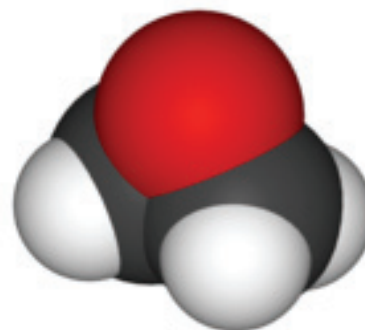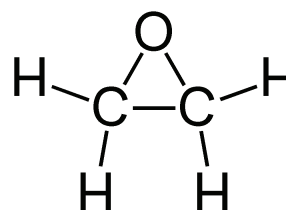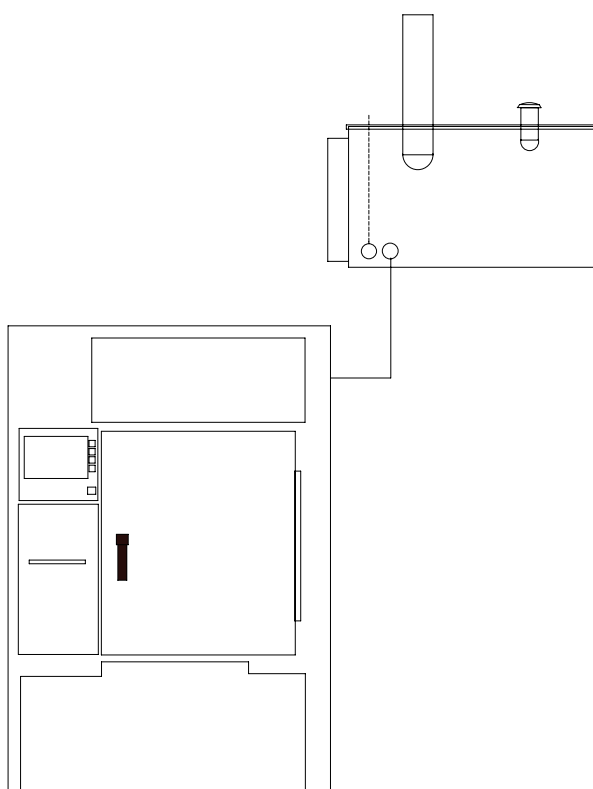# Reference Method for Source Testing:

Determination of the Ethylene Oxide Control Efficiency from Catalytic Oxidizers

Report EC 1/RM/51
July 2007

Readers' Comments

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Foreword

The procedures contained in the Environment Canada Reference Method EPS 1/RM/8 (December 1993, as amended from time to time) *"Reference Method for Source Testing: Measurement of Releases of Particulate from Stationary Sources"* and EPS 1/RM/15 (September 1990) *"Reference Method for the Monitoring of Gaseous Emissions from Fossil Fuel-fired Boilers"* are to be used in conjunction with the ethylene oxide (EtO) control efficiency method.

The complexity of the sampling and analysis procedures warrants that the operator be trained and experienced. The application of this method will entail health and safety hazards. Individuals are responsible for obtaining the required training to meet occupational health and safety standards.

Ethylene oxide is a toxic compound. Consequently all personnel involved in the analysis of EtO must be informed of proper handling procedures and potential health hazards. Do not release EtO to the laboratory atmosphere during preparation of standards or samples. All venting of samples and calibration gases must be directed to a fume hood or through an activated charcoal filter. The charcoal must be changed on a regular basis, based on the manufacturers' recommendations, prior to breakthrough of EtO.

Application of this method for release testing and analysis requires strict adherence to the method in all respects. Deviation from the method may invalidate the test results. Any modifications to equipment, reagents, materials, procedures, or calculations different from those specified in the reference method must be approved in writing by Environment Canada.

Note: Mention of trade names or commercial products does not constitute endorsement for use by Environment Canada.

Table of Contents

Section 1
Applicability

This Environment Canada reference method is used to determine the control efficiency of a catalytic oxidizer (abator) treating EtO from sterilization operations. This procedure may be applied to sterilizers using pure EtO or those that use a blend of carbon dioxide (CO_2) and EtO sterilant gas. This procedure applies only during the evacuation phase of a sterilization cycle.

Section 2
Principle

A non-condensing integrated flue gas sample is withdrawn proportionally or at a constant rate from a single point within the enclosed stack or exhaust duct during the evacuation phase of a sterilization cycle. The integrated sample is collected in a Tedlar bag and then analyzed for both CO_2 and EtO to determine the control efficiency for the abator.

The uncertainty for the determination of the control efficiency is shown in Appendix I. Note that there are no acceptance criteria for this value.

Section 3
Performance Specifications

Tables 1 and 2 provide the minimum performance specifications for the CO_2 and EtO analyzers. The procedures described in EPS 1/RM/15 (September 1990) *"Reference Method for the Monitoring of Gaseous Emissions from Fossil Fuel-fired Boilers"* are to be used to determine the specifications. The analysis of EtO is not limited to the techniques below.

Table 1. Minimum Performance Specifications for Carbon Dioxide Analyzers

Principle	Non-dispersive infrared (NDIR)
	Fourier transform infrared (FTIR)
	Photoacoustic
Range	0 – 10,000 ppm
Sensitivity	< 100 ppm
Raise/Fall time (90%)	< 60 seconds
Zero drift	<3% FS in 2 hr.
Span drift	<3% FS in 2 hr.
Deviation from linearity	<3% FS
Interference rejection ratio	H_2O > 100:1

Table 2. Minimum Performance Specifications for Ethylene Oxide Analyzers

Principle	Flame ionization detector (FID)
	Fourier transform infrared (FTIR)
	Photoacoustic
	Electrochemical
Range	0 – 20 ppm
Sensitivity	< 0.1 ppm
Raise/Fall time (90%)	< 140 seconds
Zero drift	<3% FS in 2 hr.
Span drift	<3% FS in 2 hr.
Deviation from linearity	<3% FS
Interference rejection ratio	H_2O > 10,000:1
	CO_2 > 10,000:1

FS = Full-scale

Section 4
Interferences

Infrared instruments such as FTIR, photoacoustic and NDIR will be affected by the interference from CO_2 and water vapour. The presence of hydrocarbon compounds will interfere with the FID.

Section 5
Apparatus

The following items are required:

Probe: A sample probe constructed from 6-mm (¼-inch) stainless steel tubing. Teflon tubing may be used to connect the probe to the sampling train components.

Pitot Tube: A calibrated pitot tube, or equivalent, to monitor stack gas velocity pressure during proportional sampling.

Manometer: An inclined gauge manometer, or equivalent, readable to within 0.13 mm (0.005 inch) of water column for the measurement of stack gas velocity. A manometer, or equivalent device, capable of measuring a pressure of 20 cm (7.9 inch) of water column, is also required to leak-check the sample bag.

Valve: A valve to adjust the sample flow rate.

Flow Meter: A rotameter or equivalent, capable of measuring flowrates up to 1000 cc/min to within 2.5%. If required to prevent condensation, a second rotameter capable of measuring flowrates up to 250 cc/min is required for active dilution of the abator flue gases.

Pump: A leak-free diaphragm pump able to deliver a flowrate of up to 1000 cc/min.

Sampling Bag: A 50-L capacity Tedlar bag, to hold an integrated gas sample. A sample of ambient air is also required to correct for the background levels of CO_2. Note that the size of sample required for analysis shall be compatible with the instrumental requirements for analysis. Place the Tedlar bag in a rigid container or sleeve to prevent damage to the bag and photodegradation of the sample.

Temperature Gauge: A temperature measuring system, to monitor the stack gas temperature to within 1.5% of the absolute stack temperature. The temperature sensor is attached to the pitot tube so that the temperature of stack gas may be determined during proportional sampling.

Conditioning Tube: A leak-free container, equipped with suitable fittings and able to hold at least 50 g of a desiccant and activated charcoal, to remove water vapour and hydrocarbons from ambient air used for diluting the flue gas sample, if necessary. **Caution: Do not use silica gel, as this desiccant removes CO_2.**

Miscellaneous: Assorted valves and fittings.

Section 6
Reagents

The following items are required:

Calibration Gases: Ethylene oxide and carbon dioxide in nitrogen contained in a pressurized cylinder at a concentration of about 90% of full scale to span the analyzer. Additional levels at about 50% of full scale are used to verify the linearity of the analyzer.

Zero Gas: Zero air or nitrogen in a pressurized cylinder to zero the analyzers.

Drierite (Anhydrous calcium sulfate): Indicating type 8 mesh, dried at 200 to 225°C for one to two hours, to remove water vapour from the ambient air used for dilution.

Activated Charcoal: Coconut, 8 to 12 mesh, to remove hydrocarbons from the ambient air used for dilution.

Section 7
Procedures

7.1 Pre-test Preparation

Prior to sample collection, purge and leak-check the sample bag. Alternately fill and evacuate the bag three times with zero air or nitrogen to purge the bag. The zero air or nitrogen must have no detectable concentration of EtO or contain any contaminant that causes a detectable response on the analyzer. Leak-check the bag by connecting it to a water manometer and gently pressurizing the bag with zero air or nitrogen to 10 cm H_2O. Allow the system to stand for 10 minutes. Replace or repair the bag if there is any decrease in pressure, as indicated by the manometer, during this time period. Following the leak check, evacuate the bag and connect it to the sampling system as in Figure 1.

Assemble the Integrated Bag Sampling Train as shown in Figure 1, but don't connect the probe to the abator exhaust. Turn on the pump and adjust the flow control valve to provide a sample flowrate of approximately 500 cc/min. Purge the train for five minutes and then turn off the pump. Connect the sampling line to the abator exhaust port. The sampling port must be located at the exhaust duct of the abator. Ensure that all connections are tight and leak-free.

Condensation of the abator gas may occur in the sampling system during the collection of the integrated bag sample. When conditions exist for condensation of the sample, such as very high relative humidity in the ambient air, steps must be taken to avoid condensation. Two procedures are identified for addressing this potential problem.

- Option 1 – Prior to the start of sampling, fill the sample bag to approximately one quarter of the bag capacity with dry, hydrocarbon-free ambient air. If the bag is over-filled, gently release some of the dry clean air to the desired level.
- Option 2 – Connect a sample dilution line near the extraction point. The diluent source may be a conditioning module with a desiccant and activated charcoal. See Figure 1 for details. Note that Option 2 requires a rotameter to monitor the addition flowrate of the dry clean gas. The flow rate through the dilution system shall be about one quarter of the total sampling flowrate.

Determine the flowrate variation in the exhaust stack over the cycle at a single point. If the flowrate at any point varies from the average by more than 15%, then proportional sampling is required to collect the exhaust sample. The procedure for collecting a proportional sample is described in the following section. Otherwise, sampling at a constant rate shall be used to collect the integrated flue gas sample.

7.2 Sample Collection

Commence sampling as soon as the sterilizer evacuation cycle begins. An indicator lamp at the abator should be available to announce the commencement of the evacuation of the sterilizer chamber contents to the abator. Otherwise, the exhaust CO_2 levels must be monitored and the sample collection must start as soon as the CO_2 level reaches twice the background level.

Set the initial sampling flowrate at approximately 500 cc/min. Immediately measure the stack gas velocity and temperature at the sampling point near the centre of the duct using the procedures given in Method B (Determination of Stack Gas Velocity and Volumetric Flow) of Environment Canada Reference Method EPS 1/RM/8, *"Reference Method for Source Testing: Measurement of Emissions of Particulate from Stationary Sources"*. These initial velocity pressure and temperature readings will be used to determine the proportional sampling flowrate for subsequent sampling intervals.

Following the first five-minute sampling interval, measure the velocity pressure and stack temperature at five-minute intervals throughout the test. Calculate the proportional sampling rate for each of the five-minute intervals using Equation 1. Adjust the sampling flowrate to this value. Record the parameters indicated on the Sample Collection Data Sheet (Figure 2) every five minutes. The total sampling time shall be the duration of the evacuation phase of a sterilization cycle; or no more than 60 minutes.

Equation 1

$$Q = 500 \sqrt{\frac{T_o}{\Delta p_o}} \times \sqrt{\frac{\Delta p}{T_s}}$$

Note: the expression $500 \sqrt{\dfrac{T_o}{\Delta p_o}}$ becomes the proportional sampling flowrate constant,

where:

Q = sampling flowrate as measured by the rotameter, cc/min

Δp_o = stack velocity pressure during the initial five-minute interval, kPa

Δp = stack velocity pressure, kPa

T_o = stack temperature during the initial five-minute interval, K

T_s = stack temperature, K

If using Option 2, then the dilution sample flowrate shall be one quarter of the flowrate calculated above. In this case, the setting for the rotameter immediately upstream of the bag sample will be $1.25 \times Q$.

At the end of the evacuation phase, turn the three-way valve to atmosphere and stop the pump. Disconnect the Tedlar bag and place it in a protective container or sleeve to prevent damage and photodegradation of the sample. The sample must be analyzed within one week of collection. **Caution: Do not refrigerate the sample.**

The determination of control efficiency also requires the collection of the background air in the vicinity of the abator. This sample is required to correct the sample for the CO_2 in the ambient air.

No conditioning of the background air is required for this sample. Purge and leak-check the sample bag before collection, following the procedure in Section 7.1.
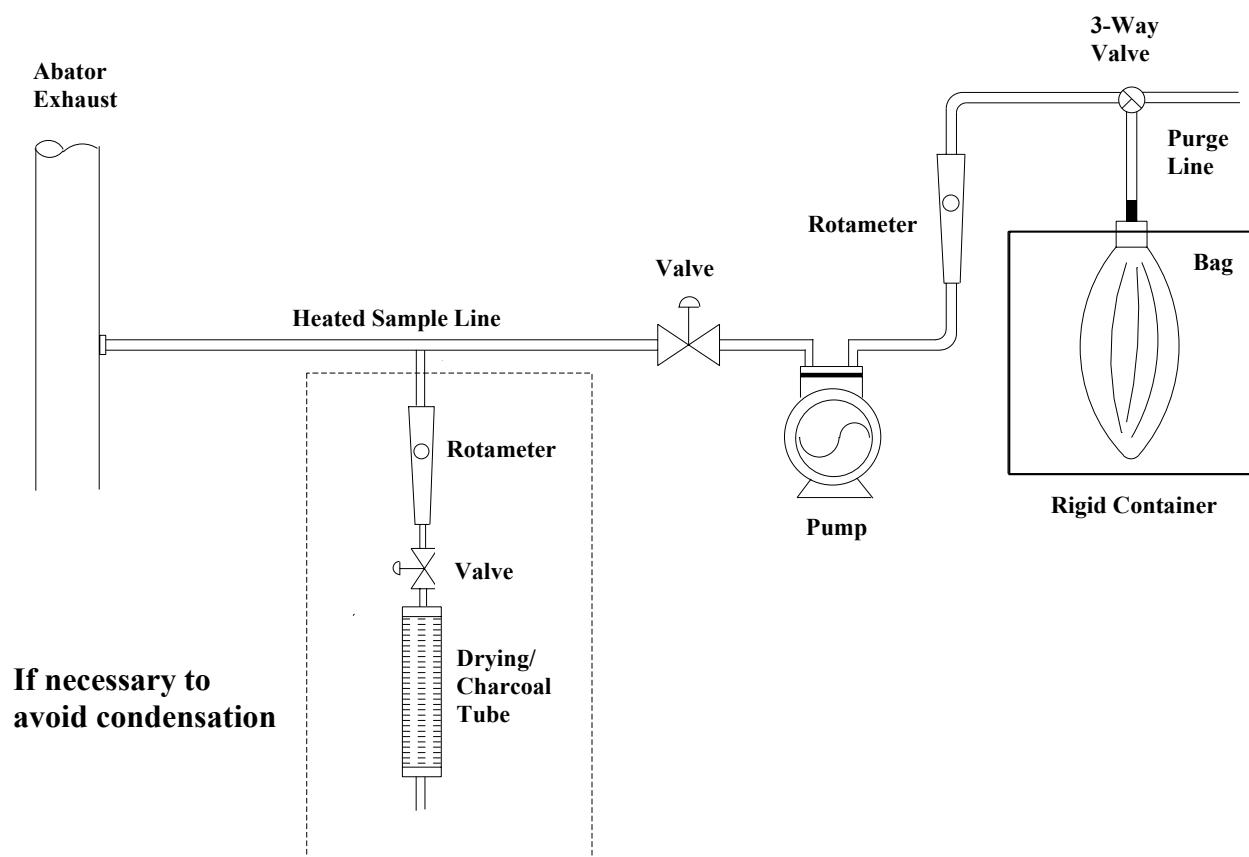

Figure 1. Integrated Bag Sampling Train

General Data		
Location	Date	
Unit Number	Test Number	
Time of Test		
Operator		

Pre-test				
Bag Leak-checked? (Y/N)		Train Purged? (Y/N)		
Proportional Sampling Constant (Determined from initial Δp and stack temperature)		$500\sqrt{(T_o/\Delta p_o)}$		

Test Data				
	Stack Gas & Sampling Parameters			
Time (min)	Stack Gas Velocity Pressure (kPa)	Temp (°C)	Calculated Sampling Rate (Q) (cc/min)	Total Sampling Rate* (cc/min)
5			500	625
10				
15				
20				
25				
30				
35				
40				
45				
50				
55				
60				

* if active dilution (Option 2) is used

Comments

_____

_____

_____

Note: data may be entered in the units for which the equipment is designed.

Figure 2. Sample Collection Data Sheet

7.3 Sample Analysis

Assemble the analytical system as shown in Figure 3. Follow the manufacturer's instructions with respect to the operation of the analyzer, taking care to allow sufficient warm-up time.

> *Caution: When calibrating the instrument with EtO or analyzing an integrated bag sample, vent the exhaust from the bags and/or analyzers through an activated charcoal trap or to a fume hood. Replace the activated charcoal trap as required to prevent the breakthrough of EtO.*

Various instrumental techniques are available for the analysis of CO_2 and EtO mixtures. Bag samples may be analyzed using a portable instrument with an electrochemical sensor and NDIR cell; a photoacoustic analyzer with water vapour, CO_2 and EtO optical filters; an FTIR analyzer or an FID for the determination of EtO. Note that analyses are not limited to the techniques mentioned above. All analyzers must meet the specifications detailed in Table 1 and Table 2.

Calibration System: Purge an empty sample bag by partially filling it with zero air from a cylinder, and evacuating it. Partially fill the bag again and connect it to the analytical system as shown in Figure 3. Turn on the pump and adjust the sampling flow rate within the analyzer manufacturer's recommended range. When the output signal has stabilized, adjust the zero control on the analyzer.

The calibration of the CO_2 and EtO instruments must be verified with known gas concentrations. Purge another sample bag by partially filling it with 90% full-scale span gas from a cylinder and then evacuating it. Partially fill the bag again with the span gas and connect it to the system as shown in Figure 3. Adjust the sampling flow rate to that used to zero the instrument. When the output from the analyzer is stable, adjust the analyzer span control.

On some analyzers, the zero and span controls are interactive, and the zero and span calibration procedures may need to be repeated several times before the desired values are obtained.

Analysis: Connect the ambient air background sample bag to the analytical system as shown in Figure 3 and turn on the pump, ensuring that the sample flowrate through the analyzer is set to the same flowrate as that used during the calibration procedure. Allow the analyzer output to stabilize and continue for another two minutes. Determine the CO_2 concentration. Repeat twice and record all values on the Sample Analysis Data Sheet (Figure 4).

Repeat the analysis procedure for the integrated abator gas sample bag. Repeat twice and record all values on the Sample Analysis Data Sheet (Figure 4). Determine the average concentrations of CO_2 and EtO for both the background air and abator exhaust on the Sample Analysis Data Sheet (Figure 4). The average level of CO_2 in the background air is used to correct the levels of this component in the abator exhaust integrated gas sample.
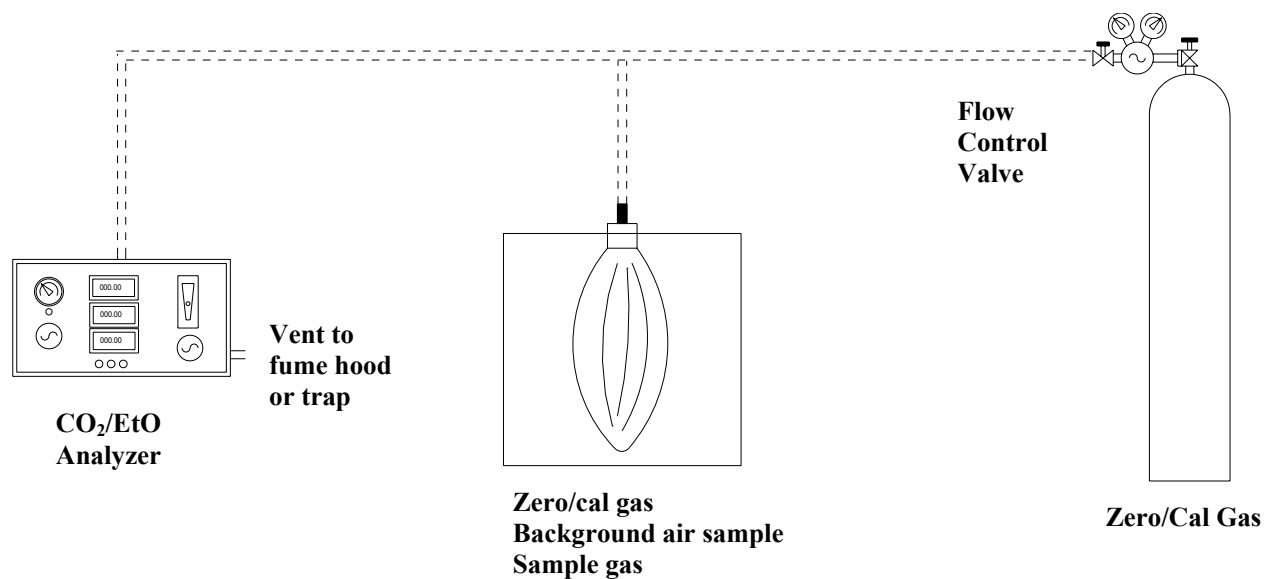
Figure 3. Carbon Dioxide and Ethylene Oxide Analysis

Analyzer Description			
Model/Type			
CO₂ Range	ppm	**EtO Range**	ppm
Analyzer 1 Flow Rate	cc/min	**Analyzer 2 Flow Rate**	cc/min

Span Gases			
CO₂	ppm	**EtO**	ppm

Instrument Response					
Zero		**Adjust (Y/N)**	**Span**		**Adjust (Y/N)**
CO₂	ppm		**CO₂**	ppm	
EtO	ppm		**EtO**	ppm	

Analysis (all values in ppm)							
Background Air			**Average**	**Sample Bag**			**Average**
CO₂				**(C1) ___**	**CO₂**			**(C2) ___**
EtO	Not required				**EtO**			**(C3) ___**

$$C_{CO2} = C2 - C1$$
$$C_{EtO} = C3$$

Enter results in Equation 2

Comments

Figure 4. Sample Analysis Data Sheet

Section 8
Calculations

Using the average values of CO_2 and EtO from the Sample Analysis Data Sheet (Figure 4), calculate the control efficiency of the abator using Equation 2.

8.1 Equations

Equation 2

$$CE = \frac{C_{CO_2} - \dfrac{1-f}{f} C_{EtO}}{C_{CO_2} + 2\,C_{EtO}} \times 100$$

8.2 Nomenclature

C_{CO2} = average concentration of CO_2 in the abator integrated gas sample, corrected for the average CO_2 in the ambient air, ppm (v/v), as sampled or diluted basis

C_{EtO} = average concentration of EtO in the abator integrated gas sample, ppm (v/v), as sampled or diluted basis

f = volume fraction of EtO in the sterilant gas mixture

CE = control efficiency of the abator for EtO, %

Appendix I

Determination of Uncertainty for
Control Efficiency of Ethylene Oxide

Determination of Uncertainty for Control Efficiency of Ethylene Oxide

$$CE = \frac{A - B}{A - B + 2*C}*100$$

Compound		Measured Value (ppm)		Standard Deviation (ppm)
Carbon dioxide - sample	A	1500	D	50
Carbon dioxide - air	B	500	E	50
Ethylene oxide	C	5	F	0.5

Calculation

$\frac{(A+0.5*D) - B}{(A+0.5*D) - B + 2*C}*100$	(G)	(H-G)	
$\frac{(A-0.5*D) - B}{(A-0.5*D) - B + 2*C}*100$	(H)		Uncertainty
$\frac{A - (B+0.5*E)}{A - (B+0.5*E) + 2*C}*100$	(I)	(J-I)	
$\frac{A - (B-0.5*E)}{A - (B-0.5*E) + 2*C}*100$	(J)		$\sqrt{(H-G)^2 + (J-I)^2 + (L-K)^2}$
$\frac{A - B}{A - B + 2*(C+0.5*F)}*100$	(K)	(L-K)	
$\frac{A - B}{A - B + 2*(C-0.5*F)}*100$	(L)		

Example

$\frac{(1500+0.5*50) - 500}{(1500+0.5*50) - 500 + 2*5}*100$	(G) 99.03382	(H-G) -0.04904	
$\frac{(1500-0.5*50) - 500}{(1500-0.5*50) - 500 + 2*5}*100$	(H) 98.98477		Uncertainty
$\frac{1500 - (500+0.5*50)}{1500 - (500+0.5*50) + 2*5}*100$	(I) 98.98477	(J-I) 0.04904	$\sqrt{(-0.049)^2 + (0.049)^2 + (0.098)^2}$
$\frac{1500 - (500-0.5*50)}{1500 - (500-0.5*50) + 2*5}*100$	(J) 99.03382		0.1201
$\frac{1500 - 500}{1500 - 500 + 2*(5+0.5*0.5)}*100$	(K) 98.96091	(L-K) 0.09803	0.12% (rounded)
$\frac{1500 - 500}{1500 - 500 + 2*(5-0.5*0.5)}*100$	(L) 99.05894		

$$CE = \frac{A - B}{A - B + 2*C}*100 = \frac{1500 - 500}{1500 - 500 + 2*5}*100 = 99\% \pm 0.12\%$$