Method no.:	PV2080
Matrix:	Air
Target concentration:	5.0 ppm (30.0 mg/m³) TWA (ACGIH TLV)
Procedure:	Samples are collected by drawing a known volume of air through glass sampling tubes containing coconut shell charcoal. Samples are desorbed with 95/5 (v/v) methylene chloride/methanol and analyzed by gas chromatography using a flame ionization detector (GC-FID).
Recommended air volume and sampling rate:	10 L at 0.20 L/min
Reliable quantitation limit:	0.05 ppm (0.32 mg/m^3)
Special requirements:	Samples should be stored in a refrigerator when not in transit.
Status of method:	Partially Evaluated Method. This method has been subjected to established evaluation procedures, and is presented for information and trial use.

Date: October 1994 Chemist: Wayne Potter

Organic Service Branch I
OSHA Salt Lake Technical Center
Salt Lake City, UT 84165-0200

1. General Discussion

1.1 Background

1.1.1 History

This evaluation was undertaken to establish a suitable sampling procedure for butyl lactate. A study for butyl lactate collected with charcoal tubes showed a average recovery of 100% from the desorption study. This report describes a similar analytical method for sampling and analysis of butyl lactate.

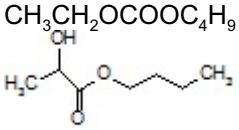
1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.) (Ref. 5.1)

n-Butyl lactate is a poison by intraperitoneal route. Local effects include irritation to the skin and eyes. Toxic concentration in air for humans is about 4 ppm.

1.1.3 Workplace exposure (Ref. 5.2)

n-Butyl lactate is used as a solvent for nitrocellulose, ethyl cellulose, oils, dyes, natural gums, many synthetic polymers, lacquers, varnishes, inks, stencil pastes, antiskinning agent, perfumes, dry-cleaning fluids and adhesives. It is also used as a chemical intermediate. No data is available on the extent of workplace exposure.

1.1.4 Physical properties and other descriptive information (Ref. 5.2)

Synonyms:	butyl α-hydroxypropionate; lactic acid, butyl ester; 2-hydroxypropanoic acid, butyl ester
CAS number:	138-22-7
IMIS:	0478
RTECS:	OD4025000; 8604 (Ref. 5.3)
Molecular weight:	146.21
Flash point:	75.5°C (168°F)(TOC)
Boiling point:	188°C
Melting point:	-43°C
Odor:	Mild odor
Color:	water-white, stable liquid
Autoignition temp:	382°C (720°F)
Density:	0.968
Molecular formula:	$CH_3CH_2OCOOC_4H_9$
Structural formula:	

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25°C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the overall procedure (DLOP)

The detection limit of the overall procedure is 0.95 µg per sample (0.016 ppm or 0.095 mg/m³). This is the amount of analyte spiked on the sampler that will give a response that is significantly different from the background response of a sampler blank.

The DLOP is defined as the concentration of analyte that gives a response (Y_{DLOP}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DLOP} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{BR} in chromatographic methods is typically inconvenient, and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for the DLOP:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

Y_{obs} = observed response
Y_{est} = estimated response from regression curve
n = total no. of data points
k = 2 for a linear regression curve

At point Y_{DLOP} on the regression curve

$$Y_{DLOP} = A(DLOP) + Y_{BR}$$

A = analytical sensitivity (slope)

therefore

$$DLOP = \frac{(Y_{DLOP} - Y_{BR})}{A}$$

Substituting 3(SEE) + Y_{BR} for Y_{DLOP} gives

$$DLOP = \frac{3(SEE)}{A}$$

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the highest sampler loading was 14.96 µg/sample. This is the amount, when spiked on a sampler, that would produce a peak approximately 10 times the background response for the sample blank. These spiked samplers, and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (A and SEE) for the calculation of the DLOP. Values of 112.87 and 35.66 were obtained for A and SEE respectively. DLOP was calculated to be 0.948 µg/sample (0.016 ppm or 0.095 mg/m^3).

Table 1.2.1
Detection Limit of the Overall Procedure

mass per sample (µg)	area counts (µV-s)
0	0
1.5	176
2.99	415
4.49	537
5.98	709
7.48	814
8.97	1044
10.47	1231
11.96	1397
13.46	1589
14.96	1680

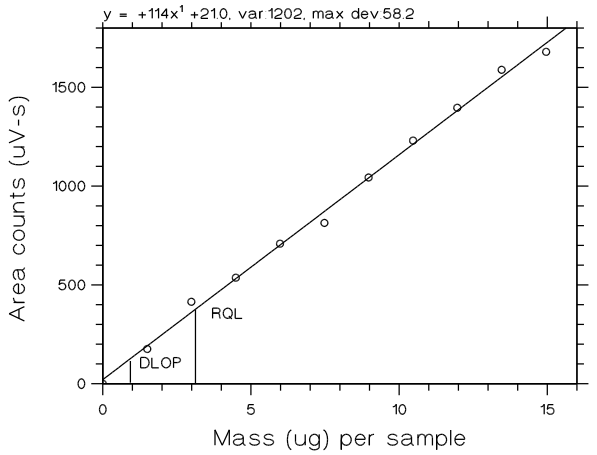


Figure 1.2.1. Plot of data to determine the DLOP/RQL.

1.2.2 Reliable quantitation limit (RQL)

The reliable quantitation limit is 3.2 µg per sample (0.05 ppm or 0.32 mg/m³). This is the amount of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements.

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line data obtained for the calculation of the DLOP (Section 1.2.1), providing at least 75% of the analyte is recovered. The RQL is defined as the concentration of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

therefore

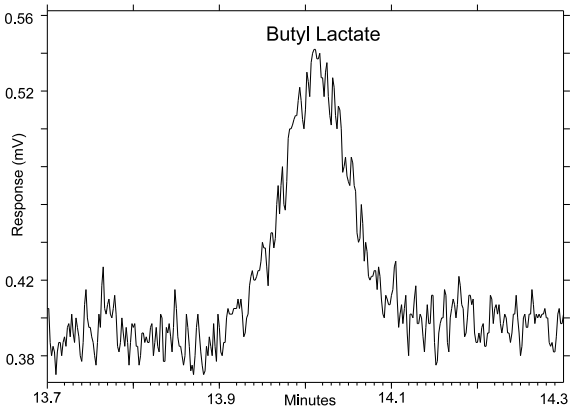


Figure 1.2.3. Chromatogram of the RQL.

$$RQL = \frac{10(SEE)}{A}$$

2. Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within ±5% of the recommended flow rate.

2.1.2 Samples are collected with solid sorbent sampling tubes containing coconut shell charcoal. Each tube consists of two sections of charcoal separated by a urethane foam plug. The front section contains 100 mg of charcoal and the back section, 50- mg. The sections are held in place with glass wool plugs in a glass tube 4-mm i.d. × 70-mm length. For this evaluation, SKC Inc. charcoal tubes (catalog number 226-01, Lot 120) were used.

2.2 Technique

2.2.1 Immediately before sampling, break off the ends of the sampling tube. All tubes should be from the same lot.

2.2.2 Attach the sampling tube to the pump with flexible tubing. It is desirable to utilize sampling tube holders which have a protective cover to shield the employee from the sharp, jagged end of the sampling tube. Position the tube so that sampled air passes through the front section of the tube first.

2.2.3 Air being sampled should not pass through any hose or tubing before entering the sampling tube.

2.2.4 Attach the sampler vertically with the front section pointing downward, in the worker's breathing zone, and positioned so it does not impede work performance or safety.

2.2.5 After sampling for the appropriate time, remove the sample and seal the tube with plastic end caps. Wrap each sample end-to-end with a Form OSHA-21 seal.

2.2.6 Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.

2.2.7 Record sample volumes (in liters of air) for each sample, along with any potential interferences.

2.2.8 Ship any bulk samples separate from the air samples.

2.2.9 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator.

2.3 Desorption efficiency

The desorption efficiencies of n-butyl lactate were determined by liquid-spiking the charcoal tubes with the analyte at 0.1 to 2 times the target concentration. The loadings on the tubes were 29.9, 149.6, 299.1, and 598.2 µg of n-butyl lactate. These samples were stored overnight at ambient temperature and then desorbed and analyzed. The average desorption efficiency over the studied range was 98.25%.

Table 2.3
Desorption Efficiency of n-Butyl Lactate

	% Recovered			
Tube #	0.1 × 29.9 µg	0.5 × 149.6 µg	1.0 × 299.1 µg	2.0 × 598.2 µg
1	98.49	97.54	98.07	100.03
2	97.70	96.99	98.01	99.97
3	97.41	97.62	99.03	98.16
4	98.26	96.68	99.51	99.67
5	96.95	95.38	99.62	100.02
6	97.36	96.00	99.93	99.49
average	97.70	96.70	99.03	99.56
overall average	98.25			
standard deviation	±1.29			

2.4 Retention efficiency

Six sampling tubes were each spiked with 598.22 µg (10.0 ppm or 59.82 mg/m³) of n-butyl lactate, allowed to equilibrate for 24 hours at room temperature, and then 10 L humid air (80% RH at 21°C) was drawn through each tube at 0.2 Lpm. They were opened, desorbed, and analyzed by GC-FID. The retention efficiency averaged 100.16%. There was no n-butyl lactate found on the back section of the tubes.

Table 2.4
Retention Efficiency of n-Butyl Lactate

Tube #	% Recovered		
	Front section	Back section	Total
1	100.54	0	100.54
2	98.85	0	98.85
3	100.56	0	100.56
4	100.02	0	100.02
5	100.79	0	100.79
6	100.22	0	100.22
		average	100.16

2.5 Sample storage

The adsorbing sections of twelve sampling tubes were each spiked with 299.1 µg (10.0 ppm or 29.9 mg/m³) of n-butyl lactate. They were sealed and stored at room temperature. The next day 10 L of humid air (80% RH at 21°C) was drawn through each tube at 0.2 L/min. Half of the tubes were stored in a drawer at ambient temperature and the other half were stored in a refrigerator at 0°C. After 7 days of storage three samples from the tubes stored under refrigeration and three samples from ambient storage were analyzed. The remaining samples were analyzed after 15 days of storage. The amounts recovered, which are not corrected for desorption efficiency, indicate that the samples should be refrigerated. The samples stored in a refrigerator had an average recovery of 94.5%.

Table 2.5
Storage Test for n-Butyl Lactate

Ambient Storage		Refrigerator Storage	
Time (days)	% Recovery	Time (days)	% Recovery
7	80.9	7	94.5
7	79.4	7	96.2
7	81.1	7	95.5
15	73.4	15	92.6
15	76.5	15	94.9
15	73.6	15	93.2
average	77.5	average	94.5

2.6 Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 10 L air samples should be collected at a sampling rate of 0.2 L/min.

2.7 Interferences (sampling)

2.7.1 It is not known if any compounds will severely interfere with the collection of n-butyl lactate on coconut shell charcoal tubes. In general, the presence of other contaminant vapors in the air will reduce the capacity of the charcoal tube to collect n-butyl lactate.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precautions (sampling)

2.8.1 Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2 Follow all safety practices that apply to the work area being sampled.

2.8.3 Wear eye protection when breaking the ends of the glass sampling tubes.

3. Analytical Procedure

3.1 Apparatus

3.1.1 The instrument used in this study was a gas chromatograph equipped with a flame ionization detector, specifically a Hewlett Packard (HP), model 5890.

3.1.2 A GC column capable of separating the analyte from any interferences. The column used in this study was a 60-m x 0.32-mm i.d. Rtx-volatiles, 1.5 µ film thickness.

3.1.3 An electronic integrator or some suitable method of measuring peak areas.

3.1.4 Two milliliter vials with Teflon-lined caps.

3.1.5 A 10 µL syringe or other convenient size for sample injection.

3.1.6 Pipets for dispensing the desorbing solution. A 1 mL dispenser was used in this study.

3.1.7 Volumetric flasks - 5 or 10 mL and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 GC grade nitrogen, hydrogen, and air.

3.2.2 n-Butyl lactate, Reagent grade

3.2.3 Methylene chloride, Reagent grade

3.2.4 Methanol, Reagent grade

3.2.5 n-Heptanol, Reagent grade (internal standard)

3.2.6 Desorbing solution was 95/5 (v/v) methylene chloride/methanol with 0.25 µL/mL n-heptanol internal standard.

3.3 Standard preparation

3.3.1 At least two separate stock standards are prepared by diluting a known quantity of n-butyl lactate with the desorbing solution. The concentration of these stock standards was 299.1 µg/mL.

3.3.2 A third standard at a higher concentration, 1196.4 µg/mL, was prepared to check the linearity of the calibration. Dilutions of the stock standards were made with the desorbing solution to obtain lower working range standards.

3.4 Sample preparation

3.4.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2 mL vials.

3.4.2 Each section is desorbed with 1 mL of the desorbing solution.

3.4.3 The vials are sealed immediately and allowed to desorb for 60 minutes with intermittent shaking.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

Injection size: 1 µL

Flow rates (mL/min)		Temperatures (°C)	
Nitrogen (make-up):	30	Injector:	200
Hydrogen(carrier):	3.0	Detector:	225
Hydrogen(detector):	30	Column:	50-170 at 10°C/min
Air:	400		

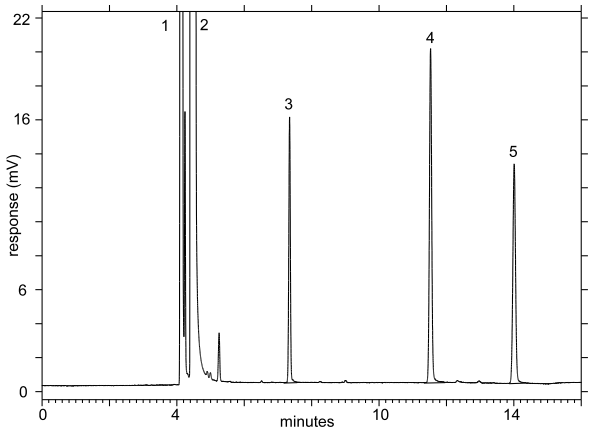


Figure 3.5.1 A chromatogram of the target concentration, where the peaks are identified as follows: 1=methanol, 2=methylene chloride, 3=ethyl lactate, 4=n-heptanol, and 5=butyl lactate.

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound that produces a response and has a similar retention time as the analyte is a potential interference. If any potential interferences were reported, they should be considered before samples are desorbed. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed by a GC-mass spectrometer or by another analytical procedure.

3.7 Calculations

3.7.1 The instrument was calibrated with a standard of 299.1 µg/mL n-butyl lactate in the desorbing solution. The linearity of the calibration was checked with a standard of 1196.4 µg/mL n-butyl lactate in the desorbing solution.

3.7.2 If the calibration is non-linear, two or more standard at different concentrations must be analyzed, bracketing the samples, so a calibration curve can be plotted and sample values obtained.

3.7.3 To calculate the concentration of analyte in the air sample the following formulas are used:

$$\text{mass of analyte in sample} = \frac{(\text{mg/mL})(\text{desorption volume})}{\text{desorption efficiency}}$$

$$\text{number of moles of analyte} = \frac{\text{mass of analyte in sample}}{\text{molecular weigth}}$$

Volume the analyte will occupy at 25 °C and 760 mmHg is number of moles of analyte times the molar volume at 25 °C and 760 mmHg.

$$\text{ppm} = \frac{(\text{volume analyte occupies})(10^6)}{\text{air volume}}$$

3.7.4 The above equations can be consolidated to the following formula.

$$\text{ppm} = \frac{(\text{mg/mL})(\text{DV})(24.46)(10^6)(\text{g})(\text{mg})}{(10\ \text{L})(\text{DE})(\text{MW})(1000\ \text{mg})(1000\ \text{mg})}$$

µg/mL = concentration of analyte in sample or standard
24.46 = molar volume (liters/mole) at 25 °C and 760 mmHg
MW = molecular weight (g/mole)
DV = desorption volume
10 L = 10 liter air sample
DE = desorption efficiency
* All units must cancel.

3.7.5 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and inhalation of all chemicals.

3.8.2 Wear safety glasses, gloves and a lab coat at all times while in the laboratory areas.

4. Recommendations for Further Study

Collection studies need to be performed.

5. References

5.1 Sax, N., "Dangerous Properties of Industrial Materials", Eighth Edition, Van Nostrand Reinhold Co., New York, 1992, p. 622.

5.2 Lewis, R., "Hawley's Condensed Chemical Dictionary", Twelfth Edition, Van Nostrand Reinhold Co., New York, 1993, p. 187.

5.3 Sweet, D., "Registry of Toxic Effects of Chemical Substances", 1985-86 Edition, U.S. Department of Health and Human Services, Public Health Service, Center for Disease Control, NIOSH, 1987, Vol. 3A, p. 3023.