LOW LEVEL METHANE ANALYSIS FOR SUMMA CANISTER GAS SAMPLES

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SUPERCEDES: SOP #1708, Revision 2.1; 04/17/91; U.S. EPA Contract EP-W-09-031.

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1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) is intended for use when analyzing Summa canister gas samples for low parts per million volume (ppmv) levels of methane.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or limitations imposed by the procedure or other procedure limitations. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

2.0 METHOD SUMMARY

A flame ionization detector (FID) gas chromatograph (GC) is used to separate and quantitate methane in gas samples. The sample is introduced into the carrier gas as a plug and passes through a gas chromatography column which then separates it into two peaks. The first peak is unresolved air; the second peak is resolved methane. Peak areas are used in conjunction with calibration plots for quantitative measurements. This separation is completed in five minutes.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Refer to U.S. EPA Method T014 concerning Summa canister cleaning and sample collection. In addition refer to Environmental Response Team/Scientific, Engineering, Response and Analytical Services (ERT/SERAS) ERTSERAS SOP #1703, Summa Canister Cleaning Procedures and SOP #1704, Summa Canister Sampling.

Canisters are stored and analyzed at room temperature.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

This section is not applicable to this SOP as interferences have not been studied.

5.0 EQUIPMENT/APPARATUS

- Gas Chromatograph - Varian 3400 gas chromatograph with flame ionization detector (or equivalent) capable of operating at 225^{o}C.
- Carrier gas cylinder - ultra high purity helium with a two stage regulator delivering a pressure of 90 psi
- 1 mL and .1 mL precision gas-tight syringes with needles for sample introduction
- Gas chromatography column - 10 ft. x 1/4 in. stainless steel column packed with Spherocarb, 100/120 mesh (or equivalent), capable of operating at 100^{o}C, injection temperature of 200^{o}C
- Electronic integrator - Spectra-Physics SP4290 integrator (or equivalent)
- Septum port adaptor for Summa canister
- Soap film flow meter (or equivalent)

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6.0 REAGENTS

- Helium - Ultra high purity grade helium (99.9999%)
- Hydrogen - Ultra high purity grade hydrogen (99.9999%)
- Air - Ultra zero grade air (<0.05 ppmv total hydrocarbon)
- Calibration standards (in the range of 5-100 ppmv) - methane standards, balance air

7.0 PROCEDURES

7.1 Gas Chromatograph

The carrier gas is turned on and the flow rate adjusted to 40 mL per minute. The air is turned on and the flow rate adjusted to 150 mL per minute. The hydrogen is turned on and the flow rate is adjusted to 30 mL per minute. The flows are checked with a soap film flow meter. The flame ionization detector is then ignited and allowed to equilibrate for ten minutes. The integrator is turned on and zeroed before samples are introduced.

7.2 Calibration

Introduce, via 1 mL syringe, aliquots of the same size as will be used on the sample injections of the standard calibration gas mixtures in the gas chromatograph injector. At least one injection each standard gas mixture is required before starting to analyze samples. The very first calibration should be performed in triplicate.

Verify the initial calibration by injection of a complete set of at least four standards (at least five different concentrations of standards are routinely available from commercial suppliers) at the commencement of each day's analytical activities. It is suggested that each sample injection be followed systematically by a standard injection so that many injection areas are tabulated and averaged in the report.

7.3 Injection of Sample

A 1-mL sample is withdrawn from the Summa septum port using a 1-mL gas-tight syringe. The sample is quickly injected, guarding against blow-back of the plunger. Simultaneously, the integrator is activated and the sample run is labeled. The integrator run is ended in five minutes and rezeroed before the next analysis.

Samples analyzed above the calibrated linear range can be reanalyzed by injecting a smaller volume, or by diluting in ultra high purity zero air to acquire responses within the linear range. These dilutions may be done by injecting a measured volume of the sample into Tedlar bag and adding a measured volume of zero air. For instance, 100 mL of sample measured with a gas tight syringe, added to 900 mL of zero air would be diluted by a factor 10. These volumes have to be recorded and taken into account in the calculations.

8.0 CALCULATIONS

A linear standard curve of ppmv versus peak area is prepared. The sample concentrations are calculated using the formula

$$y = mx + b;$$

where
y is the peak area,
m is the slope (peak area/ppmv),
b is the y intercept (peak area), and
x is the concentration (ppmv).

The above equation may be rearranged to

$$x = \frac{y-b}{m}$$

where y is measured area, corresponding to a sample injection and x is the desired methane concentration in the sample injection. If a dilution has been made then, of course, the concentration obtained must be multiplied by the ratio of the final sample volume to the initial sample volume. Most integrator packages will handle the above calculations but it is recommended that a commercial spreadsheet program be used so that the final report preparation may be expedited.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

The following quality assurance/quality control procedures are applicable:

9.1 Precision

The precision of the method is monitored during the second lowest calibration standard from the linear curve. A control range is established for the standard using three standard deviations from the mean of ten independent analyses. The standard is analyzed periodically (at the beginning and end of a series of samples or every 8 hours) and must respond within the range of three standard deviations for the system and data precision to be considered under control. If the results of the standard analysis are out of range, the system must be repaired and the standards rerun, for a new calibration curve must be performed.

9.2 Accuracy

The accuracy of the method is monitored by periodically analyzing blind performance evaluation samples. These samples should not be prepared by the same outside source that the calibration standards were obtained from.

10.0 DATA VALIDATION

Data will be evaluated based on the information provided by Section 9.0.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, refer to U.S. EPA, OSHA or corporate health and safety practices.