Casting Emission Reduction Program

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HAP Method Validation
Methyl Ethyl Ketone
WBS # 2.1.1

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Application Method

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1. **PURPOSE**

This method may be used to determine the concentration(s) of the listed analytes (see Table 1) in ambient air, workplace air, and process/facility emissions.

2. **SCOPE**

This procedure applies to the compounds listed in Table 1.

TABLE 1
Analytes

	Boiling Point (°C)	Density (g/mL)	MW (g/mole)
2-Butanone	79.59	0.804	72.11

3. **DEFINITIONS**

mg = milligram
L = liter
ml = milliliter
µg = microgram
m^3 = cubic meter
°F = degrees Fahrenheit

4. **APPARATUS AND REAGENTS**

4.4 Gas chromatograph equipped with a mass selective detector
4.4 Column - see instrument parameters
4.3 Syringes
4.4 2-Butanone - reagent (AR) grade, suitable for spectrophotometric analysis
4.5 Target Analyte(s) - reagent (AR) grade
4.6 Standard solution – 2-Butanone
4.7 Desorbing solution – Carbon Disulfide
4.8 Vials - screw cap with Teflon™ cap liners
4.9 Assorted pipets and volumetric flasks
4.10 100/50 mg charcoal tubes

5. **CALIBRATION**

5.1 Prepare, in the standard solvent, a stock solution or solutions containing the target analyte(s), each at a concentration convenient for further dilution to levels approximating the levels expected in the field samples.

5.1.1 For liquids, the volume of pure analyte(s) needed for the stock solution(s) may be calculated using Equation 1 (see section 8.1).

5.1.2 For solids, use Equation 1 without "d". "V_a" then becomes the analyte weight in milligrams.

5.1.3 For "V_S" in Equation 1, use the mean air volume expected to be sampled in the field.

5.1.4 The following procedure has been found to provide accurate calibration standards, however, other procedures may be used at the discretion of the analyst.

5.1.4.1 Weigh the approximate calculated amount of each analyte into a volumetric flask of the appropriate volume and record the weight(s) to nearest 0.1 mg.

5.1.4.2 Fill the volumetric flask to the mark with the standard solvent and mix thoroughly.

5.1.4.3 Calculate the concentrations obtained with this stock solution and the dilutions necessary to achieve the target concentrations for each of the analytes. Use concentrations in units of mass/volume, e.g., mg/ml.

5.1.5 Perform dilutions, recording all volumes used, and clearly label both in a bound notebook and on the flasks containing the solutions. Each label should also include the solution disposal date and the analyst's initials. The labels should be made as indelible as possible, keeping in mind the environment in which the solutions will be stored.

5.2 Inject a known reproducible volume, using solvent flush techniques, of each standard into the gas chromatograph such that the lowest calibration standard response is greater than five (5) times the background noise level (see Section 7, Instrument Parameters).

5.2.1 When an autosampler is being used, its control parameters must be set to assure consistently accurate sample transfer and complete syringe rinsing between injected solutions.

5.3 Analyze each standard in triplicate, record and average the peak area(s).

5.4 Prepare a calibration curve by plotting the weight of analyte in each standard versus the mean peak area(s) for each standard.

5.5 The calibration curve shall have a correlation coefficient greater than 0.98 for the curve fit used. If the coefficient of variation is less than 0.98, the cause of the problem must be identified and corrected prior to sample analysis.

6. ANALYSIS OF SAMPLES

6.1 Remove samples from storage and allow warming to room temperature.

6.2 Transfer each section of solid sorbent to an appropriately labeled vial.

6.3 Pipet an appropriate volume (1.0 mL for 100 mg/50 mg tubes) of the desorbing solvent into each vial and cap immediately.

6.4 Allow to desorb for one (1) hour using an ultrasonic bath.

6.5 Inject a known volume (same as used in part 5.2) of the solution, using solvent flush techniques, into the gas chromatograph (see Section 7, Instrument Parameters).

6.6 Record the peak area(s) of the analyte(s) present.

6.7 Calculate the concentration of analyte in the sampled environment (equations 2-7).

6.8 Report the weight, in µg, for each analyte.

6.9 Laboratory blanks, spikes, and sample duplicates will be analyzed at a minimum frequency of 5% or one (1) each per batch for batches containing fewer than twenty (20) samples.

7. INSTRUMENT PARAMETERS

7.1 Instrument parameters may vary significantly with changes in sample matrix, instrument make and model, and column condition. Appendix A contains instrument parameters that have been used to successfully determine each analyte. These parameters should be considered a starting point only and optimized for each set of samples.

8. CALCULATIONS

8.1 The volume of analyte needed to prepare appropriate standards may be calculated using the following equation:

$$V_a = 20 \; X \; \frac{(TLV)\,(V_S)}{1000 \; X \; d} \; X \; V_{Sol} \qquad 1$$

. . . where:

V_a is the volume of analyte needed to prepare the standard, µL

20 is a scaling factor to give a V_a that is conveniently measurable and a resulting stock solution concentration that is readily diluted to useful concentrations

TLV is the expected concentration of the analyte in the sampled gas, mg/m^3

V_S is the volume of air sampled in the field, L

d is the density of the analyte of interest, g/mL

V_{Sol} is the volume of the desorbing solvent used for the stock solution, mL

8.2 Using a computer application (e.g., a chromatography data system or Excel) or calculator, calculate the coefficients (m_i, b_i) of the linear regression:

$$Area_i = m_i * Conc_i + b_i \qquad 2$$

where:

$Area_i$ is the area of the analyte peak "i" when the standard containing it is analyzed

$Conc_i$ is the concentration of analyte "i" in the standard, e.g., mg/L

m_i is the slope of the linear regression between the area and the concentration

b_i is the y-intercept of the linear regression between the area and the concentration

If the y-intercept equals 0, then the slope is equivalent to the classical definition of the response factor. For EPA applications, the agency may require the linear regression to be calculated with the regression through the origin, i.e., the y-intercept (b_i) must be equal to 0.

8.3 Calculate the weight of analyte "i" in a sample as follows:

$$Wt_{Bf} = DV * (Area_{Bf} - b)/m \qquad Wt_{Bb} = DV * (Area_{Bb} - b)/m \qquad 3$$

$$Wt_{Sf} = DV * (Area_{Sf} - b)/m \qquad Wt_{Sb} = DV * (Area_{Sb} - b)/m \qquad 4$$

$$Crtd\ Wt_i = (Wt_{Sf} - Wt_{Bf}) + (Wt_{Sb} - Wt_{Bb}) * 2 \ (df) \qquad 5$$

. . . where:

Wt_{Bf} is the weight of the analyte of interest found on the front section of the blank solid sorbent tube, mg

$Area_{Bf}$ is the area of the analyte peak of interest from the chromatographic run of the blank solid sorbent tube front section, mV-sec

Wt_{Bb} is the weight of the analyte of interest found on the back section of the blank solid sorbent tube, mg

$Area_{Bb}$ is the area of the analyte peak of interest from the chromatographic run of the blank solid sorbent tube back section, mV-sec

Wt_{Sf} is the weight of the analyte of interest found on the front section of the solid sorbent tube on which the sample was collected, mg

$Area_{Sf}$ is the area of the analyte peak of interest from the chromatographic run of the sample solid sorbent tube front section, mV-sec

Wt_{Sb} is the weight of the analyte of interest found on the back section of the solid sorbent tube on which the sample was collected, mg

$Area_{Sb}$ is the area of the analyte peak of interest from the chromatographic run of the sample solid sorbent tube back section, mV-sec

DV is the volume of solvent use to desorb the sorbent media, mL

Crtd Wt_i is the total weight of analyte "i" corrected for any amounts found on the blank solid sorbent tube, mg

NOTE: If the corrected weight of analyte i found on the back section of the sample tube (Wt_{Sb}-Wt_{Bb}) is equal to or greater than 10% of the total amount of analyte present on the sample tube, then "breakthrough" has occurred. Breakthrough results should be reported, but clearly identified as such. These are to be considered ***minimum*** amounts present in the air sampled.

8.4 Calculate the concentration of analyte in the sampled air as follows:

$$C_i \left(\frac{mg}{m^3}\right) = \frac{Crtd\ Wt_i\ X\ 1000}{(V_S)\ (DE_i)} \qquad 6$$

. . . where:

C_i is the concentration of analyte i in the sampled air, mg/m^3

Crtd Wt_i is the corrected weight of analyte i in the sample, mg

1000 is the number of liters in a cubic meter, L/m^3

V_S is the volume of air sampled, L

DE_i is the desorption efficiency of the analyte

8.5 Calculate the concentration of analyte(s) in the sampled air in parts per million (ppm) using the following equation:

$$C_i\,(ppm) = \frac{C_i\,(\frac{mg}{m^3})\ X\ 24.45}{MW_i} \qquad 7$$

. . . where:

C_i (ppm)	is the concentration of analyte i in parts per million
C_i (mg/m^3)	is the concentration of analyte i in milligrams per cubic meter
24.45	is the molar volume of a gas at 70°F and standard pressure, mL/mmole
MW_i	is the molecular weight of analyte i, mg/mmole

9. **REFERENCES**

9.1

Analyte	Literature Reference
2-Butanone	Method TO-11

INSTRUMENT PARAMETERS

Capillary Columns

Analyte	2-Butanone
Column:	
Dimensions:	30 m x 0.32mm i.d. x 0.50 µm film thickness
Type:	DB-Wax or equivalent
Material:	100% Polyethylene Glycol bonded to Fused Silica
GC Temperature Profile	
Initial Temp:	40 °C
Isothermal Hold:	6 min
Final Temp.:	40 °C
Post Run Hold:	8 min
Post Run Temperature:	240 °C
Injector Profile:	
Inlet Temperature:	250°C
Mode:	Split
Split Flow:	12.0 ml/min
Pressure:	0.39 psi
Detection:	
Type:	MSD
Detector Temperature:	250 °C
Solvent Delay:	2.62 min
Carrier Gas:	
Type:	He
Column Flow Rate:	1.3 mL/min
Mode:	Constant Flow
Sample:	
Injection Volume:	1.0 µl
Solvent:	Carbon Disulfide

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2-Butanone Method Validation Average Results

Average Mass, ng	Spike Mass, ng	DE %
0.50	0.8	78
2.68	4.02	83
5.44	8.04	92

Discussion

The present work was conducted to evaluate the desorption efficiency of 2-Butanone on charcoal tubes desorbed with carbon disulfide and analyzed by gas chromatography. This method is well established. The detector in these tests was a mass selective detector (MSD). Because of the high sensitivity of the MSD, nanogram concentrations of the analyte were used in the procedure.

Calculations of desorption efficiencies for one day storage averaged 81%. This is possibly due to the establishment of equilibrium between adsorption and desorption processes between the analyte and the charcoal at the room temperature storage conditions. In addition, desorption efficiency was seen to increase as the spiked concentration increased.

The following table of results, shown for reference purposes, provides details on the analysis.

Sample Name	Misc Info	ug/ml	ug spiked on tube	Analyzed Concentration ug/ml	% Desorption Efficiency
TL1001B	10ul MEK, desorp 17 hours	8.04	0.00804	0	
TL0101B	1ul MEK, desorp 17 hours	0.80	0.00080	0	No Breakthrough
TL0100B	1ul MEK,desorp 17 hours	0.80	0.00080	0	
TL0502B	5ul MEK, desorp 17 hours	4.02	0.00402	0	
TL0501B	5ul MEK, desorp 17 hours	4.02	0.00402	0	
TL01001F	1ul MEK,desorp 17 hours	0.80	0.00080	0.5	62.2
TL0101F	1ul MEK,desorp 17 hours	0.80	0.00080	0.75	93.3
TL0502F	5ul MEK, desorp 17 hours	4.02	0.00402	2.98	74.1
TL0501F	5ul MEK, desorp 17 hours	4.02	0.00402	3.69	91.8
TL1001F	10ul MEK,desorp 17 hours	8.04	0.00804	6.77	84.2
				TOTAL AVG	81.8