CDM FEDERAL PROGRAMS CORPORATION

August 31, 1992

Mr. Peter Savoia
Monitoring and Management Branch
U.S. Environmental Protection Agency
2890 Woodbridge Avenue
Edison, NJ 08837

Project:	TES V, EPA Contract No. 68-W9-0002
Work Assignment:	C02048
Site:	Tutu Wellfield
Subject:	Submittal of SAS client request Nos.1148 & 1049.

Dear Peter:

I am submitting for your review and approval two SAS Client requests for TPH and Methyl tertiary butyl ether(MTBE), n-propylbenzene and 1,2-dibromoethane analysis of water samples to be collected at the Tutu Wellfield site. These SAS requests have been prepared based on previously approved SAS requests 1088 and 1089. Sampling is scheduled to occur during the week of September 28, 1992.

I trust that these submittals will meet with your approval. Please feel free to call me at (908)757-9500, if you have any comments.

Sincerely,

CDM Federal Programs Corporation

Vasu Desikan
CLP coordinator

cc: Caroline Kwan EPANYC
Sally Odland CDM Federal NYC
Scott Graber CDM Federal NYC

107-F Corporate Boulevard South Plainfield, NJ 07080 908 757-9500

SAS CLIENT REQUEST FORM 1148
TUTU WELLFIELD
ST. THOMAS, U.S. VIRGIN ISLANDS

EPA CONTRACT NO.: 68-W9-0002
WORK ASSIGNMENT: C02048

Prepared By: J. Letourneau for
Sally Odland

Date: 8/31/92

Reviewed By: Vasu Desikan
Vasu Desikan

Date: 8/31/92

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
300 North Lee Street, Suite 200
P.O. Box 818
Alexandria, Virginia 22314
Phone: 703/557-2490 - FTS/557-2490

SAS No.
1148

SPECIAL ANALYTICAL SERVICES

Client Request

Regional Transmittal

A. EPA Region/Client: Region II/CDM FPC - TES V

B. RSCC Representative: Kathy Kinsella

C. Telephone Number: (908) 549-3112

D. Date of Request: August 24, 1992

E. Site Name/ SS ID: Tutu Wellfield
St. Thomas, U.S. Virgin Islands
Cerclis No.: VID982272569

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical services requested:**

   Analysis of aqueous samples for Total Petroleum Hydrocarbons (TPH).

2. **Definition and number of work units involved (specify whether whole samples or fractions; Whether organics or inorganics; whether aqueous or soil and sediments and whether low, medium or high concentration):**

   Five (5) low-concentration aqueous samples (including 1 Fieldblank) for TPH analysis.

3. **Purpose of analysis (specify whether Superfund enforcement or remedial action, RCRA, NPDES, etc.):**

   TES V Enforcement, RI/FS Compliance

4. **Estimated Date(s) of collection:**

   Samples are scheduled to be collected during the week of September 28, 1992.

5. **Estimated date(s) and method of shipment:**

Samples will be shipped the day they are collected via Federal Express.

The laboratory must refrigerate all samples at 4 degrees Celcius. The laboratory must have personnel available on Saturdays (except legal holidays) to receive, log in, and refrigerate samples.

The laboratory shall have all applicable USDA permits including the USDA Compliance Agreement and the Application and Permit to Move Soil to allow entry of soil samples into the U.S. from the Virgin Islands. These permits shall be signed by the appropriate regulatory officials, and legible copies of these documents must be provided to CDMFPC prior to the initial sampling date.

6. **Number of days analysis and data required after laboratory receipt of samples:**

Samples must be analyzed within 26 days of VTSR. The complete data package containing all the sample delivery group(s) (SDG's) associated with the case must be submitted as one data package in it entirety within 35 days of verified time of receipt of the last sample in this case.

7. **Analytical protocol required (attached copy if other than a protocol currently used in this program):**

Aqueous samples must be prepared and analyzed as per MCAWW 418.1

8. **Special Technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The maximum number of samples in a sample delivery group is 20.
Any modification of the required method must be approved by SMO, prior to samples analysis.

An aqueous method blank must be prepared and analyzed along with each batch of water samples extracted by extracting 1 L of distilled, dionized water along with the water samples.

A method control sample (aqueous) must be prepared by spiking with an appropriate amount of TPH standard 1 L of distilled, dionized water, and then extracting this sample along with the water samples.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-Of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

Submit all documentation including SAS packing lists, chain-of-custody forms, SAS client request form, copy of airbill(s), copies of analyst's logbooks (signed by analyst) with date and time of sample preparation and analysis, sample data sheets with date sampled, date sample

received, extraction and analysis dates, actual method used, data results, laboratory duplicate and method blank results, all instrument calibration results, calibration curves, QA/QC information, standards information, and all raw data(including all instrument printouts).

List the instrumentation and the actual methods used for preparation and analysis. Note the EPA QC reference samples or identify equivalent reference samples or identify equivalent reference samples as to source and lot number. Documentation of "true" values and associated 95% confidence limits must be provided for any reference samples used. All results must be reported in mg/L.

The complete EPA sample numbers as they appear on chain-of-custody and CLP paperwork, must be used in the raw data and on all data reporting forms.

A written case narrative describing problems encountered in the receipt of samples or during preparation and analysis and the corrective actions taken must be provided(including telephone record logs. etc.). The entire data package must be paginated.

10. Other (use additional sheets or attach supplementary information, as needed):

The laboratory must provide a detailed example calculation that clearly demonstrates the manner in which the initial and final result was derived. Where applicable, each component of the calculation must be explained (e.g., if the calculation includes a dilution factor, it must be clear where, why, and how each dilution occurred). The laboratory must supply any and all information required to produce during independent data review, all results reported by the laboratory.

The laboratorys copy of the SAS request along with documentation of communications with SMO which resulted in the amendment of this SAS request must be included in the data package.

11. Name of sampling/shipping contact: Sally Odland or Vasu Desikan

Phone: (212) 393-9634 or (908)-757-9500

12. Data Requirements

Parameter	Detection Limit	Precision Desired +/-% or conc.)
Total Petroleum Hydrocarbons (aqueous)	1 mg/L	+/- 25%

13. **QC Requirements**

Please refer to section 7, 8, 9 and 14 for additional instructions.

Audits Required	Frequency of Audits	Limits (Percent, Conc.)
Instrument calibration	Daily and consisting of at least 4 points.	Correlation coefficient r $\geq$0.995
Lab Duplicate (A)	One per 20 samples	+/- 25% RPD
Method Blank (A)	One per 20 samples or less	less than MDL (less than the 1 mg/L detection limit)
Method Detection Limit Calibration Standard	See Footnote B.	75% - 125% Recovery
Mid Range Calibration Standard	See Footnote B.	80% - 120% Recovery
Method Control Sample	One per 20 samples or less	80% - 120% Recovery
Matrix Spike Sample	One per 20 samples or less	75% - 125% Recovery

(A) The laboratory duplicates, matrix spike and method blank samples are to be brought through the entire preparation and analytical procedure.

(B) The method detection limit calibration standard and Mid Range Calibration Standards must be analyzed immediately following initial instrument calibration and subsequently following every 10 samples.

Note: Because the entire sample will be consumed by this test, extra volume will be provided to the CLP laboratory performing the analysis and will be identified as extra volume for laboratory duplicate and matrix spike analysis.

14. **Action required if limits are exceeded**

Failure to obtain method blank values less than the detection limit requires that all samples prepared with that method blank be reprepared with a new method blank and reanalyzed. All blank data are to be reported and the necessity for reanalysis must be included in the narrative summary. If duplicate results exceed control limits, reanalyze sample and duplicate. If reanalysis fails to produce results in control, contact RSCC.

Failure to obtain recoveries of the midrange calibration verfication standard and/or method detection limit standard within the specified control limits, requires that analysis be terminated. The instrument must be recalibrated, the problem corrected and analysis of samples should be resumed only after the recoveries of the verification standards are within the specified control limits.

Failure to obtain a correlation coefficient $r \geq 0.995$ during instrument calibration requires that a new set of calibration standards be prepared and the instrument be recalibrated with this new set of standards. If the correlation coefficient is still not $r \geq 0.995$ for instrument calibration, contact SMO.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questioons or need any assistance, please contact your Regional representative at the Sample Management Office.

SAS CLIENT REQUEST FORM 1149
TUTU WELLFIELD
ST. THOMAS, U.S. VIRGIN ISLANDS

EPA CONTRACT NO.: 68-W9-0002
WORK ASSIGNMENT NO.: C02048

Prepared By: J. Stevens for
Sally Odland

Date: 8/31/92

Reviewed By: V. Desikan
Vasu Desikan

Date: 8/31/92

TOTAL P.03

TOTAL P.03

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
300 North Lee Street, Suite 200
P.O. Box 818
Alexandria, Virginia 22314
Phone: 703/557-2490 - FTS/557-2490

SAS No.

1149

SPECIAL ANALYTICAL SERVICES

Client Request

Regional Transmittal

A. EPA Region/Client:	Region II/CDM FPC - TES V
B. RSCC Representative:	Kathy Kinsella
C. Telephone Number:	(908) 549-3112
D. Date of Request:	August 24, 1992
E. Site Name/ SS ID:	Tutu Wellfield St. Thomas, U.S. Virgin Islands Site No. 2PID Cerclis ID# VID982272569

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical services requested:**

   Analysis of water samples samples for methyl tertiary butyl ether (MTBE), n-propylbenzene and 1,2-dibromoethane.

2. **Definition and number of work units involved (specify whether whole samples or fractions; Whether organics or inorganics; whether aqueous or soil and sediments and whether low, medium or high concentration):**

   Six (6) low-concentration low concentration water (including 1 fieldblank and 1 trip blank) samples for methyl tertiary butyl ether (MTBE), n-propylbenzene and 1,2-dibromoethane analysis.

3. **Purpose of analysis (specify whether Superfund enforcement or remedial action, RCRA, NPDES, etc.):**

TES V Enforcement, RI/FS Compliance

4. **Estimated Date(s) of collection:**

The samples are scheduled to be collected during the week of September 28, 1992.

5. **Estimated date(s) and method of shipment:**

Samples will be shipped the day they are collected via Federal Express

All samples must be refrigerated at 4 degrees Celcius. The laboratory must have personnel available on Saturdays(except legal holidays) to receive, log in and refrigerate samples. The laboratory will be informed by 3 pm on Friday, if Saturday delivery is to be expected.

The laboratory shall have all applicable USDA permits including the USDA Compliance Agreement and the Application and Permit to Move soil to allow entry of soil samples into the U.S. from the U.S. VIRGIN ISLANDS. These permits shall be signed by the approprite regulatory officials and legible copies of these documents must be provided to CDMFPC prior to the intial sampling date.

6. **Number of days analysis and data required after laboratory receipt of samples:**

All samples must be analyzed within ten (10) days of verified time of sample receipt. A complete data package containing all the sample delivery groups(SDG's) associated with the case must be submitted in its entirety within thirty five(35) days of verified time of sample receipt of the last sample in the case.

7. **Analytical protocol required (attached copy if other than a protocol currently used in this program):**

All samples must be prepared and analyzed per the protocols described in Section D, "Analytical Methods for Volatiles" of the current revision of the CLP RAS Statement of Work for Organics analysis OLM01.8, Rev.3/90.

Any modifications of the specified procedures must be approved by SMO, prior to sample analysis.

8. **Special Technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The maximum number of samples in a sample delivery group is 20.
All calibration, QA/QC procedures, and analytical procedures as specified in the current revision of the CLP RAS Statement of Work for Organics Analysis OLM01.8, Rev 3/90 must be performed.

In addition to this the laboratory must:

1. Perform Method detection limit studies for the analytes of interest as described in 40 CFR Pt 136, App.B(attached).

2. The analytes of interest must be included in all calibration standards.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-Of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

Submit all documentation including data sheets with data results, laboratory duplicate and method blank results, QA/QC information, raw data, calibration curves, SAS packing lists, chain-of-custody forms, SAS client request form, copy of airbill(s), sample tags, and all CLP deliverables required for the VOA fraction.

The laboratory must submit all supporting documentation to demonstrate the performance of the MDL studies.
The complete EPA sample numbers as they appear on chain-of-custody and CLP paperwork, must be used in the raw data and on all data reporting forms. The entire data package must be paginated.
Results are to be reported on CLP data forms modified to include the analytes requested in Section 2 of this SAS Request. The laboratory must submit a lab generasted mass spectrum for all compounds detected above and below the detectionn limit stated in the method.
A written case narrative describing problems encountered in the receipt of samples or during preparation and analysis and the corrective actions taken must be provided(including telephone record logs, etc.). The case narrative should explain any deviations and their effect on the final results.

The data package must be equivalent to the CLP RAS data package as specified in the Statement of Work for Organics analysis OLM01.8, Rev 3/90.

10. Other (use additional sheets or attach supplementary information, as needed):

The laboratory must provide a detailed example calculation that clearly demonstrates the manner in which the initial and final result was derived. Where applicable, each component of the calculation must be explained (e.g., if the calculation includes a dilution factor, it must be clear where, why, and how each dilution occurred). The laboratory must supply any and all information required to produce during independent data review, all results reported by the laboratory. Submit sample preparation logs, the concentrations and amounts of standards added for all QC analyses.

The laboratory's copy of the SAS request, along with documentation of any communications with SMO that resulted in the amendment of the SAS request must be included in the package.

11. Name of sampling/shipping contact: Sally Odland or Vasu Desikan

Phone: (212) 393-9634 or (908)-757-9500

12. Data Requirements

Parameter	Detection Limit	Precision Desired +/-% or conc.
MTBE	10 ug/L*	+/- 25%
n-propylbenzene	10 ug/L*	+/- 25%
1-2-dibromoethane	10 ug/L*	+/- 25%

* Although these detection limits have been specified, it is recognized that the laboratory will perform Method Detection Limit studies as specified in Section 8 of this SAS request.

13. QC Requirements

All QC requirements are per the current revision of the CLP RAS SOW for Organics OLM01.8, Rev 3/90.

MTBE, n-propylbenzene, and 1,2-dibromoethane standards must be added to all calibration standards. System Monitoring Compounds (SMCs) should be added to all samples, blanks, matrix spike, and matrix spike duplicate prior to purging. The SMCs are used to evaluate the purge efficiency.

14. Action required if limits are exceeded

Follow all actions specified in the current revision of the CLP RAS Statement of Work for Organics analysis OLM01.8, Rev 3/90.

Failure to obtain method blank values less than the detection limit requires that all samples prepared with that method blank be re-prepared and re-analyzed. All blank data are to be reported and the necessity for re-analysis must be included in the narrative summary. If the duplicate results exceed control limits, re-analyze the sample and the duplicate. If re-analysis fails to produce results in control, contact SMO.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please contact your Regional representative at the Sample Management Office.

Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2 \Big/ n\right]$$

$$S = (S^2)^{1/2}$$

where:

X_i; i=1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,1-\alpha=0.99)} \quad (S)$$

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha=.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B < 3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S^2_A + 6S^2_B}{12}\right]^{1/2}$$

if $S^2_A/S^2_B > 3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$$MDL = 2.681\ (S_{pooled})$$

where 2.681 is equal to $t_{(12,\ 1-\alpha\ =\ .99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL=0.72 MDL

UCL=1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,\ .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title ald the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which

affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]

Appendix C to Part 136—Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See Section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See Section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 *Dissolved*—Those elements which will pass through a 0.45 μm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 μm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations. (Section 9.1 plus 9.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

3.8 *Interference check sample*—A solution containing both interfering and analyte elemelts of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2.)

3.9 *Quality control sample*—A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.6.3)

3.10 *Calibration staldards*—A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4)

3.11 *Linear dynamic range*—The concentration range over which the analytical curve remains linear.

3.12 *Reagent blank*—A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 7.5.2)

3.13 *Calibration blank*—A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 7.5.1)

3.14 *Methmd of standard addition*—The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 10.6.1.)

4. Safety

4.1 The toxicity of carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is repsonsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified [14.7, 14.8 and 14.9] for the information of the analyst.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 *Spectral interferences* can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The Interference information, which was collected at the Ames Laboratory,[1] is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system.

Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

5.1.2 *Physical interferences* are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic

[1] Ames Laboratory, USDOE, Iowa State University, Ames Iowa 50011.