# BUTYL ACETATE VAPOR DETECTION METHODS

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Polar Ice Coring Office

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## INTRODUCTION

The modern work place requires the monitoring of potentially dangerous fumes for the prevention of deleterious health effects as well as for fire or explosion. For this purpose, numerous methods exist to monitor specific or general classes of pollutants. Factors to consider in the choice of the method of analysis include: cost, accuracy (required as well as achievable) and the ambient conditions of the work place (temperature, altitude). Normally the latter can be neglected, but in the case of high altitude glaciers, they cannot be ignored.

Butyl acetate vapors in the work place are permissible at an average concentration of 150 ppm (v) (710 mg $m^{-3}$) for the entire normal 7-hour-contact work day period (e.g., Sax and Lewis, 1989). However, it is desirable that the airborne burden of butyl acetate vapors be kept well below the 50 ppm level (a purely arbitrary value).

We offer three points of information. First, while 150 ppm is the routine legal standard, periodic concentrations of 200 ppm for 20 minutes each are also permissible, provided the work day average does not exceed 150 ppm. Second, butyl acetate vapors are not considered to be truly dangerous for a few minutes exposure until the concentration reaches 10,000 ppm (OSHA/NIOSH). That is also approaching the lower flame limit. At temperatures of 0°C, it is physically impossible for the partial pressure of butyl acetate to exceed 4340 ppm; ca. 1050 ppm at -20°C (Gosink *et al.*, 1990). Third, the only place that butyl acetate vapors pose a potential fire hazard in heated areas is in closets where solvent wetted protective clothing is stored. Warm areas heavily impacted by butyl acetate should be kept below 10°C, and under no circumstances be allowed to go over 15°C (59°F) (Gosink, Kelley and Koci, 1990).

The following is an absurd but true fact to emphasize the point that, in even nominally ventilated areas, the concentration of butyl acetate will not become a problem in a cold environment. Given no blower fans and only four air exchanges an hour in a 52 ft (15.8 m) diameter drill dome with open doors and top, it would be necessary for nearly 3 liters of butyl acetate to evaporate in an hour (normal boiling point 126°C) in order for the vapor concentration in the dome to reach 150 ppm.

In order to achieve safety goals, it is not necessary that the monitoring device provide information accurate to ±1 or 2 ppm. It is desirable that the system be reliable at ±10% of the reading at higher levels, and at lower concentrations (≤50 ppm), even ±20% data would be usable and acceptable. Fume concentrations in the drill dome and science trench are expected to be highly variable, for seconds to minutes, but well within the legal limits. One or two routine inspections per shift in all impacted work areas, plus investigation of any suspicious concentrations, should be more than adequate.

## Criteria

The criteria for butyl acetate vapor detector(s) are: (a) reliable detection at or below the 50 ppm(v) concentration level, (b) the ability to function at -20°C (and colder) and (c) provide meaningful data at 3300 m altitude. (Past records indicate an average pressure at Summit, Greenland, to be ca. 507 mm Hg; 678 mb. Temperature varies from about -30 to 0°C, with the science snow trench being more temperature stable near -20°C.) It is desirable, but not mandated, that fumes from generator exhaust (diesel) not cause unsurmountable interference and that the method provide some concentration information over the ca. 25 to 400+ ppm range.

## Calibration

No matter what monitoring method is employed, certified calibration gas will be required. Reliable suppliers (e.g., Scott Specialty Gas Co.) can provide them for about $300 per cylinder, certified to ±2% of the reported value. Two or three cylinders each of several concentrations will be required per field season. Two butyl acetate vapor standards should be available in the normal operational range of 30 to 60 ppm. The balance of the gas in the cylinder should be zero-air.

*Note Well. The calibration must take place in a warm (≥ 60°F) environment. The trace fumes in the standard gas cylinders will condense on the cylinder walls at cool (≤50F°) temperatures, causing a major calibration error.*

*Note Well. Recalibration or calculation corrections for pressure altitude will be required. At Summit, Greenland, the calculation essentially amounts to increasing the reading by 30% (if not compensated for by proper recalibration).*

## RESULTS

In this report we consider the suitability and reliability of three routine methods for the analysis of butyl acetate fumes: (1) a photoionization detector, (2) several versions of gas leak detectors, and (3) gas reaction tubes. All of these methods assume that known interferants (e.g., engine exhaust) are not present in significant quantity.

### Photoionization Detector

One modern gas monitoring method is the photoionization meter. An air sample is continuously drawn into a chamber where it is subjected to ultraviolet radiation. The radiation is strong enough to ionize molecules with an ionization potential of 10.2 eV or less, such as butyl acetate. A charged plate in the chamber collects the ionized particles, and the resulting current is displayed in ppm concentration units, based on a known gas calibration standard.

We have considered the merits of model HW101 from the Massachusetts based manufacturer, HNU Systems, Inc., which offers numerical data over a wide range of vapor concentration (1 to 2000 ppm). Purchase price for the system was $5960. It is billed as a portable hazardous waste analyzer. This is a misnomer since it does not analyze the vapor, but only indicates the presence of ionizable organic vapor. Linearity is not perfect, but usable. Stability between daily calibration also was not perfect, but still usable for our purposes. The zero setting drifted several ppm, and the span setting varied by 10-20% (ca. 10-15 ppm). Significant span control changes have been routinely observed between uses, and the device is sensitive to freezing temperatures. The instrument gave readings ca. 50% high in the 20 ppm range when calibrated with the 140 ppm butyl acetate calibration span gas.

*Note Well. Routine application of this type of device for flammable gases uses a butene standard to set the span control. In the case of butyl acetate, this would lead to serious calibration error.* The span settings between butene and butyl acetate differ by a factor of nearly 20, which would cause the reading butyl acetate to be several hundred percent low. The meter must be calibrated with butyl acetate standards.

The radiation chamber is normally unaffected by pressure changes, which operates at 775±30 mb. However, Summit, Greenland average pressures are 678 mb. This serious problem can be rectified by recalibration at the work site. Instead of directly connecting the HNU probe to the hose nipple of the low flow regulator on the calibration gas supply cylinder, the standard is connected to the luer connection of a 10-ml syringe, and the HNU probe inserted into the barrel of the syringe. Given a flow of ca. 300 cc/min, this will insure that there is a small overflow of calibration gas, and the detector will only collect enough gas to compensate for the altitude.

The zeroing operation consists of drawing the air sample through a tube of activated charcoal. Nearly one minute of continuous sampling is required to obtain an accurate reading. (The system must be in the standby or ON mode for 5 minutes before any use, zeroing or calibration.)

The system was unstable in cold temperatures, part of which can be ascribed to the problem described earlier in the calibration section. The manufacturer specifies

0°C as the lower operational temperature limit. A battery heated insulated sock over the main body of the probe was investigated in an effort to overcome its temperature sensitivity. The main pack was also placed in an insulated jacket for extra protection. The inside of the sock covering the probe remained at 25°C over a 15 min test period in -20°C air temperature, and the system was found to be accurate after one hour at -24°C. (A pair of "mini-mini" mycoal pocket warmers stay very warm for seven hours, and can be added to the main pack and to the battery compartments to prolong life in a particularly cold environment. Retail cost $1.59. Manufacturer is: Mycoal Warmers Co., Ltd., Japan. Distributed by Grabber, 205 Mason Circle, Concord, California.)

If it is deemed necessary, the photoionization detector probably can provide some continuous monitoring data. (The life of the lamp is variable, from as little as 200 to as much as 1000 hours, and is the limiting factor.) To monitor continuously it will be necessary to mount the entire device inside the heated drill operators room. An extension tube of teflon (up to 10 m) can be mounted through the wall of the drill operators shed into the drill dome. (Aluminum or stainless tubing will cause the reading to be low by 30% or more.) The direction of the ventilation drafts will greatly affect the readings.

All things considered, this is the best system we have seen. It functions with acceptable accuracy and numerical readout over a range of 1 to 2,000 ppm.

See appendix for specifics for calibration and operation.

## Gas Leak Detector

Several gas leak detectors are available on the market. Most employ platinum or palladium doped tin oxide on a heated screen which changes in electrical conductivity when ppm concentrations of flammable gases in air pass through the screen. The technology has been common for several decades, has been used in some fire detectors, and even in small, inexpensive, dedicated field gas chromatographs.

See appendix for calibration and operation of these devices.

Version One

A battery-operated (2 D cells) flashlight sized device is manufactured by the California based Sierra Monitoring Corporation, and retails for $345. In the warm laboratory with the sensitivity level control increased, the proportional counter will begin to give a series of audible clicks when the concentration of butyl acetate vapors exceeds ca. 30 ppm. The sound becomes rapid at about 50 ppm. An alarm level can be preset so that the device is silent until the 50 ppm level is exceeded, at which the siren goes off. A ten-fold second alarm is triggered only if the concentration level reaches 500 ppm. These concentration levels are very rough (± ca. 30%), but quite usable.

This device is rated to operate at -5°C and was found to be operational at lower temperatures. If the device is placed in a cold room at -20°C for an hour, it fails to turn on. (Probably a battery rather than a detector problem.) However, if turned on inside a warm area, the battery compartment kept warm by the operators gloved hand, or kept under his or her parka, the device was observed to function at -30°C during a 15-minute test period. The accuracy at -10 to -15°C temperatures was investigated. At -10°C, after one-half hour in the cold while switched on, both the proportional and alarm 1 features of the device still operated. At -15°C the ALARM 1 level failed after 10 minutes, but could be restored by just a short exhaled breath onto the detector. Changes in humidity noticeably affect the sensitivity of the device. Moderate humidity increases its sensitivity. (In the work spaces on glaciers, the humidity will be constant and low.) Nevertheless, the proportional function continued to operate, but at a noticeably slower rate after fifteen minutes. The battery portion of the device was kept under the investigator's parka, but the detector nose-piece was thoroughly exposed to the -15°C outside air.

Another important factor is the quality of the batteries. It seems that only the Duracell brand offers the best performance. In the lab, one pair of new batteries lasts for 6 or 7 hours of continuous operation. In the cold, this drops to about 1 or 2 hours. Rechargeable Ni-Cad batteries offer less operational time. However, considering that only brief periodic monitoring is required, and that the device is easily carried under the operator's parka, a pair of batteries should last at least one work day. Rechargeable batteries should be replaced once or twice a day. Calibration is achieved by placing the sensor nose piece into a funnel (folded aluminum foil) connected to the appropriate gas standard. Sensitivity and alarm level turn-pot screws are located under the main switch. Counter-clockwise increases sensitivity (left pot) and lowers the ALARM 1 level setting (right pot).

Version Two

There is an AC-powered version of the same detector (converted to 9v DC) which is specified to operate at -20°C. The cost is $320 for the monitor, which will handle two detectors ($290 each) up to 1500 ft away. This version only offers the ALARM 1 level, which can be set to ca. 50 ppm. Calibration consists of introducing a stream of calibration gas from a teflon bag of standard. A pair of lights in the sensor compartment (and at the monitor in the driller's hut) indicates the status of the sensor. A turn pot in the sensor compartment adjusts the sensitivity of the detector. The systems can be coupled to a long term readout.

There is yet another fully-automatic version offered by Sierra Monitoring Corporation, which was considered last year but was declined because of the lack of reliability at the 50 ppm level and the high cost (ca. $11,000 for the complete system, including a data logging system.)

Gas Reaction Tubes

Gas reaction tubes have long been utilized in the industrial environment to monitor a wide variety of pollutants. The various available chemical packing in the tubes are reasonably specific for the gas in question. A fatal problem is that this particular color reaction tube is highly temperature dependent. Errors of 200-400% (low) will occur if the tube is not maintained near 15 to 20°C during the entire sampling period. (Reaction tubes for other gases have temperature errors of 0-20%.) Batch quality control problems from the production of the tubes was also observed. There are, in addition, several inherent method weaknesses that can be exacerbated by an inexperienced technician. Given all of these problems and caveats, this method cannot be recommended.

Recommendations

One pair of the AC-operated gas leak detectors should be mounted in the science trench, with the monitor in the driller's shed. Another pair should be mounted in the drill dome, with the monitor in the driller's shed. Total cost would be less than $2000, and both pairs can be monitored by a simple computer readout.

The hand-held, battery-operated gas leak detector can be used to supplement the stationary detectors by carrying them into side rooms in the science trench, low areas or poorly ventilated areas when the need arises. For the price, 15 gas leak detectors can be obtained for the cost of one photoionization system. While it does not provide numerical data, only a concentration range or minimum, it is compatible with the needs of this operation. It should be stored warm when not in use and batteries replaced daily.

The photoionization detector can be utilized to obtain more detailed information when required and if deemed necessary provide some continuous data on the air in the drill dome. It also can be periodically monitored by the same computer readout mentioned above.

## REFERENCES

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# APPENDIX

## PICO Vapor Detector Procedures
## Calibration and Operation

The following pages contain the procedures to be employed in daily maintenance, periodic calibration, and routine operation of three butyl acetate vapor detectors at the GISP drill site at Summit, Greenland.

The three devices are:

1. the portable HNU vapor detector,
2. the portable Sierra leak detector, and
3. the permanently mounted Sierra gas leak detector system.

The calibration methods described herein compensate for the considerable altitude correction factor.

These calibration and operation procedures also allow for the consequential effects of low temperature.

## HNU Vapor Monitor

### Nightly Routine

The device is to be stored overnight in the OFF position with the battery charger engaged. The wall plug is to be inserted into the 115 v.a.c. wall outlet *after* the battery charger connection is made, and unplugged *before* the battery charger is disconnected. In the event of prolonged continuous usage (>2 hrs in the cold), the battery charger should be re-engaged during the operational day. The system can be simultaneously operated, and the battery recharged.

The four rechargeable D-cells in the side pocket of the insulating jacket (auxillary heat) are to be removed and placed in their recharging unit overnight. They should be exchanged in the event of prolonged usage (2 hours) in the cold.

### Calibration

Assuming reasonable past performance by the system (drift less than 10%, and not in the same direction), this need not be a daily procedure. It should, nevertheless, be carried out every 2 or 3 days.

Turn the system on as described below as if preparing for full operation. (It is not necessary to turn on the auxiliary heat.)

Attach the probe to a tube of activated charcoal. After 1 minute, adjust the meter to zero with the ZERO setting knob. (Replace the charcoal every few days, making *sure* that *no* charcoal dust gets past the filter to contaminate the probe.)

Detach the charcoal tube and place the probe deep within the oversize delivery tube from the standard. Turn on the standard and wait at least 1 minute before adjusting the SPAN control so that the meter reads the same as the standard value.

*NOTE: This is not the same procedure as found in the manufacturer's manual. This modified method corrects for the altitude of the operation.*

*NOTE: The calibration <u>must</u> take place in a warm (>55F) shelter, and the standard gas cylinder <u>must</u> also be warm. A cylinder stored at floor level could be 10 to 30° F cooler than bench level. The standard gas cylinder and content pose absolutely no hazard.*

Turn OFF the standard gas supply.

A log (and plot) should be kept of the zero and span settings so that drift can be monitored and possible malfunction spotted before the problem becomes serious.

Operation

After calibration, the auxiliary heat for the probe is to be turned on several minutes before taking the device out into a cold area. This is accomplished by connecting the wire junction inside the side pouch holding the 4 D cells. (The auxiliary heat supplied by the 4 D cells is to be turned off -- disconnect the wire junction -- while the device is not in use. Replace the 4 D cells as described in the second paragraph of "Nightly Routine.") DO NOT leave the auxiliary heat on the drillers' hut for more than ca.-15 minutes.

If the system is not already ON, turn the main switch to STANDBY (pump should be audible).

Continue turning the main switch to BATTERY and observe that the needle is in the green region.

Continue turning the main switch to the appropriate range setting (usually 200 ppm full scale).

The system is now ready to carry out into the cold areas for operation. Allow a <u>full minute</u> of sampling in the test area before accepting the reading.

*NOTE: A wavering or drifting reading may very well reflect the transient ambient conditions rather than equipment malfunction.*

Log and plot the data.

Upon return to the heated storage area either:

1. turn the system OFF if it is not to be used in the next hour, or
2. turn to standby.

Disconnect the auxiliary heat D cells. (If the usage was prolonged, [>2h] recharge the batteries as described in the "Nightly routine" section.)

Other

Follow the manufacturer's instructions if repairs such as battery or lamp replacement are required. A spare battery and several lamps and other parts are available as well as a cell window cleaning kit.

## Portable Leak Detector

Each Shift

Replace the two rechargeable D cells. Place the used pair in the recharging unit. (Recharge the batteries after 1 or 2 hours of use.)

The system must be stored in a warm (>40°F) area.

Calibration Check

Turn the system on as described below.

Place the probe end into an aluminum foil cone on the delivery tube of the 50 ppm standard.

Observe the rapid audible clicking rate when the switch is in the PROPORTIONAL position and the siren in the ALARM 1 position.

If the system fails:

1. Exhale 1 breath on the detector (it should respond), then recheck the calibration.
2. Exchange the batteries. Only then change the sensitivity or alarm level as described below.

## Operation

Turn the system ON and wait about a minute. Note that the alarm will come on after a few seconds, persist for about 30 - 40 seconds, and then decrease in volume and clicks until it is silent. The system is now ready to use.

Carry the system under your coat when not in actual use. With the switch in the PROPORTIONAL setting, wave the device in the test area for a few seconds. Silence means the concentration is below about 30 ppm; audible clicks indicate a concentration above 30 ppm, but below the alarm level; a persistent siren alarm with the switch in the ALARM 1 mode indicates that the vapor concentration is above the alarm 1 setting of ca. 50 ppm. (ALARM 2 is always automatically 10 times that of ALARM 1.)

*NOTE: Other exhaust fumes or flammable chemicals will also set off the detector.*

Turn the device OFF after the inspection tour is made. Return the device to a warm area for storage. Replace and recharge the batteries if required.

## Other

If it is necessary to change the sensitivity or alarm level settings, a jewelers screw driver and a small allen wrench are required (as well as a gas standard).

Turn the system to the ALARM 1 position. Remove the switch knob with the two allen screws. Observe the 2 screw driver operated turn pots. Counterclockwise increases the sensitivity, or lowers the alarm level setting. The turn pot on the left is the sensitivity; alarm level is on the right. Given that the sensitivity is already near maximum, you will probably only have to manipulate the right turn pot (ALARM 1 level).

## Permanently Mounted Leak Detector

### General

This system is ON continuously as long as there is 110 v.a.c. power. The sensitivity and alarm level has been preset to ca. 50 ppm of butyl acetate. Its function is to alert personnel that the fume concentrations are rising. An alarm by this device does not indicate dangerous concentrations of fumes. It means that a check needs to be made with either the HNU or portable gas leak detectors. It could also mean a transient due to the presence of engine exhaust, or any number of other temporary pollutants.

### Operational check

Nearly fill the teflon bag with 50 ppm standard, and carry it to the detectors. (The hose nipple rotates to open or close the nipple. Do not use bagged gas samples after ca. 20 min. There is some loss in the bag.) Unscrew the detector housing cover and observe the small red and green lights (Green=OK; Red=alarm). (The active part of the detector is outside the electronics cylinder - in the lower extention.) Hold the teflon bag with bare hands and slowly squeeze out the contents over the partially covered detector for at least 30 seconds. (Use the back of your fingers to prevent excessive loss of vapors around the detector.) If the red light does not come on after about 30 seconds, the sensitivity needs to be increased (counterclockwise). If the red light does not return to green after 60 seconds (with the detector fully uncovered and open to air circulation), the sensitivity should be decreased slightly. (A small turn pot in the detector assembly controls the sensitivity. Counterclockwise = more sensitive.)

### Other

Follow the manufacturer's instruction for any repairs or modifications.