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Detector Tubes for MITC Measurements
The Pesticide Stewardship Alliance Conference

Albuquerque, NM
February 24, 2009

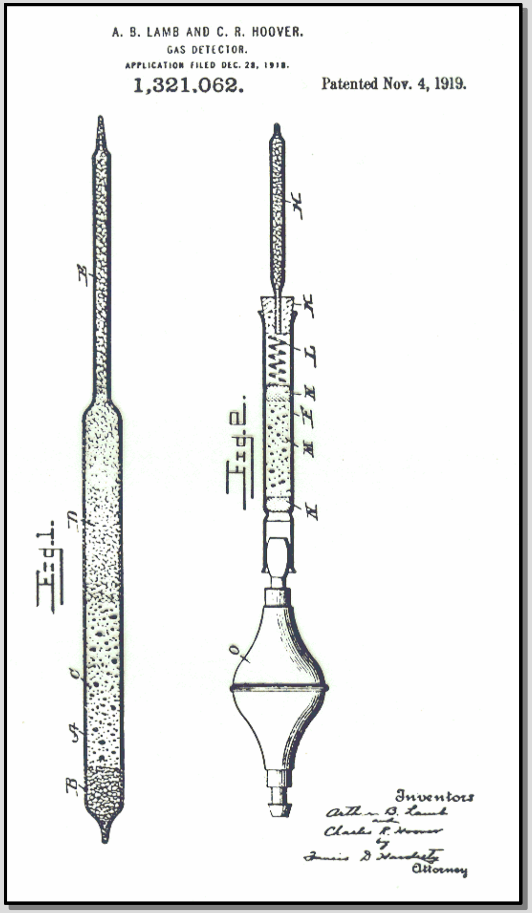
MITC Measurements with Detector Tubes

What is a Detector Tube?

"A detector tube is a hermetically sealed glass tube containing an inert solid or granular material such as silica gel, alumina, resin, pumice, or ground glass. The inert material is impregnated with or mixed with one or more reagents which change color when specific types of air contaminants are introduced. The length of the color change or stain, or the intensity of color change as compared to a comparative standard indicates the amount of material present."

Source: Air Monitoring Instrumentation, C. J. Maslansky/S. P. Maslansky

MITC Measurements with Detector Tubes
The First Detector Tube



- The first detector tube patent appeared in the United States in 1919.
- Two Americans, Lamb and Hoover, impregnated pumice with a mixture of iodine pentoxide and sulfuric acid. They filled this mixture (named “Hoolamite”) into a glass tube.
- In contact with carbon monoxide the impregnated pumice discoloured from white to a shade of green.
- Though this first detector tube was only a qualitative test, it nevertheless was the first chemical sensor to detect carbon monoxide.
- The basic principle of a detector tube was born.

MITC Measurements with Detector Tubes

Advantages of Detector Tubes

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- Inexpensive
- Portable and simple to use
- No calibration
- Wide variety of gases & vapors
  - Quantify over 500 gases and vapors
- 2-year shelf life
  - Storage at room temperature - 77° F
- Quality control by batch

MITC Measurements with Detector Tubes
When to Use Tubes

To identify a gas concentration at a specific time & location

To screen a known or unknown atmosphere to determine exposure potential

To determine the type of gas or vapor and relative concentration present at a hazardous material release

To take appropriate measures for personal protection

All of these situations could be applicable to the measurement of MITC in the field

MITC Measurements with Detector Tubes

The Dräger-Tube®

Hermetically-sealed glass tube housing

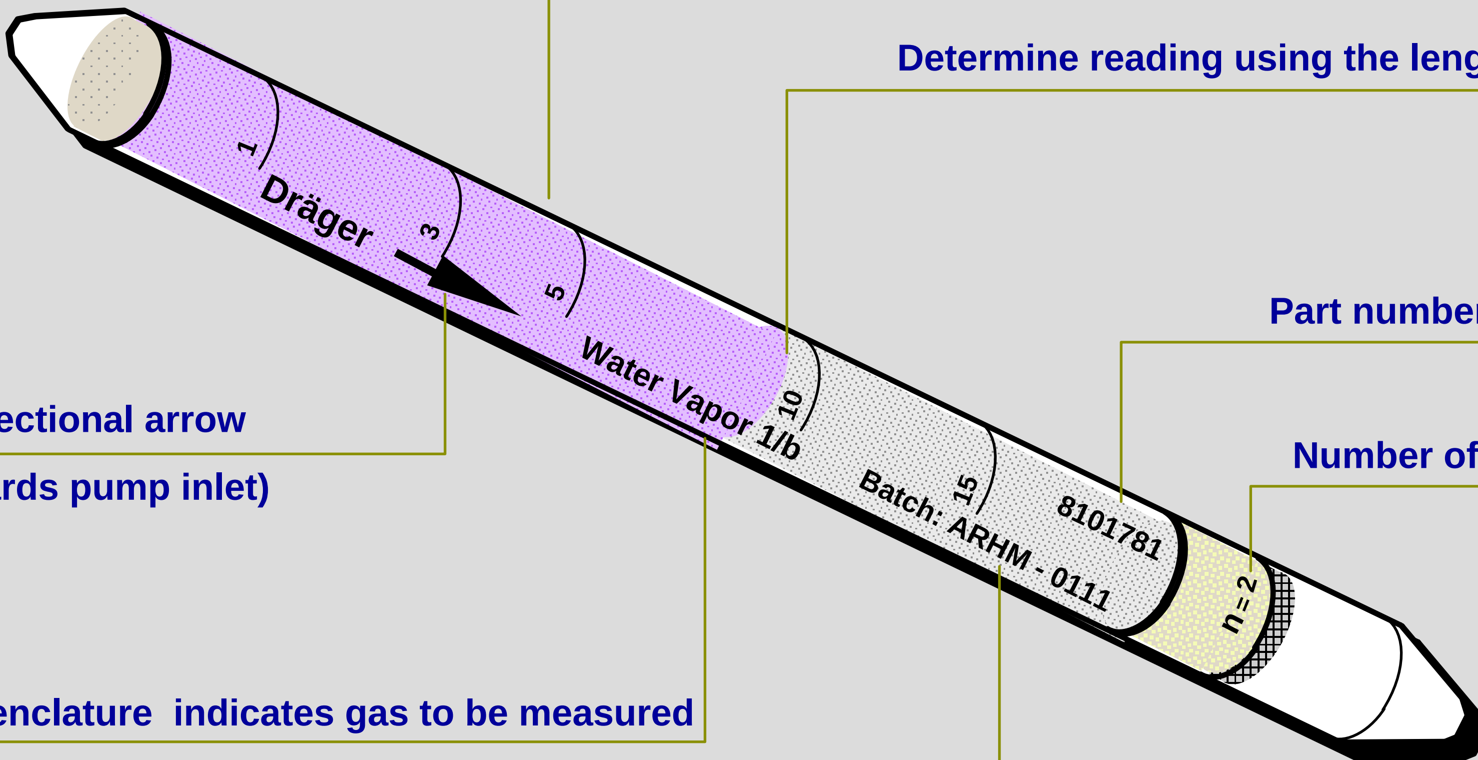
Determine reading using the length of color stain

Part number

Number of pump strokes

Airflow directional arrow

(Aim towards pump inlet)



Tube nomenclature indicates gas to be measured

Quality control batch number

MITC Measurements with Detector Tubes

The Dräger accuro® Pump

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Quality control batch number

End of stroke indicator

Pump stroke counter

Airflow directional arrow

(Facing pump inlet)

Ceramic tube opener

Scissors & spring mechanisms provides uniform pump stroke

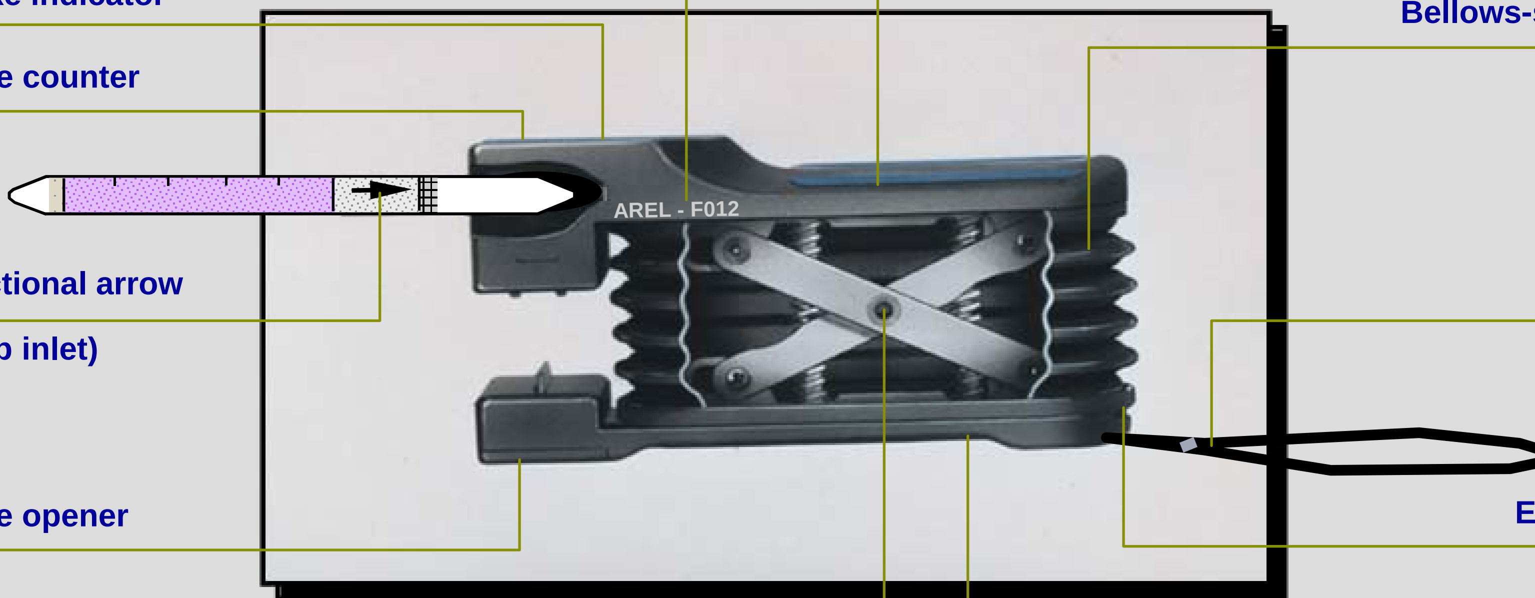
Durable EPDM rubber housing

Bellows-style pump

Wrist strap

Exhaust port

Allen screw for pump maintenance



As of 1st of January 2005 the use of **Methyl Bromide** was limited as specified by the Montreal Protocol.

The **Montreal Protocol on Substances That Deplete the Ozone Layer** is an international treaty designed to protect the ozone layer by phasing out the production of a number of substances believed to be responsible for ozone depletion. Participants of 86 countries and the Commission of the European Community signed this document.

Methylisothiocyanate (MITC) is one substitute used instead of Methyl Bromide for fumigation purposes.

MITC Measurements with Detector Tubes

Dräger-Tubes for Fumigating Agents

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Chloropicrin

1,3-Dichloropropene

Ethylene Oxide

Ethyl Formate

Formaldehyde

Hydrocyanic Acid

Methyl Bromide

Methylisothiocyanate

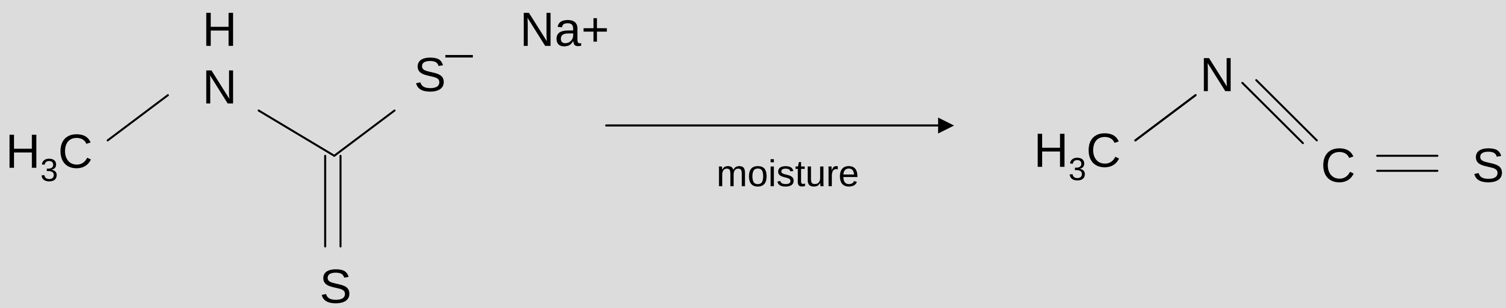
Phosgene

Phosphine

Sulfuryl Fluoride

Simultaneous Test Sets

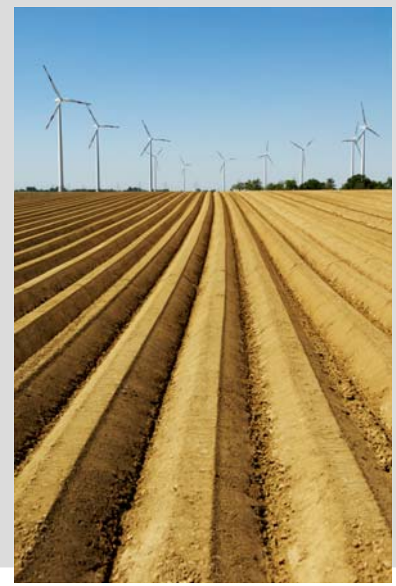
MITC Measurements with Detector Tubes
MITC Generation



Metam-sodium

Methylisothiocyanate

Metam-sodium is applied to fields by various methods and generates methylisothiocyanate gas upon reaction with moisture/water. The MITC gas is what is detected by the detector tube via a colorimetric chemical reaction.



MITC Measurements with Detector Tubes

MITC Exposure

“Based on monitoring data, it is clear that bystander exposures to concentrations of MITC in air after a metam-sodium/potassium application are possible. Therefore, the focus in assessing inhalation bystander and occupational exposures resulting from metam-sodium/potassium applications is on concentrations of MITC.”

Re-registration Eligibility Decision (RED) for Methyldithiocarbamate Salts (Metam-Sodium, Metam-Postassium) and Methyl Isothiocyanate (MITC). USEPA, 7/08, page 16

MITC Measurements with Detector Tubes
Toxicological Effects

“Metam-sodium and metam-potassium are broad spectrum fumigants with fungicidal, herbicidal, insecticidal, bactericidal, algaecide and nematicidal properties.” *(RED, page 14)*

Methylisothiocyanate is a lachrymator also causing burning sensation in nose, throat and lungs

Other reported exposure symptoms include headache, nausea, abdominal pain, diarrhea, weakness, chest pain, cough, wheezing and skin rash

Up to now no threshold values have been established

MITC Measurements with Detector Tubes
Monitoring Applications

- Possible monitoring applications include:
  - Exposures during fumigant application
    - ✓ Handlers/Workers/Bystanders
  - Buffer zones and areas between zones and residences (for prescribed period)
  - Leaky (loose) tarps
  - Emergency response

MITC Measurements with Detector Tubes
Target Air Concentrations

- Target air concentrations from Human Health Risks section of RED
  - 22 ppb - level of concern for acute exposure (from irritation and odor threshold study)
  - 220 ppb – no observable adverse effect level (NOAEL)
  - 800 ppb – lowest observable adverse effect level (LOAEL)

- There is currently no economically available monitoring equipment sensitive enough to show the 22 ppb level has been exceeded

MITC Measurements with Detector Tubes
Detection Technology Limits for MITC

- "Based on (1) the reversible sensitive end point selected, (2) the limited monitoring technology currently available, (3) the potentially physically stressful response to respirators, and (4) the apparent fact that the current technology allows detection at levels 8 times lower than the LOAEL of 800 ppb selected, the Agency is allowing a monitoring program for MITC to 100 ppb in place of respirators for some handler tasks."

  RED, page 53

- As of today, the Draeger Methylisothiocyanate 0.1/a detector tube is the available simple, inexpensive technology capable of attaining a100 ppb detection limit

MITC Measurements with Detector Tubes
MITC Tube Operating Parameters

Tube Details

Measuring Range:	0.2 – 6 ppm / 0.1 – 1.2 ppm
Pump Strokes (n):	6 / 20
Measuring Time:	~60 sec. / ~200 sec.
Standard Deviation:	± 10% to 15%
Color Change:	Yellow to Brownish-Grey
Order Code:	P/N# 8103485

Operating Conditions

Temperature Range:	0°C to 50°C (32° to 122°F)
Humidity Range:	< 55 mg/L*

** There will be correction factors applied at extremes of temperature and humidity*

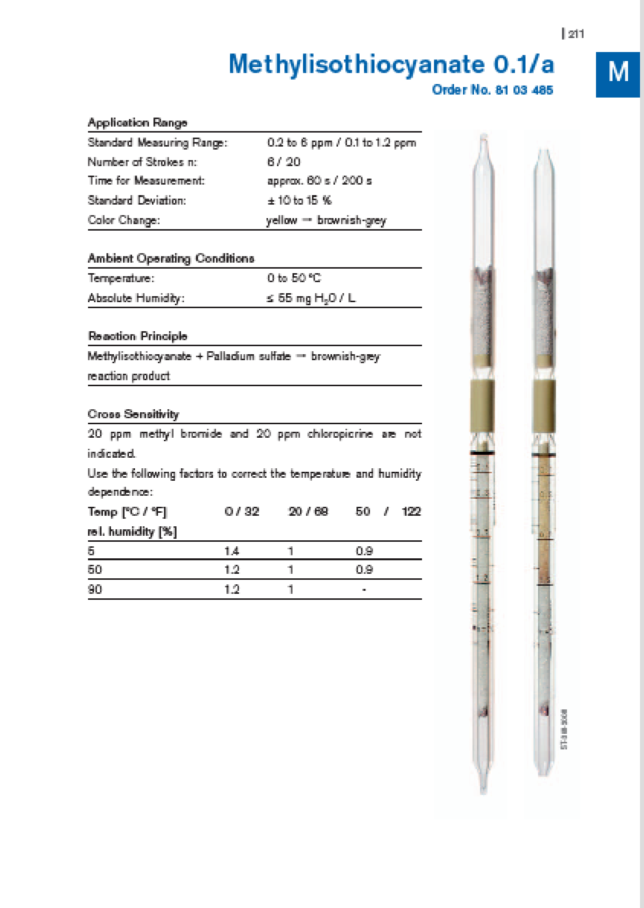
MITC Measurements with Detector Tubes
MITC Tube Reaction Chemistry

Colorimetric chemical reaction for the MITC 0.1/a is:

MITC + Palladium sulfate $\longrightarrow$

Brownish-grey reaction product

Cross sensitivity – 20 ppm of methyl bromide or 20 ppm of chloropicrin do not affect the reading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Methylisothiocyanate 0.1/a

M

Order No. 81 03 485

Application Range

Standard Measuring Range:	0.2 to 6 ppm / 0.1 to 1.2 ppm
Number of Strokes n:	6 / 20
Time for Measurement:	approx. 60 s / 200 s
Standard Deviation:	± 10 to 15 %
Color Change:	yellow → brownish-grey

Ambient Operating Conditions

Temperature:	0 to 50 °C
Absolute Humidity:	≤ 55 mg H_2O / L

Reaction Principle

Methylisothiocyanate + Palladium sulfate → brownish-grey reaction product

Cross Sensitivity

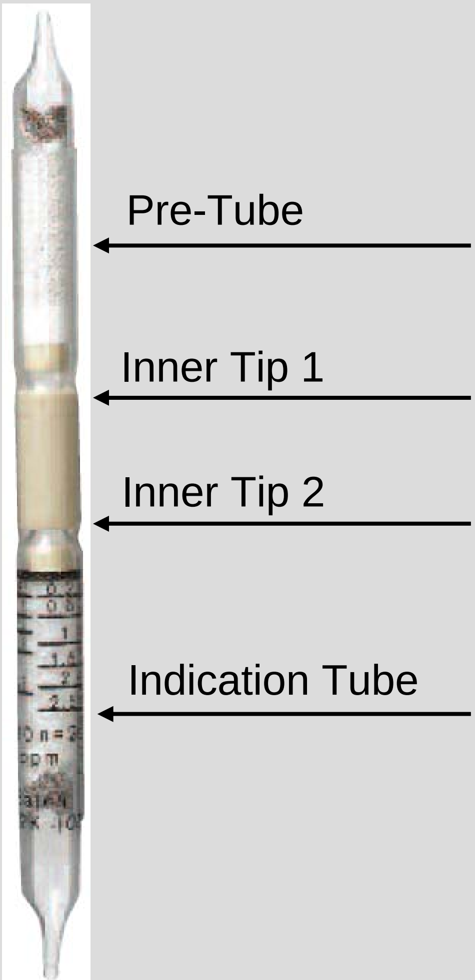
20 ppm methyl bromide and 20 ppm chloropicrine are not indicated.

Use the following factors to correct the temperature and humidity dependence:

Temp [°C / °F] rel. humidity [%]	0 / 32	20 / 68	50 / 122
5	1.4	1	0.9
50	1.2	1	0.9
90	1.2	1	-

MITC Measurements with Detector Tubes

The “Double Tube” System



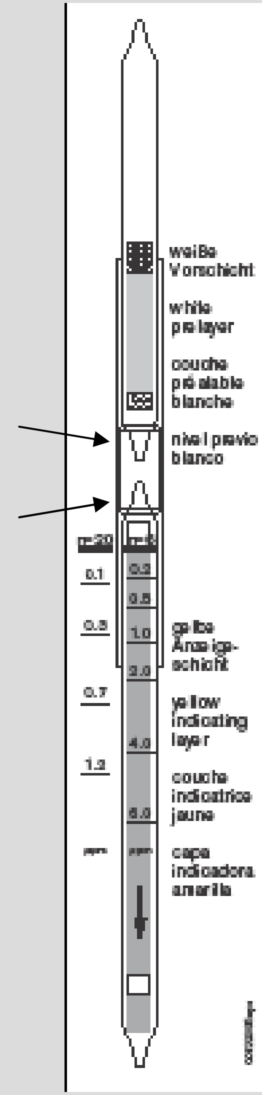
- Two tubes, a pre-tube and an indication tube, are connected with a shrink wrap tubing.
- The preparation in the pre-tube serves a purpose similar to a pre-layer of a single tube, i.e. to remove interfering substances and/or moisture
- This system is used when pre-layer material cannot be in direct contact with indicating layer material as it would interfere with the measurement chemistry
- The pre-layer tube in the MITC 0.1/a is a calcium chloride desiccant

MITC Measurements with Detector Tubes

Taking a Sample

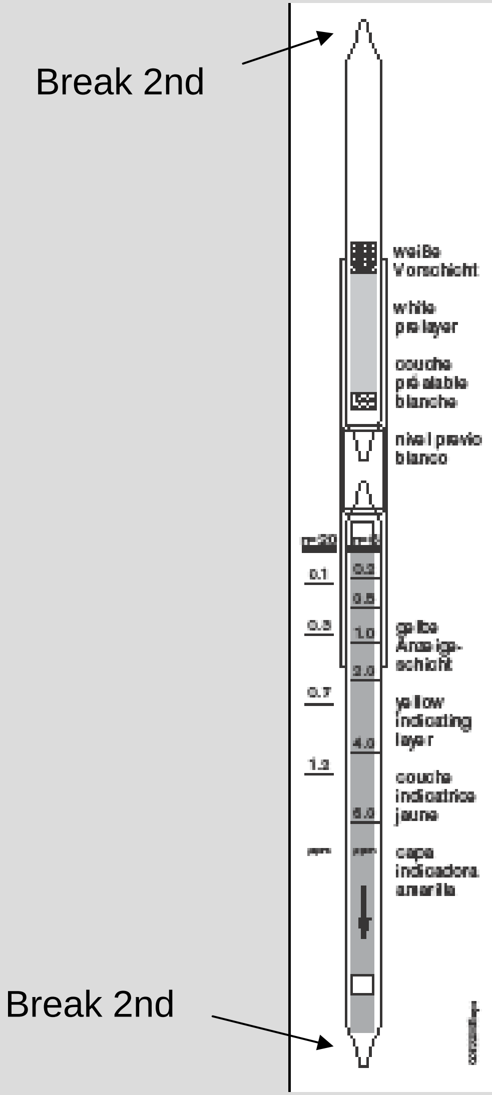
1. Break the inner tube tips covered with shrink-wrap plastic tubing by holding one end of the tube and bending the other end until the inner tip breaks off. Repeat the procedure for the second tip.

Break 1st



MITC Measurements with Detector Tubes
Taking a Sample

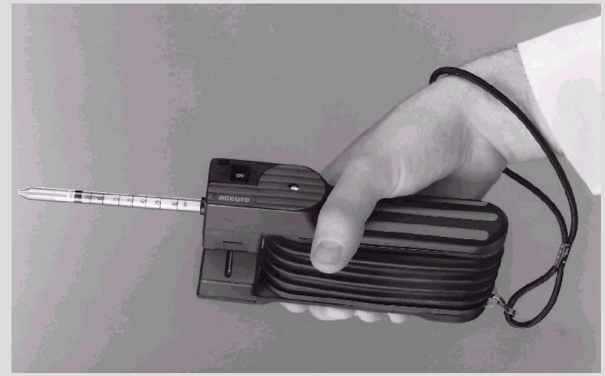
2. Break off both outer tips of the tube in the Tube Opener

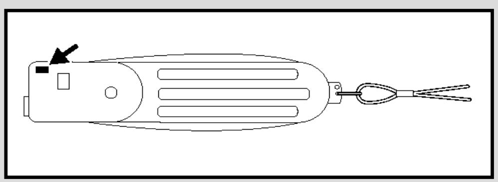


MITC Measurements with Detector Tubes
Taking a Sample

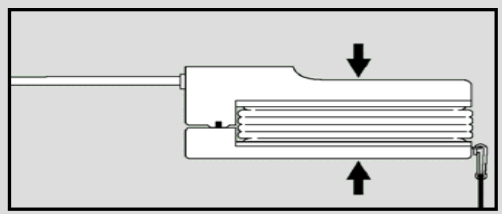
3. Insert the tube tightly in the pump. Arrow points toward the pump.

4. Suck air or gas sample through the tube with required number of complete pump strokes

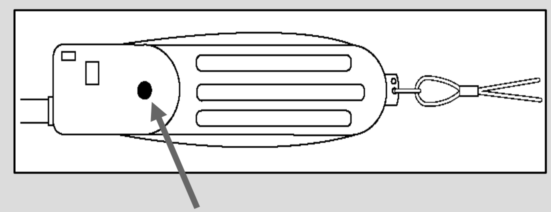




Set stroke counter to zero before starting test



Squeeze the pump until it will no longer compress (the stroke indicator will have advanced)



Allow bellows to re-expand and wait for end of stroke indicator (white dot) to re-appear before taking next stroke

MITC Measurements with Detector Tubes

Taking a Sample

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5. Read the entire length of the discoloration right after completion of the last stroke

Adequate lighting - but no direct sunlight

Hold the tube against a light background

Scale tubes:

a) full length of discoloration
(sum of all colors)

b) diffuse indication
(end point of the slightest discoloration)

Compare with an unused tube

Diagonal leading edge:
average between the shortest and longest discoloration

1.2 ppm

MITC Measurements with Detector Tubes
Correction Factors

$$\text{Concentration} = \text{Indication} \times \frac{1013 \text{ mbar}}{\text{Actual Press. (mbar)}}$$

Example: At 500 m (1640 ft.) atmospheric pressure is 950 mbar so F = 1.07

Correction Factors for the MITC 0.1/a at Various Ambient Conditions

Temperature °C/°F → % Relative Humidity ↓	0/32	20/68	50/122
5	1.4	1.0	0.9
50	1.2	1.0	0.9
90	1.2	1.0	---

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Questions?

¿Preguntas?

Questions?

Thank you for your attention

Merci beaucoup de votre attention

Grácias por su atención