SOP 712: Glycols
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U.S. EPA Region 6 Laboratory
Standard Operating Procedure

SOP 712: Glycols by Direct Injection Analysis

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SOP Review - Tracking Form

Review Date	Revision	SOP changes
4/2012	0	New SOP

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SOP 712: Glycols by Direct Injection Analysis

1.0 SCOPE AND APPLICATION (Additionally addresses TNI SOP requirements for Identification of Test Method, Applicable Matrices, Reporting Limits and Components to be Analyzed)

This method is applicable to the determination of glycols in water and solid matrices. This method uses modified QC criteria from Method 8270D. A current published version of Method 8270D should be reviewed and available on the bench for referral before performing this extraction and analysis. The following table displays the current analytes and reporting limits for this method:

Analytes	Reporting Limit, Water mg/L	Reporting Limit Solid mg/Kg
Ethylene Glycol, CAS 107-21-1	0.5 – 2.0	0.5 – 2.0
Propylene Glycol, CAS 57-55-6	0.5 – 2.0	0.5 – 2.0
2-Butoxyethanol, CAS 111-76-2	0.5 – 2.0	0.5 – 2.0
Di(propylene glycol)monobutyl ether, CAS 29911-28-2	0.5 – 2.0	0.5 – 2.0

2.0 SUMMARY OF METHOD

This method is used to determine various glycols in water and solid matrices using gas chromatography/mass spectrometry (GC/MS). Aqueous samples are injected directly onto a wax column with no extraction. Solid samples are sonicated in DI water and then analyzed as an aqueous sample.

3.0 DEFINITIONS

2BE - 2-Butoxyethanol
BS – Blank Spike
CCC – Continuing Calibration Check
DPGBE - Di(propylene glycol)monobutyl ether
DOC – Demonstration of Capability
FRB – Field reagent blank
EG – Ethylene glycol
GC - Gas Chromatograph
IDC – Initial Demonstration of Capability, same as DOC
LRB – Laboratory Reagent Blank
LFB – Laboratory Fortified Blank also known as LCS
LCS – Laboratory Control Sample
PG – Propylene glycol
RL –Reporting Limit
RSD – Relative Standard Deviation
TNI – The NELAC Institute

4.0 INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and / or elevated baselines in the chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks through the entire extraction, cleanup, and analysis process. It is highly recommended that all glassware be baked out in a muffle furnace at 400°C for 12 hours (SOP 001).Contamination during sample preparation can be minimized by the use of precleaned disposable glassware.

Carryover of glycols in the GC syringe is known to occur with this procedure. Additional syringe washes should be used between analyses to prevent this from occurring.

Degradation of the column occurs more rapidly with this method. The analyst should analyze low level calibration standards periodically to ensure adequate sensitivity is maintained.

5.0 SAFETY

5.1 General Lab:

All standard laboratory safety practices should be observed while in the lab area. Absolutely no food, drinks, or smoking is allowed in the lab areas. No food or drinks should be stored in the refrigerator/freezer. Lab coats should be worn when in the lab areas. Protective glasses and gloves should be worn when handling hazardous chemicals. No one should go to the solvent storage building without another person with them and should use full face protection when handling bulk chemicals. Flammable liquids (such as methanol) should be stored in explosion proof cabinets (up to 1 gallon flammable working reagents may be present in each lab room outside the cabinets) and should be used in a well ventilated area away from any spark or flame. Always be aware of the location and use of the nearest fire extinguishing equipment and it should be checked on a monthly basis. Be aware of fire exits, eyewash and shower equipment. Caution should be used when handling syringes as to avoid puncture. Syringes should always be returned to their rack after each use.

5.2 Compressed Gas Cylinders:

Compressed gases can be very hazardous and should be handled with caution. If the top of a compressed gas cylinder were to be knocked off, the tank could become a deadly projectile. Compressed gas cylinders should always be secured by chains or brackets above the midpoint of the tank (the more secure the better). When transporting cylinders, always attach the top cover (cap) to the tank and transport it chained to a hand cart (except for 6-packs which are already on a cart). Tanks in-use are located in the gasses room with entrance from the outside back of the building and is kept locked. Tanks that are not in use (full or empty) are stored in a locked cage area separate from the main building next to the chemical storage.

For additional information see SOP SH-04 *Gas Handling*.

5.3 Solvents:

The toxicity or carcinogenicity of each reagent used in this procedure has not been precisely defined; however, each chemical compound should be treated as a potential health hazard.

Methanol - Warning! Flammable liquid. May cause skin irritation. May cause central nervous system depression. May be absorbed through the skin. May cause kidney damage. May cause respiratory and digestive tract irritation. May be fatal or cause blindness if swallowed. May cause fetal effects. Causes severe eye irritation and possible injury. Target Organs: Kidneys, central nervous system, eyes.

Consult the current OSHA regulations and the Material Safety Data Sheets for all materials used in this procedure.

See Chemical Hygiene Plan on the Share drive. Analyst should read these manuals and become familiar with the hazards associated with the chemicals.

For more safety information contact the Health and Safety officer.

6.0 EQUIPMENT AND SUPPLIES

• Auto sampler vials and caps with Teflon faced septa, 1.8 ml.

• 40 ml VOA vials

• Micro syringes of 10, 25, 100, and 1000 µl capacity, glass (for sample measurement and spike preparation)

• Disposable pipettes

• Analytical balance

• Vortexer

•Sonicator with water bath

• GC/MS System: must be capable of temperature programming and should be equipped with a mass spectrometer and a capillary column split/splitless injector. The inlet liner is a Restek drilled double gooseneck Uniliner (installed with hole at top) cat # 20509 (or equivalent).

• GC column: Restek Stabilwax 30m, 0.32 mm ID, 1.0 µm film cat# 10654 (or equivalent)

•GC Method Parameters:

Initial temp of 80°C hold for 1 minute. Ramp 8°C/min to 200°C. Hold 8 minutes.
Total run time: approximately 24 minutes.
Pressure Pulse: 20 psi for 0.6 minutes
Column flow: 1.9 ml/min
Inlet temperature: 225°C
Syringe washes: 6 from both Wash A and Wash B with 1:1 MeOH/Water for 12 washes total.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

• Methanol - pesticide or UV grade or better

• Reagent water

• Ottawa sand, muffled at 400°C for at least 4 hours

7.2 Standards

• All stock standards, purchased or prepared must be in methanol or water. Standards may be diluted from neat or prepared by vendor if available.

• Intermediate and Working Standard Solutions- Use stock standard solutions to prepare intermediate or working standard. Intermediate standards are prepared in methanol or water and working standards are prepared in DI water.

• Calibration Standards – Calibration standards are prepared from stock standards at concentrations ranging from 0.5 µg/ml to 200 µg/ml in DI water.

• Alternate source check: This is a standard that contains the same analytes in the stock standards but is obtained from a different vendor or if obtained from the same vendor, contains a different manufacture lot number. It is prepared exactly like a mid calibration point and analyzed directly after the curve and before any samples or QC is analyzed.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

8.1 Sample Collection

Water and soil samples are collected in appropriate glass containers without chemical preservation. Small containers such as VOA vials should be used for collecting waters because less than 10 ml are needed for analysis.

8.2 Sample Preservation and Storage

Water and soils are stored at 4°C±2°C. Because no data for hold time is known at this time, all samples are to be analyzed within 7 days of collection

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

See Attachment 1 for a summary of quality control requirements.

9.1 Initial Demonstration of Capability

Prepare 4 LFBs in blank sand and 4 LFBs in reagent water at a midlevel curve concentration (or 1-2 times the reporting limit for TNI). Calculate the mean concentration found in mg/L and the relative standard deviation of the concentrations. The average recovery should be between 70%-130% of the true value. The RSD should be ≤30%. If these results are met, performance is deemed acceptable. If not, correct the source of the problem and repeat the test. Repeat this procedure anytime there is a significant change in instrument type, personnel, or methodology.

9.2 Laboratory Reagent Blank (LRB)

A blank is required with each matrix for up to 20 samples that are prepared together. Blanks are prepared using blank sand or reagent water. Target concentrations should be less than the reporting limits for analysis to proceed.

9.3 Laboratory Fortified Blank (LFB)

LFBs are required for each matrix prepared. Spike blank sand or reagent water at a midlevel curve concentration. One LFB is required for each matrix for up to 20 samples that are prepared together. The recovery of the LFBs should be 70%-130% of the expected value until such time that the lab develops in house limits (±3 standard deviations of the average).

9.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Fortify two additional aliquots of each environmental matrix at a midlevel curve concentration. One MS/MSD is required for each matrix for up to 20 samples that are prepared together. The recovery of the MS/MSD should be 70%-130% of the expected value until such time that the lab develops in house limits (±3 standard deviations of the average), and the RPD should be ≤30%.

9.5 Surrogates

Surrogates are not currently used with this method.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration standards are usually prepared at 0.5, 1, 2, 5, 10, 25, 50, 100, 150 and 200 µg/ml in DI water.

10.2 Analyze each calibration standard. Create a calibration curve by plotting peak area versus the concentration in the standard. The %RSD should be ≤ 20% for an average of response fit. If a linear or quad fit is used (6 points must be used for quad) the r or r^2>0.995 must be met.

10.3 Analyze the alternate source standard immediately after the curve. The alternate source standard should fall within ±30% of the expected value. If this cannot be met, the alternate source should be reanalyzed or the analyst should find another source to confirm the calibration standards.

10.4 Verify the calibration daily by the analysis of 1 or more calibration standards. A CCC is to be analyzed at the beginning of each period of operation (unless an initial curve is being run), after every 10 samples, and at the end of the run. Blanks should be run after the CC to lessen the level of carryover. It is recommended to include a low level point for one of the CCCs. The % difference or drift should be ≤20%. If CCCs do not meet this criterion, reanalyze all samples since the last passing CCC. Sample reanalysis may not be necessary if samples do not contain targets greater than the reporting limit and adequate sensitivity is demonstrated.

11.0 PROCEDURE

11.1 Solid Samples

11.1.1 Remove samples and standards from storage. Allow to reach room temperature.

11.1.2 For field samples weigh 10 g ±0.01 g into 40 ml VOA vial(s) and record the weight.

11.1.3 For blank and blank spike weigh 10 g ±0.01 g of blank sand into 40 ml VOA vials and record the weight.

11.1.4 For matrix spikes weigh two more aliquots of a representative sample at 10 g ±0.01 g into separate 40 ml VOA vials and record the weights.

11.1.5 Add 50-100 µl of 10,000 µg/ml calibration standard into BS, MS and MSD using a Class A syringe.

11.1.6 Add 10 ml of DI water to all samples and QC using a Class A pipet or syringe Sonicate for 1 hour at ambient temperature and let particulates settle for a minimum of 10 minutes. Centrifugation may be employed to separate phases.

11.1.7 Place approximately1 ml of the aqueous portion of the extract into a GC vial and analyze as water. It is not necessary to measure the volume exactly.

11.2 Water Samples

11.2.1 Remove samples and standards from storage. Allow to reach room temperature.

11.2.2 For field samples place approximately 1 ml of sample into a GC vial. It is not necessary to measure the volume exactly.

11.2.3 For blank and blank spike measure 1 ml reagent water into GC vials using a Class A syringe.

11.2.4 For matrix spikes, measure two 1 ml aliquots of a representative field sample into separate GC vials. The aliquots should be taken from separate vials or bottles than the source if extra volume is provided.

11.2.5 Add 5-10 µl of 10,000 µg/ml calibration standard into BS, MS and MSD using a Class A syringe. Mix by vortexing or hand shaking.

11.3 Non-aqueous Liquids

Liquid samples that are insoluble in water are not amenable to this method.

11.4 Sample Analysis

11.4.1 Analyze the BS, MS, and MSD directly after the calibration curve or calibration check.

11.4.2 Analyze two reagent blanks to ensure that carryover from spiked samples is minimized.

11.4.3 Analyze field samples.

11.4.4 Because carryover is known to occur with this procedure in the syringe, reanalysis of samples after high concentrations may be necessary.

12.0 DATA ANALYSIS AND CALCULATIONS

See Attachment 2 of this SOP

12.1 Use the calibration curve to directly calculate the concentrations of analytes in the sample. Extracts that contain results beyond the calibration range must be diluted and reanalyzed. Do not use the daily calibration verification standard to quantitate method analytes in samples

12.2 The calibration curve was established using µg/ml which is equivalent to the final reporting unit for water samples in mg/L. If a dilution is performed, then the concentration must be multiplied by the dilution factor as follows:

Liquid Concentration, mg/L = (C_i)(D)

Where C_i = uncorrected concentration in µg/ml (equivalent to mg/L)
D = Dilution Factor

Solids are calculated using the following equation:

Solid Concentration, mg/Kg = $\frac{Ci\ x\ FVxD}{Ws}$

FV = final volume in ml
W_S=solid weight in g

12.3 Significant figures: Results should be reported as 3 significant figures and/or one decimal place.

12.4 All results should be reported 30 days from receipt of samples at the lab unless a special extension has been granted. Printed final reports should be submitted, along with appropriate QA/QC and raw data. Results should be reported to three significant figures. Reports should be submitted at least 5 days before the expiration of the 30 days. Earliest possible submissions are greatly encouraged in case a sample should, upon examination of the reports, require re-analysis or re-extraction. Final reports are reviewed by the analyst who performed the work, a peer, the team leader, the QA Coordinator and the lab manager.

12.5 Raw data packages, whether hardcopy or electronic, should contain chromatograms, quantitation reports, final LIMS report, calibration data, BS/MS spike data, bench sheets, and any notes or other data that might be useful. These data packages when completed should be stored in

the central data storage area for archiving. For all known criminal investigations the raw data should be stored in a specially designated locked area.

12.6 A CD (CD-RW) back-up of the raw data is recommended. This is only a secondary backup for easy access to the files by the chemists. A log should be kept in the lab indicating the contents of each CD. Each CD should be clearly marked in a manner to prevent confusion. Once the data is backed up by this method in the lab, files should be moved over to the R6 Houston lab server for permanent storage. This should be done at the close of every work week.

13.0 METHOD PERFORMANCE

LOQs: A Limit of Quantitation (LOQ) check will be performed annually for each quality system matrix, method and analyte at 1-2 times the claimed LOQ. The LOQ will contain all targets and will be processed the same way as samples and standards. A successful analysis is one where the recovery of each analyte is within the laboratory established method acceptance criteria or client data quality objectives for accuracy.

Demonstration of Capability: Four replicate blank spikes in DI water or sand are prepared and analyzed initially or anytime there is a significant change in instrument type, personnel, or methodology to assess performance. The average recovery should be between 70%-130% of the true value. The RSD should be ≤30%. If these results are met, performance is deemed acceptable. If not, correct the source of the problem and repeat the test.

The following table contains average blank spike and matrix spike recoveries:

Analyte	BS Average %Recovery*	MS/MSD Average %Recovery*
PG	83.9	78.9
2-BE	87.3	83.7
DPGBE	86.4	82.4

*** Data from Oil Trust Fund Work**

14.0 POLLUTION PREVENTION

This method utilizes very small volumes of water for analysis and utilizes water for extraction of soils, thus making it safer for use by the laboratory analyst and less harmful to the environment. For information concerning pollution prevention that may be applicable to lab operations, consult “Less is Better: Laboratory Chemical management for Waste Reduction” available from the “American Chemical Management for Waste Reduction” available from the American Chemical Society’s Department of Government Relations, and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at point of generation. Numerous opportunities for pollution prevention exist in laboratory operation.

The Environmental Protection Agency (EPA) has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When waste cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

15.0 DATA ASSESSMENT AND ACCEPTABILITY CRITERIA FOR QUALITY CONTROL MEASURES

Some quality control elements are evaluated using limits set by the method that is referenced. Other quality control elements are evaluated using limits determined in-house. In-house limits are generated yearly if adequate data are available for calculation (more than 20 points.) If the analyte still remains outside the action limit even after re-analysis or re-extraction, the possible reason for this is noted on the summary of the report, the team leader is notified and the result is still reported. In general the following acceptability criteria will be used:

15.1 Initial Calibration Curve and Continuing Calibration Check: The initial calibration curve is for the purpose of establishing linearity. The curve is considered linear if % RSD$\leq$ 20 for an average of response curve fit or r or r^2>0.995 for a linear or quadratic curve fit. The Continuing Calibration Check must be less than 20% percent difference or drift compared with the true value established with the initial calibration curve (unless a special provision is made by the team leader or the method states wider criteria). If the continuing calibration check cannot make the established criteria, then a second shot is performed. When the continuing calibration check indicates linearity may have changed, a new multi-point curve will be analyzed to re-establish linearity.

15.2 BS/LCS/LFB: The BS is used to evaluate target recoveries in a clean matrix and to determine if recoveries outside limits are matrix related or due to laboratory problems. The BS will be evaluated using 70-130% recovery. Target compounds outside limits high but not present in the associated samples will not affect the data. If targets are recovered low, this may require the batch to be re-analyzed or re-extracted. The BS will be evaluated for effect on the data and a determination will be made as to whether qualification or re-analysis is necessary. If the same compound(s) continues to be outside limits, the lab must investigate the issue and correct the problem.

15.3 Matrix Spikes: Matrix spikes are generally used to evaluate recoveries of target compounds in a specific matrix and also to check the precision of the laboratory and sampling techniques. Matrix spike recovery and RPD limits are determined by the method or in house limits. Matrix spike recoveries and RPDs outside limits that are matrix related do not require re-extraction but may require qualification of the associated data.

16.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

Corrective actions for out-of-control data, as used in this section, must be significant enough to warrant an official corrective action form (See Quality Manual). Most re-extractions require an official corrective action form with supporting data to be generated (see section 17.3 for exceptions). Major deviations from standard operating procedures without prior approval (which may or may not have resulted in out -of-control data) will also require the generation of a corrective action. The following are example situations in which an official corrective action should be generated (see SOP QA - 04: *Corrective Actions)*:

Failed Quality Control limits will be evaluated for effects on the data. If the data with failed Quality Control are determined by the reviewer (and possible consultation with the customer) to meet the objectives of the project, re-extraction may not be necessary.

16.1 BS/LCS/LFB: If the BS shows a compound outside limits that is present in the associated samples, the customer should be contacted to determine the importance of the analyte in question. If the customer deems this to be of importance, the samples and BS should be re-extracted and reported. Alternately, the associated data may be qualified. Because a BS is to be prepared simultaneously with samples, it will be rare that an BS will be extracted again without samples associated with it.

16.2 Matrix Spike: If the sample analysis shows a matrix spike outside limits and within

limits on the BS, then the problem is deemed to be matrix related. The matrix spikes are not re-extracted but qualification of the source sample and possibly other similar samples in the batch may be necessary. If a spiked compound is outside limits on both the matrix spike and the BS, then the problem is deemed to be a laboratory problem. If this compound is present in the associated samples, then the customer may be contacted to determine its importance, the data will be qualified, or the sample batch will be re-extracted.

17.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Minor excursions from procedure or exceedances of quality control limits may not require an official corrective action form. In these cases the minor corrections may be performed at the time a problem is discovered. The problem and the action taken should be documented in a logbook, bench sheet, or notes but the official corrective action form is not required. Some of these actions include the following:

17.1 Extraction issues: Accidentally spiking the wrong volume (e.g. matrix spikes double) or mislabeling of an unspiked sample versus a spiked sample are such examples. In these cases the analytical results can be used to correct the problems. However, if this problem occurs the analyst should be suspicious that sample versus sample may also be mislabeled. If problems are reoccurring, a corrective action form must be generated.

17.2 Analysis Issues: Failed QC requirements at the time of analysis can include many things such as instrument performance checks, calibration, chromatography, etc. Most of these issues can be resolved by the analyst and are a normal part of analytical process. Once problems are discovered the analyst should correct the problem and reanalyze the problem sample(s) or QC checks. The following are examples of problems that can be corrected without the official corrective action form: Instrument maintenance including inlet, column, and oven; re-analysis of failed samples, instrument performance checks, calibration, etc.; re-quantitation of failed results; or qualification of data.

17.3 Qualification: Concentrations reported outside the calibration curve must be qualified with a J flag (estimated). The analyst should make every effort to report concentrations within the curve. Concentrations found in the samples that are less than 10x the amount found in the associated extraction or analysis blank are qualified with a B. Samples extracted or analyzed past holding time will be qualified in the narrative as minimum concentrations. Compounds suspected to have a low or high bias will be qualified with the L and K flags, respectively.

Sections 15.0, 16.0, and 17.0 do not contain a comprehensive list of all of the problems that can arise due to failed quality control or laboratory problems. The items listed are so the user has a sense of what issues would constitute an official corrective action or a minor corrective action (contingency). Failed Quality Control limits will be evaluated for effects on the data. If the data with failed Quality Control is determined by the reviewer (and possible consultation with the customer) to meet the objectives of the project, corrective action may not be necessary.

18.0 WASTE MANAGEMENT

Dispose of wastes generated by the laboratory in accordance with the Waste Management Program for the Houston Environmental Laboratory "See SOP, SH-02"

19.0 REFERENCES

"Techniques to Optimizing GC Analysis of Ethylene Glycol in Water", Restek Application Note 59187.

Method 8270D: Semi-volatile Organics by Gas Chromatography/Mass Spectrometry: Capillary Column Technique", Test Methods for Evaluating Solid Waste, SW-846, Update IV.

ATTACHMENT 1
Adapted from Method 8270D

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action for failure
Minimum five-point initial calibration	Initial calibration prior to sample analysis	Mean RSD ≤20% for Avg RF or correlation coefficient ≥0.995	Correct problem then repeat initial calibration.
Calibration verification (CCC)	At the beginning of each shift, after every 10 samples, and at the end	±20% of expected value	Reanalyze samples since last passing CCC or reanalyze initial calibration if passing CCCs cannot be obtained
Demonstration of Capability	Initially prior to analysis of any samples or if major change in instrument type, personnel, or methodology occurs	Average %R within 70-130% and RSD ≤30% or within laboratory limits	Recalculate results; locate and correct problem with system and then rerun demonstration for those analytes that did not meet criteria.
Method blank.	One per analytical batch of 20 samples or less	No glycols detected ≥ RL	Correct problem then re-prep or re-analyze method blank and all samples processed with the contaminated blank. If sample concentrations are >10X blank, re-prep and re-analysis is not necessary.
BS/LCS/LFB	One BS per matrix of 20 samples or less	%R within 70 - 130% or within laboratory limits	Reanalyze, re-extract and re-analyze, or qualify the associated data.
MS/MSD	One MS/MSD per every 20 samples per matrix	%R within 70 - 130% and RPD ≤ 30% (using concentration) or within laboratory limits	Qualify the source sample, if appropriate

ATTACHMENT 2

Equations used in Calculations

1. % Difference (Relative) or RPD:

= {[A-B]/((A+B)/2)}*100 or the difference ÷ average

A and B are any two values.

2. % Drift:

% Drift = {[True Value- Calculated Value]/True Value}*100

3. Standard Deviation (s):

$$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}}$$

N is the number of replicates
$\bar{x}$ **is the average from replicates**

4. Relative Standard Deviation:

$$\%RSD = \left(\frac{s}{\bar{x}}\right)x100$$

S is standard deviation

5. % Recovery (Matrix spikes)

$$\%\mathrm{Re}c = \frac{C_f - C_u}{C_S} \times 100$$

Cf is the final determined concentration in spiked sample in mg/L or mg/Kg
Cu is the final unspiked concentration in source sample in mg/L or mg/Kg
Cs is the theoretical spiked concentration in mg/L or mg/Kg