at concentrations that would provide a high signal-to-blank ratio. Two levels of a fuel blend, prepared by combining RFO and SRC, were incorporated into the study as control fuels to obtain a measure of the reliability of each laboratory's results.

All fuels were prepared in bulk, mechanically agitated, and then sampled to ensure that identical samples would be sent to each laboratory.

Selection of laboratories. – Five laboratories were selected for the study; this laboratory served as the sixth participant. To maintain anonymity, the laboratories are designated by Roman numerals (I-VI). The study was conducted on a fee basis, rather than cooperatively, to enable this laboratory to specify the fuel preparation scheme used as well as to determine the state of the art in trace metal analysis of liquid fuels. The laboratories selected to participate possessed at least one major instrumental technique with comprehensive analytical capabilities and had some previous experience in analyzing fuel samples.

Analytical measurement techniques. – The particular techniques used in this study were chosen because they were either readily available in most laboratories or had multielement capability. The analytical methods used are included in table 2. Not all analytical techniques under study were performed at each laboratory, as indicated in

[1]The Roman numeral designation with solvent-refined coal refers to a processing method. This designation will hereinafter be dropped to avoid confusion with laboratory codes.

table 4. Analyses by one multielement technique and AAS were conducted for the eight elements Al, Cr, Fe, Mg, Mn, Na, Ni, and Zn. Twelve additional elements, B, Ba, Ca, Cd, Co, Cu, K, Pb, Si, Sr, Ti, and V, were analyzed by using the multielement technique only. Since AAS is an instrumental method available in almost every laboratory, it was the common technique selected for all participants.

Sample preconcentration. – When possible, a direct measurement of the component of interest is desirable to lessen the risk of losses and contamination from reagents and handling. However, because of the low concentration levels of the elements to be measured in the fuel samples, as well as the difficulties encountered when measuring in an organic matrix, preconcentration was necessary. A single preparation was desired to put the sample in a form suitable for measuring all of the elements. A dry-ashing procedure was provided to each laboratory in an effort to reduce an otherwise uncontrolled source of variation. Samples were weighed directly into Vycor crucibles (high-purity silica) and a specified high-purity ashing additive was added. A blank was prepared by following the identical procedure that was employed for the fuel samples. The samples were evaporated to a solid mass on a hot plate and then ashed in a quartz-lined muffle furnace at 450° C. Dry-ashing techniques may be susceptible to losses of some elements by volatilization or retention in the ashing vessel. The lower ashing temperature and the ashing additive were used to minimize such potential element losses. The ashing additive was included in the interlaboratory study to test its effectiveness in the ashing process.

For the analytical techniques that required preparation of an aqueous solution, the ash was dissolved in minimum quantities of high-purity HCl and HNO_3 and diluted to measurable concentrations in polyethylene containers. As shown in table 4, in some techniques the dissolution step was eliminated because the sample could more readily be analyzed as the ash.

The conclusions drawn from studies conducted in this and other laboratories, that is, the preferred use of high-purity reagents and the importance of a clean-air facility, aided the specification of the sample preparation method provided to each laboratory. However, a clean-air facility may not be generally available in most chemical laboratories. In the interlaboratory study only laboratory VI prepared all samples in a clean-air facility.

Results and Discussion

Blank Study

High and variable blanks may arise from elemental contamination caused by the ashing additive and the ashing procedure. Errors in the measurement of a given element in a sample may occur by retention of the analyte onto the ashing vessel or by contamination from crucible components or previously trapped elements.

The means and detection limits (defined herein as two times the standard deviation) for the blanks are shown in table 5. Eleven of the 19 elements measured in the silica crucibles, most notably Ca, Cr, Fe, Si, Ti, and Zn, had possessed both a higher mean and greater variability when prepared open to the laboratory air. Clearly there is a considerable advantage to using a clean-air facility for trace analysis. Results of the analysis of blanks prepared in platinum crucibles are also shown in table 5. Levels of Al, B, and Si were lower in the platinum crucible than in the silica crucibles[2]. Early work in this laboratory employed platinum crucibles as the ashing vessel. Blank levels for a number of different elements appeared uncontrollable. This was attributed to "memory effects," that is, the release of elements previously trapped in the crucible[3]. When high-purity silica crucibles were substituted in the preparation procedure, the blank variability notably decreased. The results of this work demonstrated no significant memory effects with platinum crucibles. Whether this was due to the cleaning procedure or to the relatively small amounts of ash material obtained with the hydrocarbon test samples is not known. Our recommended procedure is to use platinum crucibles in a filtered-air environment. However, because of the possibility of memory effects with platinum crucibles, it is recommended that crucibles with unknown history be cleaned thoroughly and that several blanks be determined before putting them into service for the determination of trace constituents.

Metal Recoveries Using Fuel Ashing Procedure

Recovery studies using H_2SO_4 additive in the sample preparation procedure were performed by AAS and dc arc spectrometries. The concentration of several metals was measured in a number of Conostan C-21 samples of varying quantities ranging from 20 to 300 μg of each element. The metal concentrations in the standard are claimed to be accurate to 1/2 percent relative standard deviation. Mean percent recoveries, standard deviation, and the number of samples contributing to these calculated statistics are presented in table 6. The recoveries obtained by dc arc measurements are low and are attributable to the incomplete washing of the acidified ash from the crucible. The dc arc procedure used in this study involves the use of micropipettes to remove the acidified ash from the crucible. However,

[2]Silica crucibles are composed of SiO_2, Al_2O_3, and B_2O_3.

[3]In earlier studies the platinum crucibles were cleaned by fuming in H_2SO_4 only.

considering the orders-of-magnitude range of results typically reported by different laboratories on a given sample, the errors that could be attributed to the low recovery are negligible. The results of the metal recoveries do indicate that the use of the dry-ashing procedure merits consideration as a viable fuel preparation method.

Interlaboratory Study

General observations. – The response variable in this study was the metal concentration in the fuel expressed in ppm. Laboratories were instructed to report a detection limit for each element if they could not actually measure the concentration. The metal concentrations reported by each laboratory are given in the appendix. Large variations were evident for several elements in all fuel types. The range of results for the laboratories varied up to five orders of magnitude for the low-concentration-level fuels and up to three orders of magnitude for the high-concentration-level fuels. The ranges, presented in table 7, are shown for the data obtained by all the analytical measurement techniques and for that obtained by using only AAS data. One would expect more difficulty in achieving agreement between several methods of measurement than between different instruments and operators of a single technique. But although the AAS data range for most elements was smaller, considerable variation still exists.

Each laboratory was asked to supply information concerning their estimate of precision of the analysis by both AAS and the particular multielement technique used. These estimates are given in table 8. Although all of the reported precision values within a laboratory were less than or equal to 60 percent of the amounts reported, few elements, as evident from table 7, actually fell within this precision range when comparison was made among laboratories. Table 9 compares intralaboratory means and precision with those calculated between laboratories for a few example elements. The calculated precision, expressed in percent relative standard deviation, in each laboratory, was obtained by summing their results over techniques and ashing additives. Inspection of the precision within a given laboratory indicates that with the exception of laboratory I, for the elements listed, the calculated precision was generally poorer than their precision estimates shown in table 8.

The means and 95-percent confidence limits for the elements in each of the fuels were calculated for all laboratories; those results below the detection limits of the methods used were excluded. The calculation was not performed if less than three significant results were reported or if they were not obtained by at least two different laboratories. In a number of instances statistical outliers could be flagged by using rejection test guidelines provided by the American Society for Testing Materials (ref. 10). However, unless a nonstatistical reason for rejecting the datum (or data) can be identified, rejection may bring about an unrealistic assessment of the overall analysis (ref. 11). Since this work was conducted in several different laboratories, rejection of data by the author could not be justified and because the object was to aid identification of sources of variance, no data were rejected. The number of significant results reported, the means, the standard deviations, and the 95-percent confidence limits for all of the data and for the AAS data alone are shown in table 10.

As noted in table 4, instrumental neutron activation analysis (INAA) results were obtained on an intact fuel sample and on the H_2SO_4-aided ashed sample only. This method offers good limits of detection under the ideal conditions of a single-element matrix; however, with a complex matrix, such as the fuel samples, these limits were substantially higher. In fact, in the fuel matrices of this study, analysis of B, Cd, Cu, Ni, Pb, and Si could not be obtained by INAA. The advantage of analyzing the sample without a preconcentration procedure was attractive; however, only five elements, Co, Cr, Mn, V, and Zn, in any of the fuels could be measured above the detection limits of this method by using an unprepared sample (see appendix, p. 42). The upper concentration limit reported for the other elements was of the order of 10^2 to 10^5 ppm and provided no really useful information about the metal levels. Some elements were reported as not detected because a meaningful upper limit could not be obtained. This undoubtedly was due to the small sample volume that could be irradiated and because samples contained low metal concentrations. Results of the H_2SO_4-ashed-sample analysis for nine elements, Al, Ba, Co, Cr, Fe, Mn, Na, V, and Zn, were used to calculate the interlaboratory means, but no INAA data were incorporated into the statistical analysis.

Analysis of variance. – Statistical evaluation of the interlaboratory data was performed by using the analysis of variance technique (ANOVA)(refs. 12 and 13 and private communication with Charles A. Barrett of Lewis). A normal distribution of the data was assumed (ref. 14). ANOVA is a statistical method used to analyze data by partitioning the total variation of the experiment into its individual components and testing the significance of the effects of each. A commercially available computer program was used to perform the analysis (ref. 15). The testing is done by computing the F-test statistic for each source of variation and comparing that value with the tabulated distribution value at the appropriate degrees of freedom and the tolerable error (type I or α error). The particular characteristics of the factors incorporated into the study and how the data were collected dictate the mathematical model that describes the experiment and just how the F-test statistic should be calculated. Variations in the reported metal concentrations in the fuel samples may be

due to the changing of the levels of the factors, interactions between the factors, and extraneous sources of variation that cannot be assigned to the factors under study. The factors chosen for this study were considered potentially major sources of variation. Any source that has not been incorporated as a factor will contribute to the residual variance (random error) of the experiment. Overlooking an important factor may inflate the random error and lead to masking of the significant effects. The large variation of the results reported in this study should not adversely affect the outcome of the analyses unless a major source of variation has indeed been overlooked.

Experimental design models. – Two models were used to represent the analysis of the study's data. In both cases complete randomization of the data was assumed. The first equation describes a full factorial design of three independent factors that are all at fixed levels:

$$Y_{ijkl}=\mu+L_i+C_j+LC_{ij}+P_k+LP_{ik}+CP_{jk}+LCP_{ijk}+\epsilon_{l(ijk)}$$

where

Y_{ijkl}	response variable, concentration of the element in ppm
μ	true mean of the population
L_i	laboratory, $i=6$ ($i=5$)[4]
C_j	concentration, $j=2$
P_k	preparation (ashing additive), $k=3$
$LC_{ij}, LP_{ik}, CP_{jk}, LCP_{ijk}$	factor interactions
$\epsilon_{l(ijk)}$	random error of experiment
i,j,k,l	levels of the individual factors

This model was used in analyzing the eight elements measured by AAS. It was also used to describe the statistical treatment of the multielement technique data for all 20 elements.

To obtain information concerning the effect of AAS and different multielement analytical techniques on the reported concentration level, a second model was used to describe a four-factor design:

$$Y_{ijklm}=\mu+L_i+C_j+LC_{ij}+P_k+LP_{ik}+CP_{jk}+LCP_{ijk}+T(L)_{il}+CT(L)_{ijl}+PT(L)_{ikl}+CPT(L)_{ijkl}+\epsilon_{m(ijkl)}$$

In this situation, although the three factors are identical to the first model, the fourth factor, technique, is *nested* under laboratories, represented by $T(L)_{il}$. This takes into account the fact that identical techniques were not performed at each laboratory.

The random error of an experiment is usually determined by analysis replicates. In this experiment, replicates were not obtained, so the variance due to the highest order interaction (LCP_{ijk} in the first model and $CPT(L)_{ijkl}$ in the second) and that of the random-error term cannot be separated. Therefore the variance due to the interaction was assumed to be zero and the calculated variation will be attributed to ϵ. This is a reasonable assumption because of the size of the experiment and the unlikely presence of these higher order interactions.

Statistical significance testing. – A major difficulty when attempting to analyze trace-level data is how to handle results reported as not detected. Some useful information can still be rendered if a detection limit is known for those elements reported as not detected. The multifactored ANOVA requires that results for every planned treatment combination be included for statistical analysis. Generation of missing data is possible but only to a limited extent (ref. 13). When the statistical analysis required inclusion of a result reported as not detected, the ANOVA was conducted in two ways: first, by using the value of the limit of detection; and second, by replacing the number with zero, that is, no element present. The uncertainty of the actual elemental concentration will only allow testing of the two extremes. An identical set of significant effects was not always obtained for the element in a given fuel. When a difference in outcome did exist, it is noted in the tables. In most situations the calculated test statistics would lie just above the 1 percent level of significance. The results of the statistical testing are presented for each factor. Tables 11 to 14 list the elements that were determined to have statistically significant factors ($\alpha=0.01$).

This study was undertaken because of the poor precision between laboratories, and therefore the large number of elements that showed a significant difference in the results reported by the laboratories (table 11) was not unexpected. However, the carefully outlined preparation procedure supplied to each laboratory was anticipated to help reduce the large variations. Analysis of the AAS results, since a common technique and preparation was used, suggests that at least for some of the elements studied in a given fuel matrix, a large portion of the variation may not be attributable to the analytical technique used for measurement. Rather, the operator, improper instrument calibration, uncontrolled environmental factors, and inherent error in the preparation scheme may be responsible. However, the results of the metals recovery reported in the previous section, using the same procedure, did not indicate an excessively large variation due to dry ashing of the fuel sample. Several elements possessed significant laboratory

[4]Results of only five of the six laboratories were used in the analysis of data from multielement techniques.

effects in all, or a majority, of the fuels analyzed. The Newman-Keuls range test was performed to determine which of the laboratories' mean concentrations differed significantly from the others (ref. 12). The laboratory (or laboratories) identification code is listed next to each element. Variation due to the particular multielement technique most probably affected the statistical results since the technique was not incorporated as a factor.

The concentration level of the element in a particular fuel matrix also proved to be a highly significant source of variation, particularly in the ERBS and SRC fuels. Fewer elements had a significant concentration factor in the RFO sample (table 12), where the low concentration levels of most metals were considerably higher than the low concentration levels in the ERBS and SRC fuels. As the concentration of the elements in the fuel samples increased, one would expect smaller relative errors introduced from high and variable blanks. Three elements, Co, K, and Sr, are not present in the C-21 reference material used to increase the metal concentration in ERBS and SRC samples. The fact that a significant concentration effect is indicated for these elements suggests that the total concentration of analyte elements could be an important factor. The manner in which the blended data were analyzed did not permit an evaluation of the effect of different concentration levels as was performed for the other fuel samples. But rather the difference between the expected concentration, based on RFO and SRC measurements, and the observed concentration at two levels of the blended fuel was tested. Only Cd and Co exhibited a statistically significant difference.

The use of either H_2SO_4 or HNO_3 or no ashing aid during the dry-ashing preparation showed few instances of contributing a significant source of variation, as noted in table 13. The majority of elements that tested as dependent on the ashing additive were in the ERBS fuel.

Although a common preparation procedure was used, regardless of the analytical measurement technique, the actual form of the sample when analyzed may have differed between techniques. These differences are shown in table 4. Certain techniques may be restricted by the usable sample size and be susceptible to interferences not common to all. These considerations may contribute to variations caused by different techniques. Table 14 contains the elements in the ERBS, RFO, SRC, and blended fuels in which the results obtained by multielement technique analyses were significantly different than those obtained by AAS. The elements Cr, Mn, and Zn tested as technique dependent in at least two of the four fuel types analyzed.

The source of variance components includes a number of interaction terms. An interaction exists between factors when a change in one factor causes a different change in the reported metal concentration at one level of a second factor than at other levels of this factor. Several interaction terms tested as significant at $\alpha = 0.01$. A complete summary of those elements having significant effects, with AAS and multielement method data considered individually, is presented in table 15.

The laboratory-concentration interaction ($L \times C$) tested as significant more frequently than any other interaction term for the ERBS, RFO, and SRC fuels. For a given element the difference in the concentrations determined by each laboratory was not the same for the two concentration levels measured. As an example, figure 1 demonstrates the significant terms for the determination of Ca in SRC. The low-level concentration data have been normalized by the known concentration difference so that both low and high concentrations could be presented on the same graph. The curve implies a much larger variation in the high-concentration curve; however, this is actually not the case on a relative basis. The relative standard deviations for the low- and high-concentration samples were 148 and 59.2 percent, respectively. The large interval between the two curves illustrates the presence of a significant concentration effect, while the shape of each curve, over the five laboratories, indicates a large variation between laboratories. The graph demonstrates the significant interaction between concentration and laboratory by the lack of parallelism of the two concentration curves. There were fewer significant interactions for the elements analyzed in the blended fuels. The predominant interaction for the blends was the laboratory–ashing additive interaction ($L \times P$).

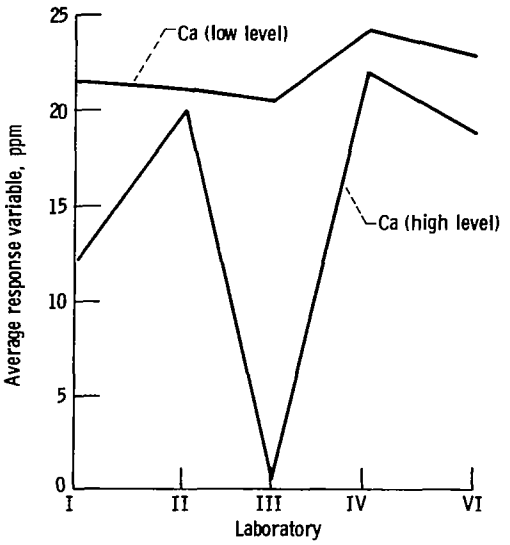

Figure 1. - Graphical presentation of statistically significant (α = 0.01) laboratory and concentration main effects and the laboratory-concentration interaction effect observed for reported calcium concentrations in solvent-refined coal.

Table 16 contains those results with the technique factor incorporated into the design. Again, the $C \times L$ term was the predominant significant interaction for the three fuels. No interaction effects tested as significant in this same analysis of the blended samples, and therefore interaction effects have not been included in the table.

Relative accuracy. – Because the true concentrations of the elements in the fuels studied were unknown, it is impossible to comment on the absolute accuracy of the reported concentrations. No standard reference materials were available that could serve as a control for a comprehensive multielement analysis of the low-metal-concentration fuels. The analysis of such a material by each laboratory would provide information concerning the accuracy attained and thus a measure of the laboratory bias (refs. 16 and 17). However, since the metal concentrations in a given fuel were varied by known amounts, the relative accuracy can be calculated by comparing the actual concentration change with that observed. The ERBS and SRC fuels were spiked with known quantities of the C–21 reference material, 23.9 and 20.6 ppm, respectively. This represents a rather large concentration difference for these fuels. Smaller concentration differences were used between the levels of the RFO and the RFO + SRC blended samples. The RFO was diluted with xylene such that the low and high metal concentrations differed by approximately a factor of 2. A separate analysis of the xylene revealed that it introduced no significant amount of any element. The change in the levels of the two blended samples varied by element, depending on the original concentration in the RFO and SRC fuels.

The mathematical expressions shown in table 17 were used to calculate the error E in the measured change of the metals between the higher and lower concentration levels of the fuels. In all five equations the terms enclosed in absolute value symbols would be equal to 1 if the observed relationship between the levels were equal to the known values. Table 18 presents, by fuel type, the calculated relative differences, expressed in percent, for the analyzed elements. Both the range and the mean averaged for all laboratories are shown. The results obtained by using AAS were generally lower than the corresponding multielement averages. Comparison of the average relative differences for the multielement techniques indicates that the laboratories more accurately measured the larger change in concentration between low and high levels, that is, in the ERBS and SRC fuels, than in those fuels with smaller metal concentration differences. For the AAS data the higher concentration change of the ERBS and the SRC fuels was more accurately determined only for Mn, Na, and Ni.

Since the results of the ANOVA for several elements indicated considerable variation in the concentrations reported by each laboratory, each laboratory's performance was assessed independently. A merit point system was used to evaluate a laboratory's ability to measure the concentration change accurately for all of the elements analyzed in the samples. The assignment of the scheme, shown in table 19, was quite arbitrary, but it adequately allows a comparison of the performance of each laboratory relative to a measurement of accuracy. The merit points assigned for the analysis of each element by a laboratory were summed for all elements to obtain a single number for each fuel. The totals for each laboratory are shown in table 20, for multielement techniques and AAS separately. Laboratories II and VI were the top ranked laboratories in the analysis by the multielement methods; both laboratories used dc arc techniques. Laboratories I and VI obtained the highest number of points for the results obtained by AAS. These results do not necessarily indicate that these laboratories have obtained accurate results for all eight fuels. In fact, examination of these laboratories' actual reported values (appendix, pp. 34, 36, and 46) shows quite a difference for some elements.

Concluding Remarks

Known adverse effects of some metals at part-per-billion levels in fuels have made their accurate determination mandatory and interlaboratory agreement a requirement to ensure interchangeability of analytical results. However, the results of this experiment indicate that the required accuracy, as well as an acceptable interlaboratory precision, have not been achieved.

It is not uncommon for the results of an interlaboratory study to show a large variation between individual laboratories. In this study a single preparation procedure was specified for all analyses and a common measurement technique was performed at each laboratory. For most elements this approach did not reduce the laboratory variation as greatly as anticipated. A single preparation procedure capable of rendering the sample in a form for which all the elements could be measured was of interest. Certainly in some instances better results could have been achieved by tailoring the method for an individual element.

Statistical analysis of the data suggests that the observed variations in reported metal concentrations, in the fuels analyzed, are not caused by a single factor. Several of the elements studied showed that the laboratory and metal concentration factors tested as significant at the 0.01 level. The analysis of variance technique also indicated that the use of various ashing additives, in general, does not produce a significant effect during the dry-ashing sample preparation.

The independent studies in this laboratory concerning the blank variability of several elements using the fuel ashing preparation procedure may give insight into the poor precision between laboratories and in some cases within laboratories. With particular reference to the experimental referee broadened-specification and solvent-refined coal fuels used in this interlaboratory study, it appears that the levels of many of the elements are close to blank levels and that some results may actually represent the blank variability in the measurements. It seems most evident that, until better control can be obtained by each laboratory on the blank level, better precision cannot be expected in results from an interlaboratory study of low-metal-concentration samples. Preparation of the sample in a clean-air environment, with continued use of high-purity reagents, appears to be essential in maintaining low blanks.

Too few results were obtained by any one multielement technique to suggest that one method was more suitable than another; however, the direct analysis of the fuel by instrumental neutron activation analysis does not appear to be an acceptable method for many of the elements of interest in low-metal-concentration fuels. For most of the eight elements analyzed by both atomic absorption spectroscopy (AAS) and a multielement technique, the lowest errors were obtained by using AAS.

For the preparation and measurement procedures used in this experiment, table 21 presents the lowest errors in distinguishing the change in the two concentration levels obtained within a laboratory and by any laboratory participating in this experiment. The best results from within a laboratory and with a single analytical technique are not acceptable for the requirements of the fuels research programs aimed at determination of part-per-million and part-per billion concentration levels.

An extensive amount of work remains to provide for interchangeability of results. Until accuracy and precision can be demonstrated by different laboratories and by different analytical techniques, reliability in determining trace metals in fuels is questionable. Rigid standardization of the analytical methods involved in fuels analyses and control of the entire analytical procedure, using both internal quality control and interlaboratory analyses, will be required to achieve agreement. Comparability of analytical results will require extensive use of standard reference materials (SRM). Control of conditions within a laboratory is typically easier than between laboratories, so that through use of SRM's, biases introduced by a laboratory can be determined and corrected.

This study indicates that the fuels researcher cannot adequately determine the true lower concentration limits of the metals that promote adverse effects on fuels and fuel system components. Research into the potential use and specification of broadened-property fuels will be hampered until the chemical processes responsible for the adverse effects, including the influence of the metal concentration levels, can be characterized.

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National Aeronautics and Space Administration
Cleveland, Ohio, August 19, 1982

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TABLE 1. - SCHEME FOR THE STUDY OF BLANKS AS A FUNCTION OF EXPERIMENTAL CONDITIONS

Ashing environment				
Laboratory air		"Clean" air[a]		
Crucible				
Silica (A)	Silica (B)	Silica (C)	Platinum (D)	Platinum (E)
Sequence				
Blank 1[b] (33)[c] Blank 2 (100) Blank 3 (273) Blank 4	Blank 5 (32) Blank 6 (78) Blank 7 (320) Blank 8	Blank 1 (25) Blank 2 (22) Blank 3 (137) Blank 4 (322) Blank 5	Blank 1 (20) Blank 2 (226) Blank 3	Blank 4 (13) Blank 5 (240) Blank 6

[a]Laminar-flow air filtered through high-efficiency particulate air (HEPA) filter.
[b]Represents preparation and measurement of a blank.
[c]All numbers in parentheses are equivalent amounts, in micrograms, of each of 21 elements contained in sample that was ashed followed by cleaning of crucible and measurement of next blank in sequence.

TABLE 2. - FACTORS AND LEVELS OF EXPERIMENT DESIGN FOR MULTIELEMENT FUELS ANALYSES

Laboratory levels	Analytical technique[a] levels	Concentration levels	Preparation levels (ashing additive)
I II III IV V VI	Atomic absorption spectrometry Direct-current arc emission spectrometry Direct-current plasma emission spectrometry Spark source mass spectrometry Instrumental neutron activation analysis	Lower Higher	H_2SO_4 HNO_3 None

[a]Analytical technique factor was nested under laboratory. Each laboratory performed one multielement technique and atomic absorption spectrometry.

TABLE 3. - FUEL SAMPLES ANALYZED IN INTERLABORATORY STUDY

Relative trace metal concentration level	
Lower	Higher
Experimental referee broadened-specification fuel (ERBS)	ERBS plus 23.9 ppm of C-21 standard[a]
48 Percent residual fuel oil (RFO) in xylene	RFO
Solvent-refined coal (SRC)	SRC plus 20.6 ppm of C-21 standard[a]
28 Percent RFO plus 72 percent SRC	65 Percent RFO plus 35 percent SRC

[a]Conostan reference material (Continental Oil Co.).

TABLE 4. - SUMMARY OF ANALYTICAL TECHNIQUES PERFORMED BY EACH LABORATORY AND PREPARATION OF FUEL SAMPLE ASH

Laboratory code	Analytical technique	Preparation of fuel ash
I	Atomic absorption spectrometry (AAS) Spark source mass spectrometry	Aqueous solution Ash and graphite formed into an electrode
II	AAS Direct-current arc emission spectrometry (dc arc)	Aqueous solution Ash- and graphite-packed electrode
III	AAS dc arc	Aqueous solution Ash- and Li_2CO_3-packed electrode
IV	AAS Direct-current plasma emission spectrometry	Aqueous solution Aqueous solution
V	AAS Instrumental neutron activation analysis	Aqueous solution Intact sample and ashed sample[a]
VI	AAS dc arc	Aqueous solution Ash-acid slurry on AgCl-treated graphite electrode

[a]Ashing performed using H_2SO_4 additive.

TABLE 5. – SUMMARY OF BLANK STUDY RESULTS FOR DRY-ASHING FUEL PREPARATION PROCEDURE (H_2SO_4 AIDED) COMPARING ADVANTAGES OF USING LAMINAR-FLOW HOOD AND EFFECT OF CRUCIBLE COMPOSITION (CONDUCTED AT LEWIS)

Element	Crucible					
	Silica[a]		Silica[b]		Platinum[b]	
	Mean, µg	Detection limit[c]	Mean, µg	Detection limit[c]	Mean, µg	Detection limit[c]
Al	0.02	0.03	0.20	0.20	0.02	0.03
B	.16	.59	.75	2.78	<.01	(d)
Ba	<.03	(d)	<.03	(d)	<.03	(d)
Ca	.06	.08	.03	.03	.04	.07
Cd	<.06	(d)	<.06	(d)	<.06	(d)
Cr	.02	.05	.002	.006	.007	.026
Cu	.005	.014	.003	.004	.006	.006
Fe	2.2	7.6	.12	.37	.20	.88
Mg	.01	.03	.007	.018	.004	.006
Mn	.03	.07	<.001	(d)	<.001	(d)
Mo	<.003	(d)	.016	.06	<.002	(d)
Na	<.3	(d)	<.3	(d)	<.3	(d)
Ni	.02	.07	.02	.06	<.003	(d)
Pb	.01	.01	<.01	(d)	<.01	(d)
Si	.4	1.2	.2	.6	.07	.15
Sn	<.03	(d)	<.03	(d)	<.03	(d)
Ti	.22	1.2	.002	.007	<.001	(d)
V	<.003	(d)	.004	.004	<.003	(d)
Zn	.13	.28	.06	.04	<.05	(d)

[a]Preparation performed in laboratory environment.
[b]Preparation performed in clean-air facility.
[c]Detection limit defined as two times standard deviation.
[d]Standard deviation was zero.

TABLE 6. – PERCENT RECOVERY[a] OF METALS IN CONOSTAN C-21 REFERENCE MATERIAL

Element	Measurement technique					
	Direct-current arc emission spectrometry			Atomic absorption spectrometry		
	Number of observations	Mean, percent	Standard deviation	Number of observations	Mean, percent	Standard deviation
Al	8	62.8	8.1	--	-----	----
B	6	42.9	8.3	--	-----	----
Ba	4	88.9	20.4	--	-----	----
Ca	8	87.0	16.0	--	-----	----
Cd	↓	81.2	22.6	16	101.5	6.4
Cr	↓	86.8	15.1	16	89.3	7.2
Cu	↓	77.0	11.5	16	98.4	5.2
Fe	↓	69.7	15.1	16	96.0	11.4
Mg	7	84.6	10.8	--	-----	----
Mn	8	92.2	14.8	16	103.0	2.3
Mo	8	91.4	5.8	--	-----	----
Na	6	74.2	9.8	15	97.1	6.0
Ni	8	75.3	17.1	--	-----	----
Pb	↓	70.1	6.8	16	96.8	10.8
Si	↓	68.5	17.7	--	-----	----
Sn	↓	67.6	17.4	--	-----	----
Ti	↓	66.5	8.3	--	-----	----
V	↓	75.1	6.6	--	-----	----
Zn	↓	74.9	9.1	16	100.6	2.8

[a]Measurements made at 20-, 100-, and 300-µg levels of each element; refer to table 1. Sample preparation with H_2SO_4 ashing aid in clean-air facility.

TABLE 7. – TRACE METAL CONCENTRATION RANGES REPORTED BY SIX LABORATORIES USING A PRESCRIBED SAMPLE PREPARATION PROCEDURE

Element	Fuel							
	Experimental referee broadened-specification fuel				Residual fuel oil			
	Relative concentration level							
	Lower		Higher		Lower		Higher	
	Technique							
	MET[a] + AAS[b]	AAS	MET + AAS	AAS	MET + AAS	AAS	MET + AAS	AAS
	Trace metal concentration ranges, ppm							
Al	0.001–3.5	0.5–2.2	12–37.3	13–37.3	0.4–16.0	<2–15.8	2–70	5.25–34.22
B	<0.002–200	———	0.6–20.5	———	0.02–8	———	0.05–19	———
Ba	<0.002–1.7	———	5.4–46	———	<0.3–7.6	———	0.8–4.2	———
Ca	0.005–12.0	———	0.2–31.0	———	0.2–16.0	———	0.2–26.0	———
Cd	(<0.002–<26)[c]	———	0.66–46	———	(<0.01–<25)	———	(<0.01–<23)	———
Co[d]	<0.0001–0.04	———	<0.02–0.19	———	0.4–2	———	0.9–5	———
Cr	0.0002–9.7	<0.04–2.6	3.8–51.99	3.8–51.99	0.09–1.3	0.09–0.55	0.28–4.4	0.28–1.53
Cu	0.03–0.11	———	9.6–36	———	0.03–7.8	———	0.2–2	———
Fe	0.02–88	<0.05–19	5–47.62	8–47.62	2–37.0	5.4–37.0	3–195	13–39.0
K[d]	<0.02–4.7	———	0.13–15.5	———	0.2–3.5	———	0.6–7.0	———
Mg	0.001–375	<0.01–306	1–48	17.2–36	0.2–7	1.2–6.0	2–31.8	3.98–31.8
Mn	0.00008–2	<0.03–0.67	4.6–96.1	14–96.1	<0.0007–0.6	0.07–0.26	0.07–2	0.07–0.8
Na	<0.02–32	<0.02–29	6.0–41	17.5–30	1.5–47.5	11.0–47.5	1.4–204	18.6–49.5
Ni	0.001–13	<0.16–1.8	9.2–71	9.5–71	2–20.55	3.94–20.55	5.8–34	8.4–34
Pb	0.009–12.0	———	<3–56	———	<0.08–2	———	<0.01–8.4	———
Si	0.005–230	———	2–33	———	0.2–180	———	6.2–160	———
Sr[d]	<0.001–0.007	———	0.004–0.06	———	0.08–0.2	———	<0.2–1.6	———
Ti	0.0009–0.19	———	2.4–46	———	0.07–1.5	———	0.1–2.2	———
V	0.001–0.07	———	3.5–31	———	1–4.5	———	3.8–9.8	———
Zn	0.01–1.2	0.03–1.2	5.5–84	8.8–84	0.71–13	3.1–5.81	1.8–23.7	5.32–23.7

Element	Fuel							
	Solvent-refined coal				Solvent-refined coal and residual fuel oil blend			
	Relative concentration level							
	Lower		Higher		Lower		Higher	
	Technique							
	MET[a] + AAS[b]	AAS	MET + AAS	AAS	MET + AAS	AAS	MET + AAS	AAS
	Trace metal concentration ranges, ppm							
Al	0.1–16	0.5–11	6.0–39.8	6.0–39.8	0.3–16	0.63–4.9	1–21.1	<2.5–21.1
B	0.1–2.5	———	2–21.1	———	0.4–5	———	0.17–10	———
Ba	0.01–2.4	———	0.5–44.1	———	<0.2–2.1	———	<0.2–6.4	———
Ca	0.02–3.3	———	0.1–25.0	———	0.1–6.6	———	1.0–16.0	———
Cd	<0.01–22	———	1.1–31.7	———	(<0.01–<24)[c]	———	<0.01–20	———
Co[d]	<.004–0.25	———	<0.01–0.18	———	0.17–2	———	0.4–2	———
Cr	<0.25–3.5	<0.25–2.53	2.1–50.5	2.1–38.19	0.22–4.79	0.22–4.79	<0.25–2.5	<0.25–1.3
Cu	0.02–0.36	———	4–32	———	0.04–1.65	———	0.09–2.3	———
Fe	<0.05–21	<0.05–21	6.5–42.26	6.5–42.26	1.7–54	1.7–40.0	2–47	8–36.0
K[d]	0.08–8.1	———	0.12–18.9	———	0.2–2.8	———	0.2–4.5	———
Mg	0.01–0.8	0.01–0.7	<0.006–37.9	8.6–27.9	0.5–6.1	0.74–6.1	0.5–6.3	1.86–6.0
Mn	0.04–0.33	<0.05–0.33	<0.5–37.9	13–34.03	0.05–2	0.05–0.33	0.05–0.93	0.05–0.5
Na	<0.02–10	<0.02–10	<7.4–53	8.9–33.7	0.8–24	3.08–24	2.1–42.72	7.85–42.72
Ni	0.01–2.5	0.14–2.4	5.3–40.09	5.3–40.09	1.1–40.09	2.27–41.10	2–18	5.0–14.76
Pb	<0.01–6.9	———	2–22	———	0.02–2	———	0.2–3.0	———
Si	<0.3–2.7	———	3.7–37.9	———	0.77–32	———	1.1–48	———
Sr[d]	0.0007–0.01	———	0.004–0.11	———	0.01–0.16	———	0.08–0.2	———
Ti	<0.05–0.7	———	<0.88–50.5	———	0.2–2	———	0.07–1.4	———
V	0.005–0.2	———	<0.29–25.2	———	0.62–3.6	———	0.3–8.6	———
Zn	0.03–20	0.05–1.6	4.3–29.64	4.3–29.64	0.44–5.8	1.5–5.8	1.03–7.85	2.8–7.85

[a]Multielement techniques.
[b]Atomic absorption spectrometry.
[c]Parentheses indicate limits of detection reported.
[d]Not present in multielement reference material.

TABLE 8. - LABORATORIES' ESTIMATES OF PRECISION FOR REPORTED CONCENTRATIONS

Laboratory	Method of measurement	
	Atomic absorption spectrometry	Multielement technique
	Precision, percent[a]	
I	±21	±50–60
II	±15	±10
III	±5–10	±10
IV	±10	±6
V	(b)	±10
VI	[c]±20	[d]±20
	[e]±10	[f]±50

[a]Additional analyses of fuel samples would provide results within concentration range defined by this percentage and results reported in this study.
[b]No estimate reported.
[c]Estimate for Al, Mg, Cr, and Ni.
[d]Estimate for all elements except B, Ba, Cd, and Sr.
[e]Estimate for Fe, Mn, Na, and Zn.
[f]Estimate for elements listed in c.

TABLE 9. - MEAN AND RELATIVE STANDARD DEVIATION COMPARING INTRALABORATORY AND INTERLABORATORY PRECISION FOR EXAMPLE ELEMENTS

Element	Relative concentration level													
	Lower							Higher						
	Laboratory													
	I	II	III	IV	V	VI	All	I	II	III	IV	V	VI	All
	Experimental referee broadened-specification fuel													
Fe	[a]1.4 [b]92.9	2.0 65.0	2.8 46.4	17 11	0.34 8.82	0.12 125	7.8 223	19 63	29.8 33.2	13 43	32 27	21.1 9.0	20.1 19.9	22.7 44.5
Na	0.20 40.0	0.31 3.2	6.6 156	11.2 134	0.06 33.3	0.03 33.3	4.0 232	15.7 46.5	22.6 46.9	21 36	17.8 5.6	21.3 10.8	18.0 33.3	19.4 35.0
	Residual fuel oil (RFO)													
Mg	2.3 34.8	3.3 63.6	2.2 114	4.5 31.1	2.1 66.7	2.6 25.2	2.9 58.6	6.2 71.0	6.7 53.7	7.0 80.0	9.6 26.0	13.5 118	4.9 24.5	7.5 76.0
Ni	6.2 25.8	8.1 81.5	5.8 36.2	6.1 4.9	4.3 7.0	6.0 16.7	6.2 48.4	10.0 25.0	10.8 30.6	11.9 33.6	19.3 51.3	10.7 9.3	12.9 21.7	12.8 44.5
	Solvent-refined coal (SRC)													
Cr	1.5 13.3	2.0 50	1.2 8.3	1.1 45.4	1.6 50	2.0 25.0	1.6 43.8	11.9 42.0	30.2 39.1	15.8 46.8	4.5 46.7	27.4 48.9	20.1 14.9	17.9 65.4
Fe	6.5 38.4	6.2 50	5.3 43.4	17.8 22.5	6.0 45	9.4 16	9.1 58.2	23.4 55.1	29.5 25.1	13 46	23 22	22.6 36.7	21.7 18.0	22.1 39.8
	RFO + SRC blend													
Cr	1.1 18.2	2.1 71.4	1.4 28.6	0.5 80.0	1.1 18.2	1.4 21.4	1.4 57.1	1.0 40.0	2.0 80.0	1.1 18.2	0.6 16.7	0.6 16.7	0.9 22.2	1.1 72.7
Zn	2.3 52.2	2.3 34.8	3.5 57.1	1.9 26.3	1.6 50	2.5 20	2.3 43.5	4.1 29.3	4.3 48.8	5.4 25.9	4.8 6.2	4.8 52.1	6.3 27.0	4.9 34.7

[a]Top numbers are mean concentrations in ppm.
[b]Bottom numbers are relative standard deviation in percent.

TABLE 10. – OVERALL INTERLABORATORY MEAN, STANDARD DEVIATION, AND 95-PERCENT CONFIDENCE LIMIT OF RESULTS FOR EACH ELEMENT IN EIGHT FUEL SAMPLES

(a) Experimental referee broadened-specification fuel

Element	Relative concentration level															
	Lower								Higher							
	Technique															
	MET[a] + AAS[b]				AAS				MET + AAS				AAS			
	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit
Al	20	1.0	0.9	±0.4	5	1.3	0.7	±0.9	34	22.7	6.1	±2.1	18	24.2	6.3	±3.2
B	12	17.9	57.5	+36.5 -17.9	--	----	-----	-----	14	6.5	5.2	±3.0	--	----	----	----
Ba[c]	3	.7	.9	+1.6 -.7	--	----	-----	-----	16	17.6	10.2	±5.5	--	----	----	----
Ca	11	1.9	3.8	+2.6 -1.9	--	----	-----	-----	15	17.0	11.0	±6.1	--	----	----	----
Cd[c]	0	-----	------	-----	--	----	-----	-----	14	17.3	12.6	±7.2	--	----	----	----
Co[d]	4	.01	.02	+.03 -.01	--	----	-----	-----	4	.11	.06	±.10	--	----	----	----
Cr	10	.6	1.0	+.7 -.6	1	----	-----	-----	31	22.6	12.5	±4.6	18	20.6	13.0	±6.4
Cu	7	.06	.03	±.03	--	----	-----	-----	15	18.8	5.9	±3.3	--	----	----	----
Fe	27	7.8	17.4	±6.9	14	4.6	6.9	±4.0	34	22.7	10.1	±3.5	18	23.4	10.4	±5.2
K[d]	6	1.4	1.8	+1.8 -1.4	--	----	-----	-----	10	5.0	6.4	±4.6	--	----	----	----
Mg	19	39.0	107.1	+51.6 -39.0	8	42.2	106.8	+89.3 -42.2	33	24.6	8.2	±2.9	18	25.9	5.4	±5.4
Mn	11	.3	.6	+.4 -.3	3	.3	.3	+.8 -.3	34	19.6	6.3	±2.2	8	22.5	4.2	±2.1
Na	24	4.0	9.3	±3.9	12	3.0	8.2	±3.0	34	19.4	6.8	±2.4	8	22.2	3.6	±1.8
Ni	13	1.6	3.8	+2.3 -1.6	4	.4	.04	±.06	33	23.1	14.8	±5.2	8	23.6	15.8	±7.9
Pb	9	2.4	4.1	+3.1 -2.4	--	----	-----	-----	14	21.1	13.7	±7.9	--	----	----	----
Si	14	35.1	80.6	+46.5 -35.1	--	----	-----	-----	15	14.8	10.6	±5.8	--	----	----	----
Sr[c,d]	2	-----	------	-----	--	----	-----	-----	6	.03	.02	±.02	--	----	----	----
Ti	6	.04	.08	+.08 -.04	--	----	-----	-----	15	18.3	11.4	±6.3	--	----	----	----
V	5	.02	.03	+.04 -.02	--	----	-----	-----	16	19.0	6.4	±3.4	--	----	----	----
Zn	17	.2	.3	±.2	10	.3	.4	±.3	34	20.6	14.5	±5.1	18	21.9	16.4	±8.2

[a]Multielement techniques
[b]Atomic absorption spectrometry.
[c]Too few results for meaningful calculation.
[d]Not present in multielement reference material.

TABLE 10. - Continued.

(b) Residual fuel oil

Element	Relative concentration level															
	Lower								Higher							
	Technique															
	MET[a] + AAS[b]				AAS				MET + AAS				AAS			
	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit
Al	29	8.5	3.4	±1.3	13	5.2	4.3	±2.6	31	11.3	12.3	±4.5	16	9.6	7.0	±3.7
B	8	1.2	2.8	+2.3 -1.2	--	----	----	----	8	3.0	6.5	+5.4 -3.0	--	----	----	----
Ba	12	1.7	1.9	±1.2	--	----	----	----	16	2.6	1.0	±.6	--	----	----	----
Ca	15	5.7	4.0	±2.2	--	----	----	----	15	10.2	7.0	±3.9	--	----	----	----
Cd[c]	0	----	----	----	--	----	----	----	2	----	----	----	--	----	----	----
Co	15	.8	.5	±.3	--	----	----	----	15	1.9	1.2	±.6	--	----	----	----
Cr	19	.4	.3	±.1	9	.3	.2	±.1	28	.9	.9	±.3	15	.6	.4	±.2
Cu	13	.9	2.1	+1.3 -.9	--	----	----	----	15	.7	.5	±.3	--	----	----	----
Fe	34	12.6	8.0	±2.8	18	13.5	8.6	±4.3	34	26.9	31.4	±11.0	18	22.3	5.5	±2.7
K	9	1.7	1.4	±1.1	--	----	----	----	9	2.6	2.1	±1.6	--	----	----	----
Mg	33	2.9	1.7	±.6	18	2.8	1.1	±.6	33	7.5	5.7	±2.0	18	7.2	6.4	±3.2
Mn	19	.2	.1	±.1	10	.2	.1	±.05	27	.6	.5	±.2	15	.4	.3	±.2
Na	34	16.5	6.3	±2.2	18	19.9	5.3	±2.6	34	38.1	32.0	±11.2	18	38.1	8.5	±4.2
Ni	33	6.2	3.0	±1.1	18	6.9	3.6	±1.8	33	12.8	5.7	±2.0	18	13.2	5.5	±2.8
Pb	12	.8	.6	±.4	--	----	----	----	10	2.0	2.4	±1.7	--	----	----	----
Si	14	22.9	47.1	+27.2 -22.9	--	----	----	----	13	32.0	42.2	±25.5	--	----	----	----
Sr	6	.14	.06	±.06	--	----	----	----	9	.4	.5	±.4	--	----	----	----
Ti	11	.5	.4	±.3	--	----	----	----	15	.9	.7	±.4	--	----	----	----
V	16	2.2	.9	±.5	--	----	----	----	16	5.3	1.6	±.9	--	----	----	----
Zn	31	4.3	2.0	±.7	18	4.4	.7	±.3	31	9.2	4.2	±1.5	18	10.5	4.3	±2.1

[a]Multielement techniques.
[b]Atomic absorption spectrometry.
[c]Too few results for meaningful calculation.

TABLE 10. - Continued.

(c) Solvent-refined coal

Element	Relative concentration level															
	Lower								Higher							
	Technique															
	MET[a] + AAS[b]				AAS				MET + AAS				AAS			
	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit
Al	16	2.4	4.5	±2.4	4	3.9	4.9	+7.8 −3.9	34	17.8	9.0	±3.2	18	17.3	7.8	±3.9
B	12	.8	.6	±.4	--	---	---	-----	15	12.9	6.5	±3.6	--	-----	---	-----
Ba	8	.6	.8	+.7 −.6	--	---	---	-----	15	15.5	10.3	±5.7	--	-----	---	-----
Ca	14	.8	1.1	±.6	--	---	---	-----	15	14.3	8.2	±4.6	--	-----	-----	-----
Cd[c]	0	---	---	-----	--	---	---	-----	14	12.5	9.6	±5.5	--	-----	-----	-----
Co[c,d]	1	---	---	-----	--	---	---	-----	4	.11	.06	±.09	--	-----	-----	-----
Cr	27	1.6	.6	±.2	16	1.6	.5	±.3	32	17.9	11.7	±4.2	18	16.9	11.4	±5.6
Cu	10	.13	.13	±.09	--	---	---	-----	15	13.6	7.2	±4.0	--	-----	-----	-----
Fe	30	9.1	5.3	±2.0	17	9.2	4.8	±2.5	34	22.2	8.7	±3.0	18	21.9	8.2	±4.1
K[d]	6	1.8	3.1	+3.2 −1.8	--	---	---	-----	11	5.8	7.0	±4.7	--	-----	-----	-----
Mg	21	.3	.3	±.1	9	.3	.3	±.2	33	18.7	8.2	±2.9	18	19.5	6.3	±3.1
Mn	20	.14	.09	±.04	11	.14	.08	±.05	31	17.9	7.3	±2.7		19.2	5.5	±2.8
Na	26	1.1	2.0	±.8	17	1.2	.6	±.3	33	19.2	8.2	±2.9		19.9	5.4	±2.7
Ni	14	.8	.8	±.5	5	.9	.9	+1.1	33	15.3	6.1	±2.2		16.4	7.4	±7.4
Pb	7	1.5	2.4	+2.3 −1.5	--	---	---	-.9	15	13.6	5.9	±3.3	--	-----	-----	-----
Si	11	1.3	.9	±.6	--	---	---	-----	13	14.4	10.5	±6.3	--	-----	-----	-----
Sr[d]	3	.002	.002	+.005 −.002	--	---	---	-----	5	.04	.04	±.05	--	-----	-----	-----
Ti	9	.3	.2	±.2	--	---	---	-----	15	15.2	12.1	±6.7	--	-----	-----	-----
V	10	.09	.07	±.05	--	---	---	-----	15	16.6	5.0	±2.8	--	-----	-----	-----
Zn	22	1.3	4.3	+1.9 −1.3	14	.4	.4	±.2	32	14.8	6.6	±2.4	18	15.5	7.2	±3.6

[a]Multielement techniques.
[b]Atomic absorption spectrometry.
[c]Too few results for meaningful calculation.
[d]Not present in multielement reference material.

TABLE 10. - Concluded.

(d) Blended solvent-refined coal and residual fuel oil

Element	Relative concentration level															
	Lower								Higher							
	Technique															
	MET[a] + AAS[b]				AAS				MET + AAS				AAS			
	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit	Number of results	Mean, ppm	Standard deviation	Confidence limit
Al	24	2.9	3.1	±1.3	9	2.6	1.4	±1.0	29	6.0	4.2	±1.6	14	6.8	5.4	±3.1
B	14	1.3	1.3	±.8	--	----	---	----	15	1.5	2.5	±1.4	--	----	---	----
Ba	12	1.1	.6	±.4	--	----	---	----	13	1.8	1.4	±.9	--	----	---	----
Ca	14	3.2	2.2	±1.3	--	----	---	----	14	6.7	4.4	±2.5	--	----	---	----
Cd[c]	0	----	----	----	--	----	---	----	1	----	----	----	--	----	---	----
Co	15	.6	.6	±.4	--	----	---	----	15	1.0	.5	±.3	--	----	---	----
Cr	28	1.4	.8	±.3	18	1.4	1.0	±.5	27	1.1	.8	±.3	17	.8	.3	±.1
Cu	12	.4	.5	±.3	--	----	---	----	14	.5	.6	±.3	--	----	---	----
Fe	33	14.6	11.5	±4.1	18	13.8	9.0	±4.5	34	16.9	9.7	±3.4	18	16.4	6.1	±3.0
K	8	1.2	.8	±.7	--	----	---	----	9	1.6	1.3	±1.0	--	----	---	----
Mg	31	2.1	1.4	±.5	18	3.6	1.0	±.5	33	3.4	1.3	±.5	18	2.0	1.3	±.6
Mn	24	.3	.4	±.2	13	.2	.1	±.1	23	.3	.2	±.1	13	.2	.1	±.1
Na	33	10.3	5.4	±1.9	18	11.9	4.7	±2.3	34	19.7	9.8	±3.4	18	25.1	8.9	±4.4
Ni	33	4.6	7.2	±2.5	18	6.5	9.4	±4.7	33	7.8	3.2	±1.1	18	8.6	2.4	±1.2
Pb	11	.6	.6	±.4	--	----	---	----	12	1.0	.9	±.6	--	----	---	----
Si	13	6.9	8.8	±5.3	--	----	---	----	13	10.4	12.6	±7.6	--	----	---	----
Sr	6	.1	.1	±.1	--	----	---	----	6	.15	.05	±.05	--	----	---	----
Ti	10	.6	.6	±.4	--	----	---	----	11	.6	.4	±.3	--	----	---	----
V	16	1.3	.7	±.4	--	----	---	----	16	2.8	1.7	±.9	--	----	---	----
Zn	31	2.3	1.0	±.4	18	2.8	1.0	±.5	31	4.9	1.7	±.6	18	5.58	1.47	±.73

[a]Multielement techniques.
[b]Atomic absorption spectrometry.
[c]Too few results for meaningful calculation

TABLE 11. - ELEMENTS WITH A STATISTICALLY SIGNIFICANT LABORATORY EFFECT AT $\alpha = 0.01$

Analytical technique	Fuel				
	Experimental referee broadened-specification fuel	Residual fuel oil (RFO)	Solvent-refined coal (SRC)	RFO + SRC blend	
				Lower level	Higher level
	Elements				
Multielement[a]	Ba[b] (II)[c] Ca[d] Cd[e] (III) Co[d] K (II,IV) Pb (IV) Sr[d,e]	B (III) Ca[d] Cd[e] (III) Co[e] (III) Cr[e] (III) K (IV) Mn[e] (III) Pb[e,g] Sr[e] (III) Ti[e] (IV) Zn[e] (III)	Ca (III) Cd[e] (III) Co[d,e] Cr[e] (IV-III)[f] Fe (III) K[d,e] Mn[b] (IV-II)[f] Sr[d,e] Zn[e] (III)	B[e] (III) Ca[d] Cd[e] (III) Co (III) Cr[d] K[d] Mn[e] (III) Si[e,g] Sr[d] Zn[e] (III)	B (III) Ca[d] Cd[e] (II,III)[c] Co[e] (III) Cr[e] (III) K[d] Mn[e] (III) Si[e] (I) Sr[e] (II) Zn[e] (III)
Atomic absorption[h]	Al (V,VI) Fe (II,IV) Mn (III)	Al (V) Cr[d,e] Fe (IV) Mn[d,e]	Al[e] (IV-V)[f] Mg (IV)	Al[e] (V,VI) Fe (IV) Mn[d,e] Na (III)	Al[e] (V) Fe (IV) Mn[d,e] Na (IV)
Multielement methods and atomic absorption[i]	Mg (IV) Ni (IV) Zn[d]	Cr[e] (III) Mg (IV) Mn[e] (III) Zn[e] (III)	Al (IV-II)[f] Cr[d] Fe (III,IV) Mg[d] Mn[b] (II) Ni (II)	Cr[d] Fe[e] (IV) Mg (IV) Mn[e] (III) Zn[e] (III)	Cr (II) Mn[e] (III) Zn[e] (III)

[a]Analyses of 20 elements at five laboratories.
[b]Tested as significant only when using zero in place of reported upper concentration limit.
[c]Roman numeral in parentheses is code (codes) of laboratory (or laboratories) whose mean tested significantly different from those of other laboratories using Newman-Keuls range test.
[d]Several laboratories' means were significantly different.
[e]Tested as significant only when using lower value of reported upper concentration limit.
[f]Only the two laboratories' means specified tested significantly different from one another.
[g]Range test did not indicate differences in laboratory means.
[h]Analyses of eight elements at six laboratories.
[i]Analyses of eight elements at five laboratories.

TABLE 12. - ELEMENTS WITH A STATISTICALLY SIGNIFICANT CONCENTRATION EFFECT AT $\alpha = 0.01$

Analytical technique	Fuel		
	Experimental referee broadened-specification fuel	Residual fuel oil	Solvent-refined coal
Multielement methods[a]	Ba[b] Ca Cd[c] K Mn Na	Cd[c] Cr[c] Mn[c] Sr[c] Zn[c]	B Ba Ca Cd[c] Cr[c] Cu Fe K[c] Mn Ni Pb Si[b] V Zn
Atomic absorption[d]	Al[c] Mn[c]	Cr[c] Mn[c]	Al[c] Fe Ni Zn
Multielement methods and atomic absorption[h]	Al Fe[c] Mg Mn Na Zn	Cr[c] Mn[c]	Al Cr Fe Mn Ni Zn

[a]Analyses of 20 elements at five laboratories.
[b]Tested as significant only when using zero in place of reported upper concentration limit.
[c]Tested as significant only when using value of reported upper concentration limit.
[d]Analyses of eight elements at six laboratories.
[e]Analyses of eight elements at five laboratories.

TABLE 13. - ELEMENTS WITH A STATISTICALLY SIGNIFICANT DIFFERENCE IN ASHING ADDITIVES AT $\alpha = 0.01$

Analytical technique	Fuel				
	Experimental referee broadened-specification fuel	Residual fuel oil (RFO)	Solvent-refined coal (SRC)	RFO + SRC blend	
				Lower level	Higher level
Multielement methods[a]		B[b] (2)[c]		B (2) Sr[d] (1)	B (2)
Atomic absorption[e]	Mn (1)				Na (2)
Multielement methods and atomic absorption[f]	Mg (2) Ni (2-3) Zn (1)				

[a]Analyses of 20 elements at five laboratories.
[b]Tested as significant only when using value of reported upper concentration limit.
[c]The number in parentheses is ashing additive that produced significantly different mean using Newman-Keuls range test (1 - H_2SO_4, 2 - HNO_3, 3 - N additive).
[d]Tested as significant only when using zero in place of reported upper concentration limit.
[e]Analyses of eight elements at six laboratories.
[f]Analyses of eight elements at five laboratories.

TABLE 14. - ELEMENTS WITH A STATISTICALLY SIGNIFICANT DIFFERENCE BETWEEN MULTIELEMENT TECHNIQUES AND ATOMIC ABSORPTION SPECTROMETRY[a] ANALYSIS AT $\alpha = 0.01$

Fuel				
Experimental referee broadened-specification fuel	Residual fuel oil (RFO)	Solvent-refined coal (SRC)	RFO + SRC blend	
			Lower level	Higher level
Zn	Cr Mn Zn	Cr Fe[b] Zn	Cr Mn Zn	Cr Mn Zn

[a]Analyses of eight elements at five laboratories.
[b]Tested as significant by substitution of zero for value of reported upper concentration limit. All others were obtained when upper value was used.

TABLE 15. – ELEMENTS WITH SIGNIFICANT INTERACTION EFFECTS AT $\alpha = 0.01$

Sample	Analytical technique	Interaction term				
		C x L[a]	C x P[b]	L x P[c]	B x L[d]	B x P[e]
Experimental referee broadened-specification fuel (ERBS)	Atomic absorption[f]	Al[g], Fe, Mn	Mn	———		
	Multielement methods[h]	Ba[g], Ca, Co[g], K	--	———		
Residual fuel oil (RFO)	Atomic absorption	Cr[i]	--	Al[g]		
	Multielement methods	Cd[i], Cr[i], Mn[i], Sr[i], Zn[i]	--	B, Ti		
Solvent-refined coal (SRC)	Atomic absorption	Al[g], Mg	--	———		
	Multielement methods	Ba, Ca, Fe, K[g], Mn, Pb[i]	--	———		
RFO + SRC blend, lower concentration	Atomic absorption			———	---	---
	Multielement methods			Co[g], Sr[g]	---	---
RFO + SRC blend, higher concentration	Atomic absorption			Mn, Na[i]	---	---
	Multielement methods			B, Cd[i], Co[g]	---	---

[a]Concentration–laboratory interaction.
[b]Concentration–preparation interaction.
[c]Laboratory–preparation interaction.
[d]Calculated versus observed blend concentration – laboratory interaction term.
[e]Calculated versus observed blend concentration – preparation interaction term.
[f]Analyses of eight elements at six laboratories.
[g]Tested as significant only when using zero in place of reported upper concentration limit.
[h]Analyses of 20 elements at five laboratories.
[i]Tested as significant only when using value of reported upper concentration limit.

TABLE 16. - ELEMENTS WITH SIGNIFICANT INTERACTION EFFECTS(α = 0.01) FOR ANALYSIS OF ATOMIC ABSORPTION SPECTROMETRY AND MULTIELEMENT METHODS DATA[a]

Interaction term					
C x L[b]	C x P[c]	L x P[d]	C x L x P[e]	C x T(L)[f]	P x T(L)[g]
Experimental referee broadened-specification fuel					
Mg Ni Zn	Mg Ni Zn	Mg Ni Zn	Mg Ni Zn		
Residual fuel oil					
Cr[h] Mn[h] Zn[h]		Mg[h]		Cr[h] Mg[h] Zn[h]	Mg[h]
Solvent-refined coal					
Al Mg Cr Mn Fe Ni				Fe	

[a]Analyses of eight elements at five laboratories.
[b]Concentration-laboratory interaction.
[c]Concentration-preparation interaction.
[d]Laboratory-preparation interaction.
[e]Concentration-laboratory-preparation interaction.
[f]Concentration-technique interaction, nested under laboratory.
[g]Preparation-technique interaction, nested under laboratory.
[h]Tested as significant only when using value of reported upper concentration limit.

TABLE 17. - MATHEMATICAL EXPRESSIONS USED TO CALCULATE RELATIVE DIFFERENCE IN FUEL SAMPLES

Fuel	Relative difference,[a] E, percent
Experimental referee broadened-specification fuel fuel (ERBS)	$E_{ERBS} = \left[1 - \left\lvert \frac{C'_{ERBS} - C_{ERBS}}{23.9} \right\rvert \right] \times 100$
Solvent-refined coal (SRC)	$E_{SRC} = \left[1 - \left\lvert \frac{C'_{SRC} - C_{SRC}}{20.6} \right\rvert \right] \times 100$
Residual fuel oil (RFO)	$E_{RFO} = \left[1 - \left(\frac{C_{RFO}/C'_{RFO}}{2.08} \right) \right] \times 100$
RFO + SRC blend, lower concentration	$E_{LBL} = \left[1 - \left(\frac{C_{LBL}}{0.28\ C_{RFO} + 0.72\ C_{SRC}} \right) \right] \times 100$
RFO + SRC blend, higher concentration	$E_{HBL} = \left[1 - \left(\frac{C_{HBL}}{0.65\ C_{RFO} + 0.35\ C_{SRC}} \right) \right] \times 100$

[a]Where C is concentration of fuel and C' is concentration of altered fuel (i.e., spiked ERBS and SRC or diluted RFO).

TABLE 18. - CALCULATED MEAN AND RANGE OF RELATIVE DIFFERENCE OF MEASURED METAL CONCENTRATION LEVEL CHANGE IN FUEL

Element	Fuel							
	Experimental referee broadened-specification fuel				Solvent-refined coal (SRC)			
	Technique							
	Multielement		Atomic absorption spectrometry		Multielement		Atomic absorption spectrometry	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
	Relative difference, percent[a]							
Al	32.3	3.1-180	30.8	3.2-104	51.0	10.7-148	44.2	0.8-122
B	137	14.2-916	----	----------	43.8	0.4-105	----	----------
Ba	44.4	0.4-92.5	----	----------	52.2	1.6-112	----	----------
Ca	43.9	7.2-100	----	----------	34.8	1.2-99.6	----	----------
Cd	48.0	0.4-108	----	----------	59.3	3.9-207	----	----------
Cr	42.4	0.3-91.6	48.0	3.2-118	49.0	1.5-135	50.0	1.4-94.2
Cu	28.7	7.6-60.3	----	----------	42.8	6.4-82.0	----	----------
Fe	60.2	2.5-410	35.0	2.6-99.2	54.1	9.2-105	48.8	2.3-110
Mg	136	2.9-1540	91.0	1.7-1263	42.4	5.0-83.2	25.8	1.0-61.4
Mn	35.4	4.6-80.8	14.4	0.6-43.5	40.9	1.6-90.3	20.4	0.7-65.2
Na	60.4	21.3-163	21.4	0.3-142	41.9	1.9-157	23.1	2.9-69.4
Ni	45.2	12.3-169	46.0	0-190	37.4	1.4-56.3	35.8	1.0-94.6
Pb	41.7	3.8-114	----	----------	44.0	1.8-105	----	----------
Si	179	0.4-1020	----	----------	53.1	2.9-92.7	----	----------
Ti	42.8	7.5-92.5	----	----------	51.8	0.5-143	----	----------
V	27.6	7.5-85.6	----	----------	24.3	1.6-82.0	----	----------
Zn	63.5	0.4-149	39.9	1.0-249	61.0	16.5-197	35.6	0.2-80.5

Element	Fuel											
	Residual fuel oil (RFO)				RFO + SRC blend[b]							
					Concentration level							
					Lower				Higher			
	Technique											
	MET[c]		AAS[d]		MET		AAS		MET		AAS	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
	Relative difference, percent[a]											
Al	109	3.8-622	22.4	3.6-82.8	43.0	1.5-98.5	48.8	0.3-91.3	34.7	6.6-99.1	40.3	3.7-160
B	57.6	14.2-102	----	----------	218	1.4-1983	----	----------	261	2.9-2757	----	----------
Ba	99.9	7.8-345	----	----------	103	3.5-466	----	----------	86.1	6.4-657	----	----------
Ca	38.0	3.8-140	----	----------	55.3	1.4-248	----	----------	79.3	4.5-630	----	----------
Cd	(e)	----------	----	----------	(e)	----------	----	----------	(e)	----------	----	----------
Co	20.2	5.8-44.3	----	----------	47.2	4.8-78.6	----	----------	36.2	1.4-81.8	----	----------
Cr	96.7	3.8-488	27.7	1.1-194	40.6	0.6-83.7	86.6	3.4-1018	63.0	31.8-128	40.4	5.1-238
Cu	246	3.8-3107	----	----------	231	1.1-1329	----	----------	102	2.6-856	----	----------
Fe	54.4	0.6-291	25.3	3.8-79.0	104	7.0-749	43.3	0.1-335	26.7	1.8-86.9	16.4	0.4-79.1
K	106	16.3-180	----	----------	76.8	8.3-257	----	----------	70.5	31.8-105	----	----------
Mg	199	2.6-2305	43.3	0.4-512	51.8	2.0-164	32.2	1.1-147	78.5	8.0-91.5	16.3	1.0-82.6
Mn	2544 (54.8[f])	0.2-27386	41.5	3.8-106	54.7	8.7-257	78.7	3.6-257	43.6	5.7-100	22.8	2.7-60.9
Na	65.7	3.8-477	25.1	3.8-57.4	53.6	2.2-342	36.9	5.6-123	43.0	7.3-1109	19.0	0.5-63.7
Ni	69.2	0.3-214	23.6	0.2-148	54.1	9.4-150	102	0-243	53.9	5.2-377	22.7	0.6-73.9
Pb	65.8	8.2-267	----	----------	61.4	3.2-198	----	----------	240	4.4-2122	----	----------
Si	258	2.2-2064	----	----------	107	40.4-708	----	----------	43.0	6.9-94.5	----	----------
Sr	77.7	0.6-285	----	----------	(e)	----------	----	----------	(e)	----------	----	----------
Ti	190	3.8-1274	----	----------	81.4	21.4-193	----	----------	68.4	23.1-200	----	----------
V	40.3	1.6-272	----	----------	41.9	2.0-147	----	----------	36.4	1.1-106	----	----------
Zn	29.3	5.5-81.1	30.4	2.6-147	42.6	2.0-95.3	39.2	0.4-156	37.9	6.0-139	19.8	0.3-57.9

[a]Relative difference is defined as ratio of measured and known differences between higher and lower concentration levels of given fuel type relative to expected value of 1, expressed in percent (refer to table 17).
[b]Fuels prepared by blending solvent-refined coal and residual fuel oil.
[c]Results obtained using multielement techniques.
[d]Results obtained using atomic absorption spectrometry.
[e]Majority of results were reported below detection limit.
[f]Mean percent relative error when eliminating 27 386 value.

TABLE 19. - POINT ASSIGNMENTS FOR COMPARISON OF LABORATORY PERFORMANCE BASED ON RELATIVE ERROR CALCULATED FOR EACH ELEMENT IN A GIVEN FUEL

Relative error, percent	Merit point
0–5	10
>5–10	9
>10–20	8
>20–35	7
>35–50	6
>50–75	5
>75–90	4
>90–110	3
>110–150	2
>150–200	1
>200	0

TABLE 20. - COMPARISON OF TOTAL MERIT POINTS ASSIGNED TO EACH LABORATORY FOR MULTIELEMENT ANALYSIS OF FUEL SAMPLES

Laboratory code	Fuel					Total points
	Experimental referee broadened-specification fuel	Residual fuel oil (RFO)	Solvent-refined coal (SRC)	RFO + SRC blend, lower concentration	RFO + SRC blend, higher concentration	
	Merit points					
Multielement techniques						
I	99	87	107	85	90	468
II	119	103	124	95	105	546
III	71	76	78	69	81	375
IV	103	107	96	107	105	518
VI	118	118	117	123	112	588
Maximum[a]	170	200	170	200	200	940
Atomic absorption spectrometry						
I	53	66	52	61	67	299
II	59	49	60	43	61	272
III	58	53	54	45	63	273
IV	46	57	42	54	56	255
V	64	49	55	45	54	267
VI	64	56	65	54	57	296
Maximum[a]	80	80	80	80	80	400

[a]Maximum number of points obtainable for measuring concentration level change for all elements in fuel to within 5.0 percent.

TABLE 21. – LOWEST RELATIVE ERROR REPORTED BY ANY LABORATORY FOR ANALYSIS OF ELEMENTS IN EACH FUEL MATRIX

Element	Fuel									
	Experimental referee broadened-specification fuel		Residual fuel oil (RFO)		Solvent-refined coal (SRC)		RFO + SRC blend, lower concentration specification		RFO + SRC blend, higher concentration	
	Technique									
	MET[a]	AAS[b]	MET	AAS	MET	AAS	MET	AAS	MET	AAS
Al	5.5	25.3	13.4	19.4	33.2	19.7	19.2	41.9	19.0	15.9
B	61.4	----	77.6	----	11.8	----	24.4	----	36.9	----
Ba	17.3	----	29.0	----	12.2	----	26.0	----	23.8	----
Ca	22.5	----	9.5	----	12.0	----	8.2	----	19.1	----
Cd	11.6	----	(c)	----	21.7	----	9.6	----	(c)	----
Co	(d)	----	9.4	----	(d)	----	26.2	----	26.5	----
Cr	20.4	31.4	24.9	17.8	9.6	16.9	22.6	9.9	47.7	16.7
Cu	19.1	----	19.8	----	22.9	----	6.1	----	18.7	----
Fe	15.9	12.0	5.8	3.9	29.8	30.2	33.7	5.8	15.5	3.1
K	(d)	----	43.7	----	(d)	----	38.9	----	64.3	----
Mg	9.9	2.8	8.8	0.5	14.5	4.6	16.8	7.1	22.2	13.3
Mn	12.8	5.0	41.8	14.8	15.0	7.9	11.5	10.2	35.7	14.3
Na	38.9	6.6	14.1	10.7	22.0	13.3	8.5	8.3	27.1	5.5
Ni	23.3	16.2	13.8	5.5	21.1	5.7	24.0	14.3	14.4	8.6
Pb	12.3	----	59.9	----	14.9	----	52.6	----	30.8	----
Si	9.3	----	30.2	----	31.2	----	42.6	----	14.2	----
Sr	(d)	----	46.3	----	(d)	----	31.7	----	32.1	----
Ti	25.5	----	35.1	----	28.8	----	35.8	----	31.6	----
V	20.0	----	9.9	----	8.7	----	10.8	----	21.2	----
Zn	34.0	8.9	18.9	7.8	28.7	1.1	17.2	19.0	25.9	9.8

[a]Multielement techniques.
[b]Atomic absorption spectrometry.
[c]Too few results reported over detection limit.
[d]Elements not present in multielement reference material.

APPENDIX - TRACE METAL CONCENTRATIONS REPORTED BY PARTICIPATING LABORATORIES USING A PRESCRIBED SAMPLE PREPARATION

Reported by Laboratory I

Element	Fuel															
	Experimental referee broadened-specification fuel				Residual fuel oil (RFO)				Solvent-refined coal (SRC)				RFO + SRC blend			
	Concentration level															
	Lower		Higher		Lower		Higher		Lower		Higher		Lower		Higher	
	Technique															
	SSMS[a]	AAS[b]	SSMS	AAS	SSMS	AAS	SSMS	AAS	SSMS	AAS	SSMS	AAS	SSMS	AAS	SSMS	AAS
	Trace metal concentration, ppm															
Al	[c]0.15	<2	23	19	8.2	3	70	5.6	0.86	<2	30	14	0.3	3	8.0	4
	[d]1.36	2	26	13	16	4	<5.7	7.2	<3.1	<2	36	15	16	2	3.1	5
	[e].25	<2	22	18	5.2	2	14	5.6	.61	<2	19	16	5.6	<2	10	3
B	.01	----	3.4	----	.23	----	.23	----	.72	----	11	---	.48	----	.52	---
	.08	----	3.2	----	.02	----	<.24	----	.55	----	11	---	.61	----	.54	---
	.01	----	2.9	----	.03	----	.05	----	.50	----	12	---	.38	----	.18	
Ba	<.01	----	16	----	.58	----	1.3	----	<.05	----	9.8	---	.50	----	6.4	---
	.10	----	5.4	----	.85	----	2.7	----	<.43	----	15	---	.44	----	2.1	---
	<.01	----	9.5	----	.85	----	1.3	----	.01	----	12	---	2.1	----	1.4	---
Ca	.11	----	9	----	4.3	----	12	----	1.6	----	11	---	<2.3	----	<2.1	---
	.06	----	12	----	5.6	----	5.3	----	.3	----	20	---	.7	----	7.2	---
	.02	----	11	----	4.1	----	4.1	----	.12	----	7.0	---	3.6	----	3.6	---
Cd	<.01	----	1.7	----	<.01	----	.05	----	<.04	----	1.1	---	<.05	----	.04	---
	<.01	----	.66	----	<.01	----	.06	----	<.05	----	1.6	---	<.03	----	<.03	---
	<.01	----	1.0	----	<.01	----	<.01	----	<.01	----	1.6	---	<.01	----	<.01	---
Co	.01	----	.19	----	.53	----	1.4	----	<.03	----	.18	---	.17	----	.46	---
	.04	----	.10	----	.92	----	2.5	----	<.03	----	.13	---	.29	----	.79	---
	<.01	----	.11	----	.40	----	1.1	----	<.01	----	.09	---	.18	----	1.3	---
Cr	.03	<.04	24	9.0	.36	.20	4.4	.40	1.7	1.6	13	4.4	.9	1.1	1.1	.68
	.15	.04	4.5	4.8	.54	.24	.44	.28	1.5	1.2	12	10	1.4	.84	1.4	.44
	<.01	<.04	43	5.6	.14	.20	.57	.44	1.3	1.6	20	12	1.0	1.2	1.4	.92
Cu	.05	----	15	----	.2	----	.4	----	<1.4	----	16	---	<1.6	----	.4	---
	.11	----	9.6	----	.37	----	.37	----	<.20	----	11	---	.78	----	2.3	---
	.05	----	36	----	.15	----	.30	----	.02	----	12	---	.10	----	.33	---
Fe	1.7	2.0	38	12	11	6.2	62	17	3.8	7.8	34	6.5	9	11	47	10
	.14	.3	12	8	24	9.1	195	13	<8.3	4.55	32	13	11	6.4	17	8
	.57	3.6	30	13.5	11	9.6	30	16	10	6.2	38	17	19	9.3	37	13

K	.13	----	.14	----	1.2	----	7.0	---	.8	----	12	---	<.8	----	1.7	---
	.21	----	.35	----	3.2	----	1.1	---	8.1	----	1.3	---	2.8	----	1.0	---
	<.02	----	.13	----	.35	----	1.9	---	.08	----	.12	---	.35	----	.55	---
Mg	<.02	.6	13	24	3.8	2.3	15	4.8	.62	.7	23	20	<1.2	1.9	.85	3.4
	.25	<.2	18	25	1.5	2.2	3.0	4.6	<1.2	<.2	16	21	<.92	1.3	2.8	2.8
	.04	<.2	20	24.5	1.6	2.2	5.4	4.6	.02	.2	37	22	1.9	1.3	3.8	3.0
Mn	.01	<.04	10	19	.14	.08	.78	.24	.04	.12	17	14	.22	.12	.22	.16
	.05	<.04	4.8	19	.20	.12	.81	.24	.05	.08	7.9	15	.16	.12	.24	.16
	<.01	.04	25	18.8	.10	.16	.29	.28	.09	.12	20	16	.10	.12	.30	.20
Na	.12	.10	6.7	20	17	15.7	204	36	.6	.10	10	15	15	9.3	7	22
	.25	.20	6.0	21	8	17	1.4	37	<4.3	.22	17	16	<4.6	9.8	11	23
	.19	.32	19	21	10	16	38	39	.08	.20	26	17	6.6	10	18	24
Ni	.20	<.2	21	16	5.6	5.3	11	11	<.06	<.2	17	10	1.3	3	4.9	6.8
	.44	<.2	9.2	10	9.2	6.6	11	8.4	<.07	<.2	17	15	1.6	2.6	9	7.6
	<.01	<.2	17	15	4.8	5.8	5.8	13	.02	<.2	14	14	4.1	16	18	8.4
Pb	.05	----	19	----	.28	----	<.53	----	.48	----	12	---	<.51	----	.49	---
	.17	----	7.4	----	.41	----	.64	----	<.52	----	22	---	<.39	----	.85	---
	<.01	----	12	----	.26	----	.36	----	<.01	----	12	---	.13	----	.35	---
Si	.3	----	31	----	<15	----	<85	----	<13	----	<53	---	<12	----	<23	---
	8.88	----	19	----	50	----	<76	----	<25	----	<29	---	<25	----	<33	---
	3.1	----	9	----	3.2	----	61	----	<1.1	----	20	---	5.3	----	48	---
Sr	<.01	----	.06	----	.09	----	.48	----	<.03	----	<0.07	---	.01	----	.17	---
	<.01	----	.01	----	.19	----	.21	----	.01	----	.11	---	.05	----	.18	---
	<.01	----	.03	----	.11	----	.23	----	<.01	----	.06	---	.16	----	.18	---
Ti	.02	----	27	----	.07	----	2.0	----	<.05	----	29	---	.34	----	.07	---
	.19	----	11	----	.07	----	1.5	----	<.06	----	16	---	<.33	----	<.29	---
	.01	----	26	----	.27	----	.38	----	.17	----	9.6	---	.67	----	.92	---
V	.03	----	27	----	3.5	----	9.8	----	.04	----	21	---	1.1	----	2.9	---
	.07	----	3.5	----	4.5	----	5.0	----	.08	----	17	---	3.6	----	2.7	---
	<.01	----	15	----	2.5	----	6.4	----	.06	----	22	---	1.1	----	8.6	---
Zn	.03	1.2	13	18	4.3	3.6	11	9.2	.24	1.6	10	10	1.4	3.6	3.7	6.0
	.19	<.04	6.8	10	13	4.2	5.1	7.6	4.0	.12	9.2	15	1.2	4.0	5.0	3.6
	.05	<.04	18	14	2.1	3.6	2.3	6.4	.03	<.04	14	12	1.3	2.2	3.6	2.8

[a]Spark source mass spectrometry.
[b]Atomic absorption spectrometry.
[c]First row of values for an element denotes analysis performed on an H_2SO_4-aided ashed sample.
[d]Second row of values for an element denotes analysis performed on an HNO_3-aided ashed sample.
[e]Third row of values for an element denotes analysis performed on an ashed sample using no ashing additive.

Reported by Laboratory II

Element	Fuel															
	Experimental referee broadened-specification fuel				Residual fuel oil (RFO)				Solvent-refined coal (SRC)				RFO + SRC blend			
	Concentration level															
	Lower		Higher		Lower		Higher		Lower		Higher		Lower		Higher	
	Technique															
	dc Arc[a]	AAS[b]	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS
	Trace metal concentration, ppm															
Al	[c]0.5	<2.4	31	25.53	2.85	4.62	12.5	9.03	0.67	<2.5	37.9	24.35	1.65	1.13	4.7	4.51
	[d]3.5	.50	20	26.32	.5	3.30	7.5	7.11	.7	.5	19	21.27	3.0	.63	4.0	4.62
	[e].6	<26	26	24.95	7.5	6.39	11	5.25	.80	<2.5	27	14.79	3.6	<2.5	9.6	<2.5
B	<.5	-----	4.6	-----	.05	-----	.21	-----	1.35	-----	19	-----	.55	-----	2.3	-----
	.4	-----	10	-----	.3	-----	.5	-----	2.5	-----	19	-----	2.5	-----	.4	-----
	.02	-----	6.2	-----	.4	-----	.06	-----	.16	-----	21	-----	.4	-----	.22	-----
Ba	<1.0	-----	46	-----	1.1	-----	4.2	-----	.05	-----	25.2	-----	.55	-----	1.2	-----
	<1	-----	33	-----	1.8	-----	1.5	-----	.03	-----	18	-----	.8	-----	.9	-----
	<.05	-----	21	-----	1.9	-----	2.6	-----	.06	-----	21	-----	.54	-----	1.6	-----
Ca	<1	-----	31	-----	4.3	-----	12.5	-----	.40	-----	18.9	-----	1.65	-----	4.7	-----
	<1	-----	20	-----	5.0	-----	9.5	-----	.3	-----	16	-----	5.0	-----	4.0	-----
	<.5	-----	31	-----	7.5	-----	7.4	-----	.16	-----	21	-----	1.8	-----	6.4	-----
Cd	<1	-----	23	-----	<.1	-----	<.1	-----	<1	-----	12.6	-----	<1	-----	<1	-----
	<1	-----	20	-----	<.5	-----	<.5	-----	<.5	-----	10	-----	<.5	-----	<.5	-----
	<1.0	-----	21	-----	<1.0	-----	<1.0	-----	<1.0	-----	16	-----	<1.0	-----	<1.0	-----
Co	<1	-----	<1.0	-----	.7	-----	2.1	-----	<1.0	-----	<1	-----	.33	-----	1.4	-----
	<1	-----	<1	-----	1.3	-----	2.5	-----	.25	-----	<1	-----	1.5	-----	.9	-----
	<.1	-----	<1.0	-----	.8	-----	1.5	-----	<1.0	-----	<1.0	-----	.40	-----	1.0	-----
Cr	.2	<.24	46	15.08	.85	.43	2.1	.67	2.0	1.99	50.5	24.47	.33	1.86	4.7	1.19
	.3	<.16	33	23.14	.5	<.17	.6	.76	3.5	1.84	19	22.73	2.5	1.59	.9	.98
	<.2	<.26	26	51.99	1.3	<.25	1.5	1.53	.80	<.25	27	37.81	1.8	4.79	2.5	<.25
Cu	<.1	-----	15.5	-----	.21	-----	.85	-----	.07	-----	18.9	-----	1.65	-----	.47	-----
	<.1	-----	20	-----	.50	-----	.75	-----	.1	-----	19	-----	.4	-----	.4	-----
	.08	-----	21	-----	.75	-----	.75	-----	.03	-----	32	-----	.2	-----	.32	-----
Fe	3.0	<.05	23	28.60	4.3	11.62	15	22.96	2.7	8.06	25.2	26.33	3.3	10.38	9.3	17.46
	3	.40	20	33.36	11	8.7	15	22.65	8.5	9.01	21	30.09	9.6	12.75	8.5	16.24
	1.5	<.05	26	47.62	9.5	27.69	15	21.66	3.0	<.05	32	42.26	54	26.39	11	15.90

K	<4	-----	15.5	-----	<4	-----	<4	-----	<4	-----	16	-----	<4	-----	<4	-----
	<4	-----	11.1	-----	<4	-----	<4	-----	<4	-----	9.6	-----	<4	-----	<4	-----
	<4	-----	15.4	-----	<4	-----	<4	-----	<4	-----	18.9	-----	<4	-----	<4	-----
Mg	.005	9.9	31	24.68	1.6	2.37	8.5	5.59	.17	.11	37.9	18.42	1.1	1.35	3.5	3.50
	.03	.08	20	22.89	2.0	2.29	3.0	5.73	.15	.02	19	20.20	2.5	1.46	1.7	3.67
	.08	<.05	26	35.53	7	4.70	13	4.28	.16	<.05	27	27.44	.9	2.59	4.8	1.86
Mn	.02	<.05	4.6	26.89	.36	.25	.85	.42	.27	.13	37.9	21.53	.22	.22	.93	.31
	.05	<.03	20	25.97	.5	.17	.3	.73	.3	.11	19	24.77	.65	.21	.60	.28
	.04	<.05	21	21.08	.6	.26	.74	.17	.08	<.05	21	14.66	.20	.15	.48	.05
Na	<5	.30	15.5	24.91	1.5	20.55	4.2	45.23	.27	.24	12.6	20.07	1.1	3.08	2.3	24.73
	<5	.32	10	24.16	5	16.92	10	48.59	<5	.27	10	25.22	3	11.02	4	30.41
	<2	<.03	41	20.01	11	20.18	22	18.60	<2	.07	53	12.76	5.5	11.21	13	7.85
Ni	<.5	.42	15.5	26.52	1.3	8.20	8.5	14.20	.53	<.25	12.6	21.93	1.1	4.56	3.73	9.67
	<.5	<.16	20	22.34	7.5	7.17	7.5	14.15	.7	.41	17	19.45	4.0	41.10	4.0	10.86
	<.5	<.26	21	54.52	3.8	20.55	7.4	13.06	.7	<.25	21	40.09	1.8	12.53	3.2	14.76
Pb	<.5	-----	23	-----	.43	-----	2.1	-----	.03	-----	18.9	-----	.33	-----	.93	-----
	<.5	-----	20	-----	.5	-----	1.2	-----	<.5	-----	14	-----	1.0	-----	.7	-----
	.08	-----	21	-----	1.5	-----	2.2	-----	.02	-----	21	-----	.20	-----	.96	-----
Si	10.0	-----	31	-----	8.5	-----	21	-----	2.7	-----	37.9	-----	2.2	-----	7.0	-----
	9	-----	33	-----	15	-----	25	-----	2.5	-----	19	-----	5.0	-----	4.0	-----
	.78	-----	21	-----	15	-----	15	-----	1.0	-----	21	-----	7.2	-----	11	-----
Sr	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----
	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----
	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----	<5	-----
Ti	<.1	-----	46	-----	.43	-----	1.3	-----	.53	-----	50.5	-----	.22	-----	1.4	-----
	<.1	-----	28	-----	.5	-----	.1	-----	.7	-----	19	-----	1.0	-----	.8	-----
	<.08	-----	21	-----	1.5	-----	2.2	-----	.5	-----	21	-----	.55	-----	.96	-----
V	<.5	-----	31	-----	1.1	-----	8.5	-----	.15	-----	25.2	-----	1.1	-----	2.33	-----
	<.5	-----	20	-----	3	-----	5	-----	.2	-----	19	-----	2.0	-----	2.5	-----
	<.2	-----	18	-----	2.2	-----	4.5	-----	.06	-----	21	-----	1.1	-----	2.2	-----
Zn	<5	.11	15.5	23.76	1.5	4.53	4.2	10.08	.27	.18	12.6	29.64	1.1	2.94	2.3	6.81
	<5	.11	20	28.55	3	4.63	5	23.79	<5	.18	14	29.42	2	2.88	2	6.53
	<.8	<.1	26	17.00	5.6	5.81	11	5.32	<.8	<.10	27	13.00	2.0	3.07	4.8	3.19

[a]Direct-current arc.
[b]Atomic absorption spectrometry.
[c]First row of values for an element denotes analysis performed on an H_2SO_4-aided ashed sample.
[d]Second row of values for an element denotes analysis performed on an HNO_3-aided ashed sample.
[e]Third row of values for an element denotes analysis performed on an ashed sample using no ashing additive.

Reported by Laboratory III

Element	Fuel															
	Experimental referee broadened-specification fuel				Residual fuel oil (RFO)				Solvent-refined coal (SRC)				RFO + SRC blend			
	Concentration level															
	Lower		Higher		Lower		Higher		Lower		Higher		Lower		Higher	
	Technique															
	dc Arc[a]	AAS[b]	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS
	Trace metal concentration, ppm															
Al	[c]0.4	<1.6	14	23	1	5.1	2	6.3	0.2	3.1	7	16	1	4.9	2	6.2
	[d]1	<2	21	15	2	<2	11	6.3	1	<2	14	21	2	<2	8	5.6
	[e].5	<2	12	21	.4	<2	2	7.6	<.3	<2	11	18	1	<2	1	4.9
B	13	----	2	----	<3	----	2	----	<3	----	2	---	<3	----	2	----
	200	----	5	----	8	----	19	----	<3	----	6	---	5	----	10	----
	<3	----	<3	----	<3	----	<3	----	<3	----	7	---	3	----	2	----
Ba	<.3	----	12	----	<.3	----	2	----	<.3	----	2	---	<.3	----	.9	----
	<.3	----	12	----	1	----	.8	----	.2	----	10	---	1	----	1	----
	.3	----	12	----	<.3	----	2	----	<.3	----	11	---	2	----	2	----
Ca	.2	----	.2	----	.2	----	1	----	<.03	----	1	---	.2	----	1	----
	<.03	----	.2	----	.2	----	.2	----	.02	----	.1	---	.1	----	1	----
	.03	----	2	----	1	----	2	----	.02	----	2	---	2	----	2	----
Cd	<23	----	<24	----	<25	----	<20	----	<23	----	24	---	<24	----	<22	----
	<22	----	46	----	<20	----	<16	----	<21	----	19	---	<23	----	<20	----
	<26	----	24	----	<23	----	<23	----	22	----	<23	---	<23	----	<24	----
Co	<3	----	<3	----	<3	----	4	----	<3	----	<3	---	2	----	2	----
	<3	----	<3	----	2	----	<3	----	<3	----	<2	---	<3	----	<2	----
	<3	----	<3	----	2	----	5	----	<3	----	<3	---	2	----	2	----
Cr	<23	<1	<24	26.2	<25	<1	<20	<1	<23	<1.0	<24	14	<24	1.4	<22	1.1
	<23	<1.0	<24	12	<20	<1.0	<16	<1.0	<21	1.1	<20	20	<23	1.8	<20	1.3
	<26	<1.0	<24	12	<23	<1.0	<23	1.0	<24	1.3	23	6.3	<23	1.1	<24	1.0
Cu	<.3	----	19	----	.2	----	.4	----	<.3	----	14	---	.2	----	.2	----
	<.3	----	14	----	<.2	----	.3	----	<.3	----	4	---	<.3	----	.2	----
	<.3	----	22	----	<.3	----	.2	----	<.3	----	7	---	<.3	----	<.3	----
Fe	<3	<1	10	22	5	11	4	22	<3	3	7	18	5	10	4	15
	88	3.7	14	14	8	12	18	26	4	6.2	10	20	5	14	12	19
	<3	1.9	5	15	2	11	3	22	<3	8.1	7	18	<3	12	2	16

K	.2	----	.2	----	.2	----	1	----	<.3	----	1	---	1	----	1	----
	<.3	----	<.3	----	.8	----	.6	----	<.3	----	.8	---	.9	----	.8	----
		----	<.3	----	.2	----	1	----	<.3	----	<.3	---	.2	----	.2	----
Mg		.23	48	23.6	7	1.98	17	3.98	.2	<.5	12	15	5	1.1	4	2.0
		<.5	14	18	.2	2.1	10	4.7	<.3		4	19	1	2.4	2	3.5
			1	21	.4	1.8	2	4.5	<.3		5	17	.5	1.3	.5	3.2
Mn			10	23	<3	<.5	2	<.5	<3		5	15	<3	<.5	<3	<.5
	2		14	15	<2	<.5	<2	.5	<3		8	19	<3	<.5	<2	<.5
	<3		10	14	<3	<.5	2	.8	<3		7	13	2	.5	<3	.5
Na	22	2.0	24	27	12	29	58	40	3	10	24	26	12	21	22	21
	2	<1.0	12	23	20	20	16	40	1	1.0	19	21	23	13	20	31
	.3	<.5	12	30	11	21	22	49	1	1.4	11	25	2	24	12	35
Ni	<3	<2	19	23.5	5	6.92	12	10.6	<3	<2.0	12	11	2	4.3	7	7.5
	13	<2.0	23	12	8	6.0	19	13		<2.0	14	19	3	2.8	8	8.1
	<3	<2.0	12	9.5	2	6.6	7	10		<2	9	10	2	3.2	2	6.8
Pb	<3	----	<3	----	2	----	<2	----		----	5	---	2	----	<3	----
	<3	----	7	----	<2	----	<3	----		----	2	---	<3	----	<2	----
	<3	----	10	----	<3	----	<3	----		----	7	---	<3	----	<3	----
Si	230	----	10	----	24	----	56	----	<.3	----	5	---	2	----	2	----
	220	----	12	----	180	----	160	----	1	----	8	---	18	----	22	----
	<.3	----	2	----	.2	----	9	----	2	----	7	---	32	----	7	----
Sr		----	<.3	----	<.3	----	<.2	----	<.3	----	<.3	---	<.3	----	<.3	----
		----	<.3	----	<.2	----	<.3	----	<.3	----	<.2	---		----	<.2	----
		----	<.3	----	<.3	----	<.3	----	<.3	----	<.3	---		----	<.3	----
Ti		----	17	----	.5	----	.4	----	.2	----	12	---		----	.2	----
		----	26	----	1	----	2	----	<.3	----	8	---	2	----	1	----
		----	10	----	.4	----	.5	----	.2	----	9	---	.5	----	.5	----
V		----	22	----	1	----	4	----	<.3	----	17	---	.9	----	2	----
		----	26	----	2	----	5	----	.2	----	16	---	.9	----	4	----
		----	14	----	2	----	5	----	<.3	----	11	---	2	----	2	----
Zn	<23	<.2	24	19.4	<25	4.5	<20	8.8	<23	<.2	24	9.0	<24	2.7	<22	4.8
	<23	<.2	23	8.8	<20	4.0	<16	8.1	20	<.2	<20	13	<23	5.8	<20	7.0
	<26	<.2	24	15	<23	4.3	<23	7.6	<24	.2	<23	4.3	<23	2.1	<24	4.5

[a]Direct current arc.
[b]Atomic absorption spectrometry.
[c]First row of value for an element denotes analysis performed on an H_2SO_4-aided ashed sample.
[d]Second row of values for an element denotes analysis performed on an HNO_3-aided ashed sample.
[e]Third row of values for an element denotes analysis performed on an ashed sample using no ashing additive.

Reported by Laboratory IV

Element	Fuel															
	Experimental referee broadened-specification fuel				Residual fuel oil (RFO)				Solvent-refined coal (SRC)				RFO + SRC blend			
	Concentration level															
	Lower		Higher		Lower		Higher		Lower		Higher		Lower		Higher	
	Technique															
	dc Plasma[a]	AAS[b]	dc Plasma	AAS	dc Plasma	AAS	dc Plasma	AAS	dc Plasma	AAS	dc Plasma	AAS	dc Plasma	AAS	dc Plasma	AAS
	Trace metal concentration, ppm															
Al	[c]1.1	1.0	24	28	3.0	3.2	10	8.2	16	11	6.2	6.5	3.0	3.4	4.3	4.7
	[d]1.1	1.0	20	20	5.5	4.1	8.1	7.5	.97	<1	9.2	7.0	2.6	2.0	5.2	6.3
	[e]2.6	2.2	22	20	2.9	2.7	8.8	7.6	1.2	<1	7.9	6.0	2.4	2.0	4.5	4.1
B	.21	-----	9.1	----	<.2	----	<.2	----	1.2	----	6.7	----	.42	----	.32	----
	.38	-----	13	----	<.2	----	<.2	----	1.0	----	20	----	.73	----	.36	----
	.28	-----	3.9	----	<.2	----	<.2	----	.50	----	19	----	.55	----	.17	----
Ba	<.5	-----	24	----	1.2	----	3.3	----	<.5	----	10	----	1.1	----	1.9	----
	1.7	-----	15	----	7.6	----	3.7	----	<.5	----	23	----	.97	----	1.7	----
	<.5	-----	23	----	.90	----	3.7	----	<.5	----	18	----	1.0	----	1.4	----
Ca	3.3	-----	31	----	8.7	----	26	----	1.9	----	17	----	6.5	----	11	----
	5.5	-----	25	----	16	----	17	----	3.3	----	25	----	6.6	----	16	----
	12	-----	27	----	8.1	----	15	----	2.2	----	22	----	5.7	----	11	----
Cd	<.2	-----	21	----	<.2	----	<.2	----	<.2	----	9.0	----	<.2	----	<.2	----
	<.2	-----	21	----	<.2	----	<.2	----	<.2	----	20	----	<.2	----	<.2	----
	<.2	-----	22	----	<.2	----	<.2	----	<.2	----	20	----	<.2	----	<.2	----
Co	<.5	-----	<.5	----	.56	----	1.4	----	<.5	----	<.5	----	.42	----	.54	----
		-----	<.5	----	.54	----	1.3	----		----	<.5	----	.49	----	.90	----
		-----	<.5	----	.56	----	1.5	----		----	<.5	----	.52	----	.56	----
Cr		<.5	17	13	<.5	<.5	.84	.89		.90	1.5	2.1	<.5	.36	<.5	.46
		<.5	37	39	<.5	<.5	.80	.80	1.0	1.9	5.0	5.9	<.5	1.0	<.5	.51
	2.2	2.6	18	15	<.5	<.5	.70	.86	<.5	.72	6.0	6.4	<.5	.22	<.5	.73
Cu	<.3	-----	18	----	7.8	----	.83	-----	.28	----	4.1	----	.45	----	.58	----
	<.3	-----	17	----	.44	----	.74	-----	.26	----	8.7	----	.39	----	.48	----
	<.3	-----	17	----	.60	----	.81	-----	.36	----	8.7	----	.42	----	.45	----
Fe	17	19	38	36	25	37	35	39	20	20	19	18	28	25	24	21
	16	14	20	23	24	27	28	25	15	11	21	21	33	40	35	36
	16	18	37	40	20	19	28	29	20	21	28	29	26	22	26	23

K	1.6	-----	3.7	----	2.7	----	4.7	-----	1.1	----	.99	----	1.4	----	1.7	----
	1.5	-----	2.6	----	3.5	----	2.7	-----	.54	----	1.5	----	2.0	----	4.5	----
	4.7	-----	1.3	----	3.0	----	3.0	-----	.50	----	1.2	----	1.1	----	2.8	----
Mg	1.6	1.2	29	36	3.4	4.2	14	11.2	.80	.65	6.2	8.6	2.9	3.8	4.9	5.1
	25	20	30	30	6.5	6.0	8.0	8.8	.40	.40	14	10.8	2.6	3.4	6.3	6.0
	375	306	31	28	3.4	3.6	7.6	7.8	.50	.40	12	10.2	5.9	6.1	4.2	4.6
Mn	<.5	<.1	22	26	<.5	.25	<.5	.39	<.5	.33	8.0	9.6	<.5	.32	<.5	.31
	<.5	.24	20	21	<.5	.17	<.5	.29	<.5	.21	<.5	20	<.5	.25	<.5	.30
	<.5	.67	22	23	<.5	.18	<.5	.38	<.5	.25	<.5	21	<.5	.33	<.5	.28
Na	1.0	1.0	17	19	13	11	33	36	2.2	2.6	12	8.9	9.4	9.3	16	19
	2.0	2.1	17	18	18	20	30	31	1.2	1.1	18	17	9.6	10	15	15
	32	29	17	19	12	12	32	33	.66	.70	18	18	8.6	8.8	15	14
Ni	<.5	.37	38	35	6.1	6.3	13	13	1.7	1.1	5.8	5.3	2.5	2.8	9.8	12
	<.5	.34	17	13	6.0	6.6	30	34	2.5	2.4	14	12	2.8	3.2	6.4	6.8
	1.6	1.8	66	71	6.0	5.7	14	12	<.5	.60	14	14	2.5	2.8	6.0	5.0
Pb	4.8	-----	56	----	1.5	----	1.4	-----	1.8	----	9.2	----	.90	----	3.0	----
	3.9	-----	21	----	1.1	----	8.4	-----	6.9	----	19	----	.78	----	1.5	----
	12	-----	45	----	1.2	----	1.9	-----	.77	----	16	----	.85	----	2.7	----
Si	1.1	-----	2.8	----	3.0	----	8.8	-----	2.2	----	3.7	----	.77	----	1.1	----
	4.2	-----	3.5	----	2.1	----	8.0	-----	.76	----	8.5	----	1.7	----	1.7	----
	3.4	-----	5.9	----	1.6	----	6.2	-----	.79	----	7.4	----	3.6	----	3.2	----
Sr	<.2	-----	<.2	----	<.2	----	.23	-----	<.2	----	<.2	----	<.2	----	<.2	----
	<.2	-----	<.2	----	<.2	----	.21	-----	<.2	----	<.2	----	<.2	----	<.2	----
	<.2	-----	<.2	----	<.2	----	.23	-----	<.2	----	<.2	----	<.2	----	<.2	----
Ti	<.4	-----	5.0	----	<.4	----	.52	-----	<.4	----	1.6	----	<.4	----	<.4	----
	<.4	-----	2.4	----	<.4	----	.31	-----	<.4	----	4.4	----	<.4	----	<.4	----
	<.4	-----	6.9	----	<.4	----	.34	-----	<.4	----	4.2	----	<.4	----	<.4	----
V	<.2	-----	20	----	1.9	----	5.0	-----	<.2	----	3.9	----	1.1	----	2.7	----
	<.2	-----	18	----	2.2	----	4.2	-----	<.2	----	16	----	1.2	----	2.7	----
	<.2	-----	20	----	1.8	----	4.6	-----	<.2	----	16	----	.99	----	1.8	----
Zn	<.5	.51	60	84	4.5	4.3	11	10	<.5	.59	6.8	4.6	1.4	1.5	4.4	4.7
	<.5	.56	10	10	4.5	4.9	8.4	8.7	<.5	.84	13	11	2.4	2.7	5.0	5.2
	<.5	.61	14	17	4.3	4.2	12	12	<.5	.50	13	13	1.6	1.9	4.4	4.8

[a]Direct-current plasma.
[b]Atomic absorption spectrometry.
[c]First row of values for an element denotes analysis performed on an H_2SO_4-aided ashed sample.
[d]Second row of values for an element denotes analysis performed on an HNO_3-aided ashed sample.
[e]Third row of values for an element denotes analysis performed on an ashed sample using no ashing additive.

Reported by Laboratory V

Element[a]	Fuel							
	Experimental referee broadened-specification fuel				Residual fuel oil			
	Concentration level							
	Lower		Higher		Lower		Higher	
	Technique							
	INAA[b]	AAS[c]	INAA	AAS	INAA	AAS	INAA	AAS
	Trace metal concentration, ppm							
Al	[d]<3000	[e]<9.68	<3000	27.97	<3000	<16.5	<1000	13.6
	----------	[f]<11.58	----------	29.9	----------	15.8	----------	34.2
	[g]<37.5	[g]<10.33	18.3	33.5	5.95	9.0	17.8	12.5
Ba	<200	-------	<200	-----	<200	------	<100	------
	<1.12	-------	18.3	-----	.60	------	2.8	------
Ca	<60 000	-------	<60 000	-----	<60 000	------	<20 000	------
	(h)	-------	(h)	-----	(h)	------	(h)	------
Co	.1	-------	.1	-----	.4	------	.9	------
	.0007	-------	.032	-----	.48	------	1.06	------
Cr	9.7	<.10	12	35.51	11	.09	2.8	.31
	----------	<.12	----------	36.72	----------	.14	----------	.40
	.01	<.11	18.3	17.68	.12	.18	.36	.37
Fe	<200	<.26	<200	18.8	<200	9.1	<200	20.7
	----------	.32	----------	21.1	----------	7.2	----------	19.8
	<7.5	.36	21.0	23.5	6.07	5.4	16.0	20.1

Fe	<200	9.7	<200	22.0	<200	9.5	<200	15.9
	----------	6.3	----------	29.4	----------	8.0	----------	13.4
	3.34	4.8	27.9	11.1	6.63	1.7	10.94	11.0
K	<40 000	-------	<30 000	-----	<40 000	------	<30 000	-----
	(h)	-------	(h)	-----	(h)	------	(h)	-----
Mg	[d]<7000	e0.03	<7000	16.3	<9000	1.2	<5000	3.6
	----------	f<.02	----------	27.1	----------	.80	----------	2.4
	(g,n)	g<.03	<.006	14.9	(h)	.95	(h)	3.2
Mn	<20	.06	5	21.24	<20	.05	<10	.18
	----------	<.06	----------	34.03	----------	<.15	----------	<.13
	<.103	<.08	<.13	20.27	.09	.08	.14	.08
Na	<1000	.22	<1000	24.0	<1000	10.6	<1000	32.1
	----------	.18	----------	27.8	--------	9.4	----------	31.8
	(h)	.16	<7.4	14.8	9.72	15.1	15.4	26.8
Ni	----------	<.18	----------	17.42	----------	2.73	----------	8.39
	----------	<.29	----------	15.90	----------	2.47	--------	6.06
	----------	<.44	----------	11.36	----------	2.27	--------	6.22
Sr	<200	-------	<200	-----	<300	------	<200	-----
	<1.3	-------	<2.9	-----	<1.77	------	<1.71	-----
Ti	<1100	-------	<1000	-----	<1400	------	<700	-----
	<.69	-------	<.88	-----	<7.07	------	<25.6	-----
V	<50	-------	8	-----	<40	------	<30	-----
	<.2	-------	<.29	-----	.62	------	2.56	-----
Zn	3.2	.05	4.4	18.9	5.0	2.2	4.7	6.5
	----------	.08	----------	20.4	----------	2.0	--------	5.6
	.034	.08	5.88	14.2	.44	1.9	1.03	6.1

[a]The elements B, Cd, Cu, Ni, Pb, and Si could not be measured by INAA in the fuel matrix.
[b]Instrumental neutron activation analysis.
[c]Atomic absorption spectrometry.
[d]Analysis was performed on the intact fuel sample without ashing.
[e]Analysis was performed on an HNO_3-aided ashed sample.
[f]Analysis was performed on an ashed sample using no ashing additive.
[g]Analysis was performed on an H_2SO_4-aided ashed sample.
[h]Extremely large lower limit could be calculated but laboratory felt it was meaningless.

Element[a]	Fuel							
	Solvent-refined coal				Blended residual fuel oil + solvent-refined coal			
	Concentration level							
	Lower		Higher		Lower		Higher	
	Technique							
	INAA[b]	AAS[c]	INAA	AAS	INAA	AAS	INAA	AAS
	Trace metal concentration, ppm							
Al	[d]<3000 --- (g,h)	[e]<5.76 [f]<9.49 [g]<14.49	<3000 --- 29.4	23.7 39.8 17.7	<3000 --- (h)	<13.0 <27.71 <14.06	<1000 --- (h)	<13.54 <23.46 21.1
Ba	<200 1.15	--- ---	<200 44.1	--- ---	<300 1.77	---	<200 1.03	---
Ca	<200 (h)	--- ---	<60 000 (h)	--- ---	<70 000 (h)	---	<40 000 (h)	---
Co	<.3 .001	--- ---	<.3 .037	--- ---	.4 .26	---	.6 .68	---
Cr	4.3 --- .805	2.53 1.93 .97	8.5 --- 29.4	34.14 38.19 8.01	6.6 --- .88	1.24 1.39 .94	5.2 --- .68	.76 .51 .54

K	<40 000	-------	<40 000	-----	<30 000	------	<10 000	------
	<.04	-------	(h)	-----	(h)	------	(h)	------
Mg	[d]<7000	[e]<.02	<8000	20.09	<7000	2.5	<3000	31.8
	----------	[f]<.02	----------	17.2	----------	2.1	----------	4.15
	[g]<37.5	[g]<.02	<54.9	25.5	(h)	1.6	<.006	4
Mn	<15	<.05	20	23.61	<15	.07	<5	.28
	----------	<.06	----------	23.52	----------	<.15	----------	<.18
	<.19	<.06	18.3	30.39	.12	<.08	.25	.07
Na	<1000	.06	<1000	20.82	<1000	20.6	<500	49.5
	----------	.08	----------	22.7	----------	32.3	----------	38.65
	<3.75	.04	18.3	23.4	13.1	24.5	35.5	37.9
Ni	----------	<.29	----------	20.02	----------	4.58	----------	11.61
	----------	<.35	----------	19.48	----------	4.22	----------	9.67
	----------	<.31	----------	15.73	----------	4.02	----------	10.89
Sr	<200	-------	<300	-----	<200	------	<100	------
	<1.87	-------	<6.4	-----	<2.4	------	<1.8	------
Ti	<1100	-------	<1100	-----	<1000	------	<400	------
	<3.75	-------	<36.6	-----	<11.4	------	<10.6	------
V	<40	-------	25	-----	<50	------	<20	------
	<.19	-------	19.2	-----	2.02	------	5.3	------
Zn	6.3	.09	8.4	20.9	4.2	3.6	3.6	12.9
	----------	<.04	----------	20.1	--------	3.7	----------	8.6
	.007	<.04	5.5	18.9	.71	3.4	1.8	10.0

[a]The elements B, Cd, Cu, Ni, Pb, and Si could not be measured by INAA in fuel matrix.
[b]Instrumental neutron activation analysis.
[c]Atomic absorption spectrometry.
[d]Analysis was performed on intact fuel sample without ashing.
[e]Analysis was performed on an HNO_3-aided ashed sample.
[f]Analysis was performed on an ashed sample using no ashing additive.
[g]Analysis was performed on an H_2SO_4-aided ashed sample.
[h]Extremely large lower limit could be calculated, but laboratory felt it was meaningless.

Reported by Laboratory VI

Element	Fuel															
	Experimental referee broadened-specification fuel				Residual fuel oil (RFO)				Solvent-refined coal (SRC)				RFO + SRC blend			
	Concentration level															
	Lower		Higher		Lower		Higher		Lower		Higher		Lower		Higher	
	Technique															
	dc Arc[a]	AAS[b]	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS	dc Arc	AAS
	Trace metal concentration, ppm															
Al	[c].001	<4.4	28.7	37.3	3.6	<11.1	9.5	<15	0.3	<4.9	14	11.7	2.1	<14.2	5.6	<16.6
	[d].002	<1.0	16	30.0	3.3	4.3	7.4	10.3	.2	.94	14.7	20.1	1.7	3.94	3.8	4.2
	[e].003	<2.5	12.8	23.4	3	<11.0	5.9	<11.7	.1	<2.1	13.2	18.1	1.6	<9.7	4.8	17.5
B	<.002	-----	6.6	-----	<.3	-----	<.2	-----	.1	-----	11.9	-----	1.5	-----	1.0	-----
	.007	-----	20.5	-----	.4	-----	1.6	-----	.4	-----	21.1	-----	.9	-----	1.0	-----
	.003	-----	.6	-----	<.3	-----	<.4	-----	.9	-----	6.5	-----	.8	-----	1.0	-----
Ba	<.002	-----	13.1	-----	<.4	-----	2.0	-----	2.4	-----	<.5	-----	<.02	-----	<.2	-----
	<2	-----	12.2	-----	1.9	-----	3.4	-----	<.08	-----	4.6	-----	<2	-----	<2	-----
	<.002	-----	8.5	-----	<.4	-----	3.7	-----	.6	-----	9.2	-----	<.2	-----	<.3	-----
Ca	.005	-----	18.7	-----	4.8	-----	10.8	-----	.06	-----	15	-----	3.2	-----	9.4	-----
	.01	-----	22.2	-----	8.1	-----	15.6	-----	.04	-----	21.2	-----	3.8	-----	8.5	-----
	.006	-----	14.7	-----	7.8	-----	14.1	-----	.03	-----	18.7	-----	3.7	-----	8.5	-----
Cd	<.002	-----	26.3	-----	<.04	-----	<.03	-----	<.07	-----	31.7	-----	<.2	-----	<.2	-----
	<.002	-----	8.9	-----	<.2	-----	<.4	-----	<.09	-----	2.8	-----	<.01	-----	<.2	-----
	<.002	-----	5.4	-----	<.4	-----	<.5	-----	<.1	-----	5.8	-----	<.2	-----	<.3	-----
Co	.001	-----	<.02	-----	.9	-----	1.7	-----	<.004	-----	<.02	-----	.6	-----	1.3	-----
	<.0001	-----	<.02	-----	.5	-----	.9	-----	<.004	-----	<.01	-----	.3	-----	.4	-----
	<.0001	-----	<.02	-----	.5	-----	1.1	-----	<.004	-----	<.02	-----	.2	-----	.5	-----
Cr	.0003	<.24	27.6	26.1	.3	<.76	2.8	<.92	1.5	1.73	17	21.4	1.2	1.75	.9	1.14
	.0002	<.11	21.3	16.0	.2	.38	.6	.43	2.8	1.85	23.9	19.6	1.2	1.67	.7	1.12
	.001	<.14	15.6	11.7	.2	.55	.4	.58	1.8	2.46	22.1	16.4	1.4	.97	.6	.94
Cu	.03	-----	22.1	-----	.03	-----	2	-----	.1	-----	14.5	-----	.04	-----	.1	-----
	.04	-----	21.3	-----	.9	-----	1.6	-----	.02	-----	19.3	-----	.07	-----	.09	-----
	.04	-----	14.7	-----	.1	-----	.4	-----	.02	-----	14	-----	.1	-----	.1	-----
Fe	.05	.38	23.2	24.90	8.1	11.08	18	21.30	6.9	10.58	17	28.26	7.7	9.51	12.9	14.55
	.02	.05	17.8	22.75	8.8	10.10	18.4	21.8	9.3	10.91	21.2	23.30	6.6	11.81	11.1	16.40
	.02	.22	14.7	17.35	7.1	9.82	13.3	21.36	9.9	8.70	18.7	21.77	7.2	9.34	10.8	14.07

K	<.09	-----	<16.7	-----	<14.7	-----	<10	-----	<3	-----	<19	-----	<7	-----	<9	-----
	<.3	-----	<20	-----	<10	-----	<17	-----	<4	-----	<10	-----	<6	-----	<9	-----
	<.08	-----	<13	-----	<17	-----	<19	-----	<3	-----	<17	-----	<8	-----	<11	-----
Mg	.001	<.20	23.2	26.9	1.5	3.09	3.2	5.21	.02	<.22	15	27.3	1.1	1.69	2.9	4.05
	.001	<.01	23.1	32.1	2.5	3.14	4.5	6.24	.1	.06	18.4	27.5	1.2	1.77	2.5	4.34
	.001	.01	18.3	31.0	2.2	3.05	4.1	6.45	.03	.01	19.6	27.9	1.4	1.64	3	4.06
Mn	.0008	<.17	20.4	26.9	.2	<.47	.4	<.57	.1	<.19	16	23.4	.2	<.54	.2	<.70
	.0002	<.06	25.8	24.1	.3	<.30	.4	.34	.2	.06	19.3	22.0	.3	.26	.2	.29
	<.001	<.10	15.1	23.6	<.0007	<.41	.4	.43	.1	.16	23.8	21.5	.2	<.38	.4	<.37
Na	.04	<.42	18.7	27.9	15.4	23.0	29.8	45.4	<.3	.42	12	22.7	8.1	13.9	20.9	35.0
	.02	<.02	16	19.0	14.9	16.8	41.1	39.8	<.4	.59	13.8	18.4	.8	13.7	23.8	42.7
	.04	<.03	9.2	17.5	19.4	21.6	32.4	21.3	<.3	<.02	19.6	27.9	10.9	11.5	2.1	15.9
Ni	.002	<.34	27.6	23.9	5.5	7.33	15.8	15.0	.01	<.37	13	20.4	2.8	4.20	8.7	9.56
	.001	<.25	15.1	22.2	5.9	7.18	12.3	15.0	.09	.14	17.5	20.4	2.6	3.44	6.2	9.30
	.002	<1.0	14.7	15.6	4.8	5.40	9.7	9.6	.06	<.54	11.9	18.5	2.5	2.56	6	10.26
Pb	.1	-----	22.1	-----	.4	-----	.9	-----	.6	-----	14	-----	.4	-----	.6	-----
	.06	-----	17.8	-----	.3	-----	.4	-----	<.2	-----	18.4	-----	.1	-----	.2	-----
	.009	-----	14.7	-----	<.08	-----	<.01	-----	<.02	-----	13.6	-----	.02	-----	.3	-----
Si	.005	-----	19.9	-----	4.4	-----	17.1	-----	.3	-----	7.6	-----	2.8	-----	9.8	-----
	.01	-----	8.2	-----	6.4	-----	13.6	-----	.3	-----	12.9	-----	2.4	-----	6.9	-----
	.02	-----	13.7	-----	6.7	-----	15.9	-----	.4	-----	29.8	-----	6.8	-----	11.2	-----
Sr	.007	-----	.02	-----	.2	-----	1.6	-----	.002	-----	.02	-----	.3	-----	.2	-----
	.003	-----	.05	-----	.08	-----	.2	-----	.0007	-----	.03	-----	.03	-----	.1	-----
	<.001	-----	.004	-----	.2	-----	.2	-----	.004	-----	.004	-----	.05	-----	.08	-----
Ti	.003	-----	22.1	-----	.4	-----	.9	-----	.2	-----	13	-----	.2	-----	.5	-----
	.0009	-----	15.1	-----	<.1	-----	.5	-----	.2	-----	16.6	-----	.2	-----	.1	-----
	.001	-----	10.5	-----	.2	-----	.3	-----	.1	-----	14.9	-----	.2	-----	.3	-----
V	.001	-----	17.6	-----	1.6	-----	4	-----	.005	-----	13	-----	1.1	-----	3	-----
	.001	-----	20.4	-----	2.5	-----	4.9	-----	.07	-----	15.7	-----	1.1	-----	2.7	-----
	.002	-----	11.9	-----	1.9	-----	3.8	-----	.07	-----	15.3	-----	1.2	-----	.3	-----
Zn	.02	.07	16.5	25.6	2.7	5.33	7.2	17.3	.07	.16	17	20.8	2.3	3.15	5.9	6.97
	.01	.02	16.9	22.1	4.8	4.82	8.2	10.9	<.2	.10	13.8	20.4	1.9	2.95	3.2	7.41
	.02	.03	11.9	21.0	3.7	5.05	8.5	11.5	.09	.16	13.6	20.4	2	2.84	6.2	7.85

[a]Direct-current arc.
[b]Atomic absorption spectrometry.
[c]Analysis performed on an H_2SO_4-aided ashed sample.
[d]Analysis performed on an HNO_3-aided ashed sample.
[e]Analysis performed on an ashed sample using no ashing additive.

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16. Abstract

The accurate determination of trace metals in fuels is an important requirement in much of the research into and development of alternative fuels for aerospace applications. Recognizing the detrimental effects of certain metals on fuel performance and fuel systems at the part-per-million and in some cases part-per-billion levels requires improved accuracy in determining these low-concentration elements. Accurate analyses are also required to ensure interchangeability of analysis results between vendor, researcher, and end user for purposes of quality control. The metal concentration levels of the fuels of particular interest to projects at the NASA Lewis Research Center are typically less than 10 parts per million. Previous interlaboratory studies have demonstrated the inability of different laboratories to agree on the results of metal analysis, particularly at low concentration levels, yet typically good precisions are reported within a laboratory. An interlaboratory study was designed to gain statistical information about the sources of variation in the reported concentrations. Five participant laboratories were used on a fee basis and were not informed of the purpose of the analyses. This laboratory served as the sixth participant in the study. The effects of laboratory, analytical technique, concentration level, and ashing additive were studied in four fuel types for 20 elements of interest. The prescribed sample preparation schemes (variations of dry ashing) were used by all of the laboratories. The analytical data were statistically evaluated using a computer program for the analysis-of-variance technique. Independent analyses evaluating the magnitude and variability of the blank have provided information concerning possible sources of error. Metal recovery studies have supplied additional information concerning the merits of the preparation procedure used for the interlaboratory study. The results of these studies are valuable for indicating directions for further studies aimed at achieving improved interlaboratory results for trace elements in specification and alternative fuels.

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