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December 20, 2019
Project No. 1803.01.01

Mark Adams
Washington State Department of Ecology
Toxics Cleanup Program
3190 160th Avenue SE
Bellevue, Washington 98008

Re: Vapor Intrusion Assessment Work Plan
Precision Engineering, Inc., Seattle, Washington

Dear Mr. Adams:

Maul Foster & Alongi, Inc. (MFA) has prepared this vapor intrusion assessment work plan on behalf of its client, Dick Morgan, for the Precision Engineering, Inc. site (the Site). The Site includes the property located at 1231 S. Director Street in Seattle, Washington (the Property). The one building on the Property will be included in the assessment.

## BACKGROUND

Sub-slab soil gas and outdoor (referred to as "ambient") air investigations were conducted at the Site in 2006 and 2015. During the 2006 investigation, seven sub-slab soil gas samples, seven indoor air samples, and one ambient air sample were collected and analyzed for trichloroethene (TCE) and its breakdown products (MFA, 2006; see Figure 1). TCE was detected in sub-slab soil gas samples at concentrations of up to 37,000 micrograms per cubic meter (ug/$m^3$) and in indoor air at a maximum concentration of 0.2 ug/$m^3$. The indoor air concentration was below the Model Toxics Control Act (MTCA) Method B cleanup level of 0.37 ug/$m^3$.

During the 2015 sampling event, one sub-slab soil gas sample, one indoor air sample, and one ambient air sample were collected and analyzed for TCE and its breakdown products (Kennedy/Jenks Consultants, 2015; see Figure 1). TCE was detected at a higher concentration in the indoor air sample than in the sub-slab sample, and above the MTCA Method B cleanup level in both samples. TCE in the indoor air sample was 240 ug/$m^3$ compared to 95 ug/$m^3$ in the sub-slab soil gas sample. TCE was also detected above the MTCA Method B cleanup level in the ambient air sample at 0.96 ug/$m^3$.

A vapor intrusion assessment will be conducted to evaluate the potential for sub-slab soil gas and other sources, including current facility operations and potential background source(s), that may contribute to TCE concentrations in indoor air. The results will also be used to evaluate TCE concentrations in indoor air relative to the short-term exposure action levels

provided in the Washington State Department of Ecology's (Ecology) Implementation Memorandum No. 22 (Ecology, 2019).

## PRELIMINARY SITE VISIT

MFA conducted a preliminary site visit on November 20, 2019. The Ecology site manager, Jennifer Kann, was present. During the site visit, MFA completed the following tasks:

- Provided information to the building owner about the scope of the assessment and appropriate sampling conditions (i.e., windows and doors should be closed for several hours before and during the indoor air sampling).
- Evaluated preferential pathways and characteristics, such as foundation cracks, sumps, and utility penetrations, that could contribute to vapor intrusion.
- Characterized the building ventilation systems, including how, when, and where they operate, and what portions of the building are intermittently or continually open to outside air.
- Conducted site reconnaissance and interviewed the building owner to help identify and coordinate the removal of potential indoor sources of volatile organic compound (VOC) vapors. This reconnaissance will be conducted again immediately before sampling.
- Identified representative sub-slab soil gas, indoor air, and ambient (outdoor) air sampling locations.

Results of the site visit are summarized below.

No obvious indications of indoor sources of VOC vapors, or preferential pathways or other characteristics that could contribute to vapor intrusion, were identified during the site visit. Commercial products that may contain VOCs, including solvents, paints, and other oils, were identified; these were shelved in their original packaging. The products are for sale and are not used in the building. One small can of solvent, which appears to be used to clean machining equipment on site, was observed. The building foundation is concrete slab-on-grade; minimal cracking was observed. No floor drains, sumps, pits, or trench drains were observed. The former locations of trench drains, tanks, sumps, and pits associated with previous operations (see Figure 2) were observed to have been filled in with concrete, with the exception of two features: the evaporator pit, in which standing water was observed, and the hydraulic cylinder (see Figure 3). The hydraulic cylinder, located outside the building, was covered with a locked concrete cap; therefore, the interior was not observed. Standing water present in the evaporator pit is likely due to shallow groundwater seepage. No VOCs were detected in groundwater during a July 2019 groundwater monitoring event (results will be provided in a forthcoming

remedial investigation work plan); therefore, the pit was determined to be an unlikely pathway for vapor intrusion.

Since no ventilation system was identified during the site visit, no pressure differential measurements are recommended to assess the building's pressurization relative to sub-slab conditions. The building appears to be naturally ventilated, with air exchanges occurring primarily through the warehouse overhead doors located throughout the building (see Figure 3).

Since the focus of Implementation Memorandum No. 22 (Ecology, 2019) is on women of childbearing age, including pregnant women, work areas staffed by female employees were noted during the site visit. The Property owner indicated that the overhead door on the south side of Warehouse 2 is routinely open during business hours and that a female employee typically works in that area (Frazier, 2019). Female employees were also observed in the main office area.

Only Warehouse 1 and the main office area are heated. Heat is provided by a natural-gas boiler system. In Warehouse 1, air is heated by ceiling-mounted units with fans that circulate the heated indoor air. No air intake was identified.

Preliminary sampling locations were identified during the site visit, based on previous sampling results, the building configuration and ventilation system, and the presence of female employees. A proposed sampling scope is discussed below. Note that the Property owner indicated that, based on his recollection, the sub-slab soil gas and indoor air samples SG-1 and IA-SHOP, respectively (see Figure 1), collected in 2015, are incorrectly located on the map; he recalled that the samplers had been located in the center of Warehouse 1 (Frazier, 2019).

## PRE-FIELDWORK SITE VISIT

MFA will conduct another site visit before the sampling event to complete the following tasks:

- Install temporary sub-slab soil gas collection ports in the building. Public or private utility-locating services and other information sources will be used to check for underground utilities or other underground obstructions before sub-slab sampling points are installed.
- Install a temporary weather station on the roof of the building.
- Immediately before sampling, conduct site reconnaissance and interview the building owner to help identify and coordinate the removal of potential indoor sources of VOC vapors, if present. None were identified during the preliminary site visit.

## SCOPE OF WORK

Specific sampling locations were selected during the site visit and were modified based on verbal feedback from Ecology (Adams, 2019). MFA also included some additional modifications based in its technical review. The sampling scope was developed in general accordance with guidance published by Ecology (2009), including Implementation Memorandum No. 22 (Ecology, 2019), the California Environmental Protection Agency (CEPA, 2011), and the New Jersey Department of Environmental Protection (NJDEP, 2012). Specific sampling locations were selected based on the following criteria:

- Passive vapor samplers will be deployed in areas identified during the preliminary site walk as places where female employees typically work.
- Indoor air and sub-slab soil gas samples will be collected in areas with previously identified VOC contamination (specifically, TCE and its breakdown products) in soil, groundwater, indoor air, and/or soil gas (see Figures 1 and 4).
- Indoor air samples will be collected in enclosed second-story areas that have first-story open areas immediately beneath them. If the area below the second story is also an enclosed area, separate from the main warehouse, then an indoor air sample will be collected only in the first-story area. This approach is intended to provide samples representative of the various enclosed areas in the building. Where the first and second stories are enclosed in the same area, the first-story area is considered most representative of the potential for vapor intrusion.
- Ambient (outdoor) air samplers will be deployed around the building on at least four sides to capture potential off-Property VOC sources. Sample locations will be upwind of and outside the footprint of the building and the areas of VOC impacts previously identified in ambient air, soil, and/or groundwater at the Site (see Figures 1 and 4). MFA will attempt to deploy the samplers in locations that are free of discernible ambient sources of VOCs. Wind direction data from the day on which the samples were collected will be reviewed to assess which ambient sample(s) was upwind of the building.

Proposed sample locations are shown in Figure 5 and are discussed in detail below. The proposed ambient air sample locations were selected as representative of ambient conditions because they are sufficiently far away from known sources of VOC contamination.

During sampler deployment, MFA must consider that access to desirable sampling locations may be restricted by the physical configuration of the building, the presence of utilities, or the building contents. Notwithstanding these limitations, MFA will collect samples in locations consistent with the criteria identified above and on Figure 5.

## Sample Collection

### Ambient (Outdoor) Air

The ambient air sampling will be started approximately one to two hours before the start of indoor air sampling. MFA will place 6-liter, stainless steel canisters (Summa canisters), each with a 24-hour flow controller, around the perimeter of the building and VOC-impacted areas. Samplers will be placed 3 to 5 feet above the ground. Only the upwind sample(s) will be submitted for analysis. Wind direction data will be collected with an instrument such as a Davis Vantage Pro2 weather station mounted on the roof of the building, and the data will be reviewed to identify the upwind ambient air sample location(s) that will be selected for analysis.

MFA will record field data before and after the sampling, including the sampling start and stop times, the initial and final canister vacuum readings, temperature, relative humidity, barometric pressure, wind speed and direction, and observations of conditions that may influence sampling results (e.g., industrial activities and presence or use of chemicals in the vicinity). The sample will be rejected if the initial canister pressure is not at least -25 inch of mercury or if the final canister pressure is greater than -0.1 inch of mercury.

### Indoor Air

Indoor air sampling will be conducted by MFA field staff, with oversight provided by an MFA certified industrial hygienist. The samples will be collected in 6-liter, stainless steel canisters (Summa© canisters) with a 24-hour flow controller. Indoor air samples will be placed 3 to 5 feet above the floor.

MFA will record field data before and after the sampling, including the sampling start and stop times, the initial and final canister vacuum readings, temperature, relative humidity, and observations of conditions that may influence sampling results (e.g., presence or use of petroleum products, open windows/doors). Atmospheric data will be collected from the nearest U.S. weather station for the two days prior to, during, and the two days after sample collection events. The sample will be rejected if the initial canister pressure is not at least -25 inches of mercury or if the final canister pressure is greater than -0.1 inches of mercury.

### Passive Indoor Air

Radiello® passive samplers (model number 130 [R130]) will be used to collect passive (diffusive) indoor air samples over a 21-day period. A trip blank sample will also be collected. The proposed sampler model was selected based on the analytical needs and anticipated uptake rate. Samplers will be placed 3 to 5 feet above the floor, consistent with Summa canister sampling heights. Samples will be collected in accordance with the Radiello sampler manufacturer instructions (see Attachment A) as well as the following protocol:

- The adsorbing cartridge will be removed from its packaging immediately prior to placement in its previously assembled supporting plate.
- Nitrile gloves will be worn during handling of the adsorbing cartridge.
- The sample label will be attached to the supporting plate.
- Atmospheric data will be collected from the nearest U.S. weather station for the two days prior to, during, and the two days after the sample collection period.
- After the samples are collected, the adsorbing cartridges will be removed from the sampling locations, placed in their protective tubes, and kept cool for shipment to the laboratory.
- Sampling information, including sample stop and start times and details of the sample location and conditions, will be recorded.

### Sub-Slab Soil Gas

After collection of indoor air samples, MFA will collect sub-slab soil gas samples from the space immediately below building slabs. The samples will be collected in 6-liter, stainless steel canisters (Summa canisters). Detailed sampling procedures are provided in the Standard Operating Procedure, Sub-Slab Soil Gas Sampling (see Attachment B). Temporary sub-slab sampling points will not be installed in places where the slab appears to be in contact with groundwater.

MFA will record field data before and after the sampling, including the sampling start and stop times, the initial and final canister vacuum readings, temperature, relative humidity, barometric pressure, wind speed and direction, and observations of conditions that may influence sampling results (e.g., industrial activities and presence or use of chemicals in the vicinity). The sample will be rejected if the initial canister pressure is not at least -25 inch of mercury or if the final canister pressure is greater than -0.1 inch of mercury.

## Sample Analysis and Quality Assurance

Samples will be analyzed by Eurofins Air Toxics, LLC (Eurofins) of Folsom, California, on a three-day turnaround. Indoor air, sub-slab soil gas, and ambient air samples will be analyzed for TCE and its breakdown products (see the table below) by Modified U.S. Environmental Protection Agency (USEPA) Method TO-15 selected ion monitoring (SIM). For quality assurance, sub-slab soil gas samples will also be analyzed for helium by Modified ASTM International Method D-1946. Passive indoor air samples will be analyzed for TCE by Modified USEPA Method TO-17.

Eurofins will provide an individually SIM-certified, 6-liter, stainless steel canister (Summa canister) for each indoor air, sub-slab soil gas, and ambient air sample. Eurofins will also provide Radiello 130 passive samplers for each passive indoor air sample and each trip blank.

Laboratory-specific method reporting limits (MRLs) are listed in the table below.

**Table**
**Analytes and Reporting Limits**

| Analyte | CAS Number | MRL | Screening Level—Air | Screening Level—Sub-slab Soil Gas |
|---|---|---|---|---|
| **Modified USEPA Method TO-15 SIM (ug/m³)** | | | | |
| TCE | 79-01-6 | 0.10 | 0.37 | 12 |
| 1,1-DCE | 75-35-4 | 0.039 | 91 | 3,000 |
| 1,2-DCA | 107-06-2 | 0.081 | 0.096 | 3.2 |
| cis-1,2-DCE | 156-59-2 | 0.079 | NV | NV |
| trans-1,2-DCE | 156-60-5 | 0.40 | NV | NV |
| 1,1-DCA | 75-34-3 | 0.081 | 1.6 | 52 |
| Chloroethane | 75-00-3 | 0.13 | 4,600 | 150,000 |
| Vinyl chloride | 75-01-4 | 0.026 | 0.28 | 9.4 |
| **Modified USEPA Method TO-17 (ug/m³)** | | | | |
| TCE | 79-01-6 | 0.0479 | 0.37 | NA |
| **ASTM Method D-1946 (%)** | | | | |
| Helium | 7440-59-7 | 0.050 | NA | NV |

NOTES:
Screening levels are based on MTCA Method B values obtained from CLARC tables dated May 2019.
CAS = Chemical Abstract Service.
CLARC = Cleanup Levels and Risk Calculation.
DCA = dichloroethane.
DCE = dichloroethene.
NA = not applicable.
NV = no value.

The MRLs provided above for Modified USEPA Method TO-15 SIM assume a 6-liter sample size and do not account for potential sample dilution due to canister pressurization or matrix interference. In general, the dilution factor from pressurization will raise the MRLs by approximately 1.5 to 1.7 times for 6-liter canisters. MFA will coordinate with the laboratory to obtain the lowest possible MRLs.

MFA will receive the data electronically from the laboratory, and the data will be transferred to a database. The data will be validated consistent with Ecology and USEPA protocols. To document data reliability, a memorandum will be prepared summarizing evaluation procedures, the usability of the data, and deviations from specific field and/or laboratory methods.

## Reporting

Immediately after the sampling data are received, the preliminary results will be transmitted to Ecology. MFA will then confirm data reliability (as described above) and will submit a summary report to Ecology that includes the sample results, assessment findings, and preliminary recommendations.

Sincerely,

Maul Foster & Alongi, Inc.

Heather Good, LHG
Senior Hydrogeologist

Bill Beadie, CIH
Principal Industrial Hygienist

Attachments: Limitations
References
Figures
Attachment A—Radiello Manual
Attachment B—Standard Operating Procedure, Sub-Slab Soil Gas Sampling

cc: Mark Myers and Bridget Schuster, Williams Kastner
Eric Stelter

# LIMITATIONS

The services undertaken in completing this report were performed consistent with generally accepted professional consulting principles and practices. No other warranty, express or implied, is made. These services were performed consistent with our agreement with our client. This report is solely for the use and information of our client unless otherwise noted. Any reliance on this report by a third party is at such party's sole risk.

Opinions and recommendations contained in this report apply to conditions existing when services were performed and are intended only for the client, purposes, locations, time frames, and project parameters indicated. We are not responsible for the impacts of any changes in environmental standards, practices, or regulations subsequent to performance of services. We do not warrant the accuracy of information supplied by others, or the use of segregated portions of this report.

# REFERENCES


Adams, M. 2019. Personal communication (re: preliminary vapor sampling scope) with H. Good, Maul Foster & Alongi, Inc, Bellingham, Washington. November 26.

CEPA. 2011. Guidance for the evaluation and mitigation of subsurface vapor intrusion to indoor air. California Environmental Protection Agency, Department of Toxic Substances Control. October.

Ecology. 2009. Guidance for evaluating soil vapor intrusion in Washington State: investigation and remedial action. Publication no. 09-09-047. Washington State Department of Ecology. Revised February 2016 and April 2018.

Ecology. 2019. Implementation memorandum no. 22: vapor intrusion investigations and short-term trichloroethene toxicity. Publication no. 18-09-047. Washington State Department of Ecology. October.

Frazier, L. 2019. Personal communication (re: previous vapor sampling locations and female employee work areas) with H. Good, H. Good, Maul Foster & Alongi, Inc, Bellingham, Washington. November 20.

Kennedy/Jenks Consultants. 2015. Remedial investigation report, former Precision Engineering property, Seattle, Washington. August 6.

MFA. 2006. Remedial investigation and risk assessment, Precision Engineering, Inc. site. Maul Foster & Alongi, Inc., Vancouver, Washington. July 17.

NJDEP. 2012. Vapor intrusion technical guidance. Vers 2.0. New Jersey Department of Environmental Protection, Site Remediation Program. January.

# FIGURES

# Figure 1
# TCE and Breakdown Product Detections - Soil Gas and Air

Precision Engineering, Inc.
Seattle, Washington

**AMB-OUTDOOR**
Ambient air (ug/m$^3$)
Collection date: 02/07/2015
TCE: **0.96**

**IA1**
Indoor air (ug/m$^3$)
Collection date: 06/13/2006
TCE: 0.2

**A3**
Sub-slab soil gas (ug/m$^3$)
Collection date: 04/18/2006
cis-1,2-DCE: 470
TCE: **6,100**

**SG-1**
Sub-slab soil gas (ug/m$^3$)
Collection date: 02/072015
TCE: **95**

**IA2**
Indoor air (ug/m$^3$)
Collection date: 06/13/2006
TCE: 0.083

**IA3**
Indoor air (ug/m$^3$)
Collection date: 06/13/2006
TCE: 0.11

**IA4**
Indoor air (ug/m$^3$)
Collection date: 06/13/2006
TCE: 0.14

**IA-SHOP**
Indoor air (ug/m$^3$)
Collection date: 02/07/2015
TCE: **240**
VC: **0.25**

**IA5**
Indoor air (ug/m$^3$)
Collection date: 06/13/2006
TCE: **0.16**

**A5**
Sub-slab soil gas (ug/m$^3$)
Collection date: 04/18/2006
cis-1,2-DCE: 1,700
TCE: **37,000**
VC: **420**

**IA7**
Ambient air (ug/m$^3$)
Collection date: 06/13/2006
TCE: 0.046

**IA6**
Indoor air (ug/m$^3$)
Collection date: 06/13/2006
TCE: 0.15

A1 A2 A3 A4 A5 A6 A7

A Airebrook/
Carey Chauffeured

| | Sub-slab Soil Gas VI SL | Air CUL |
|---|---|---|
| | ug/m$^3$ | ug/m$^3$ |
| **cis-1,2-DCE** | NV | NV |
| **TCE** | 12 | 0.37 |
| **VC** | 9.4 | 0.28 |

## Legend

**TCE and Breakdown Product Detections**

- CUL or SL Exceedance
- Indoor/Ambient Air
- Sub-slab Soil Gas

**Sample Location Type**

- Indoor/Ambient Air
- Sub-slab Soil Gas
- King County Parcels
- Property Parcels

Notes:
Only detected concentrations are shown.
Bold values indicate SL or CUL exceedances.
SLs and CULs are provided only for detected compounds.
CUL = cleanup level.
DCE = dichloroethene.
NV = no value.
SL = screening level.
TCE = trichloroethene.
ug/m$^3$ = micrograms per cubic meter.
VC = vinyl chloride.
VI = vapor intrusion.

0 25 50
Feet

Source: Aerial photograph obtained from Mapbox.
Well locations for MW01-MW08 obtained from survey conducted by Duncanson, Inc.

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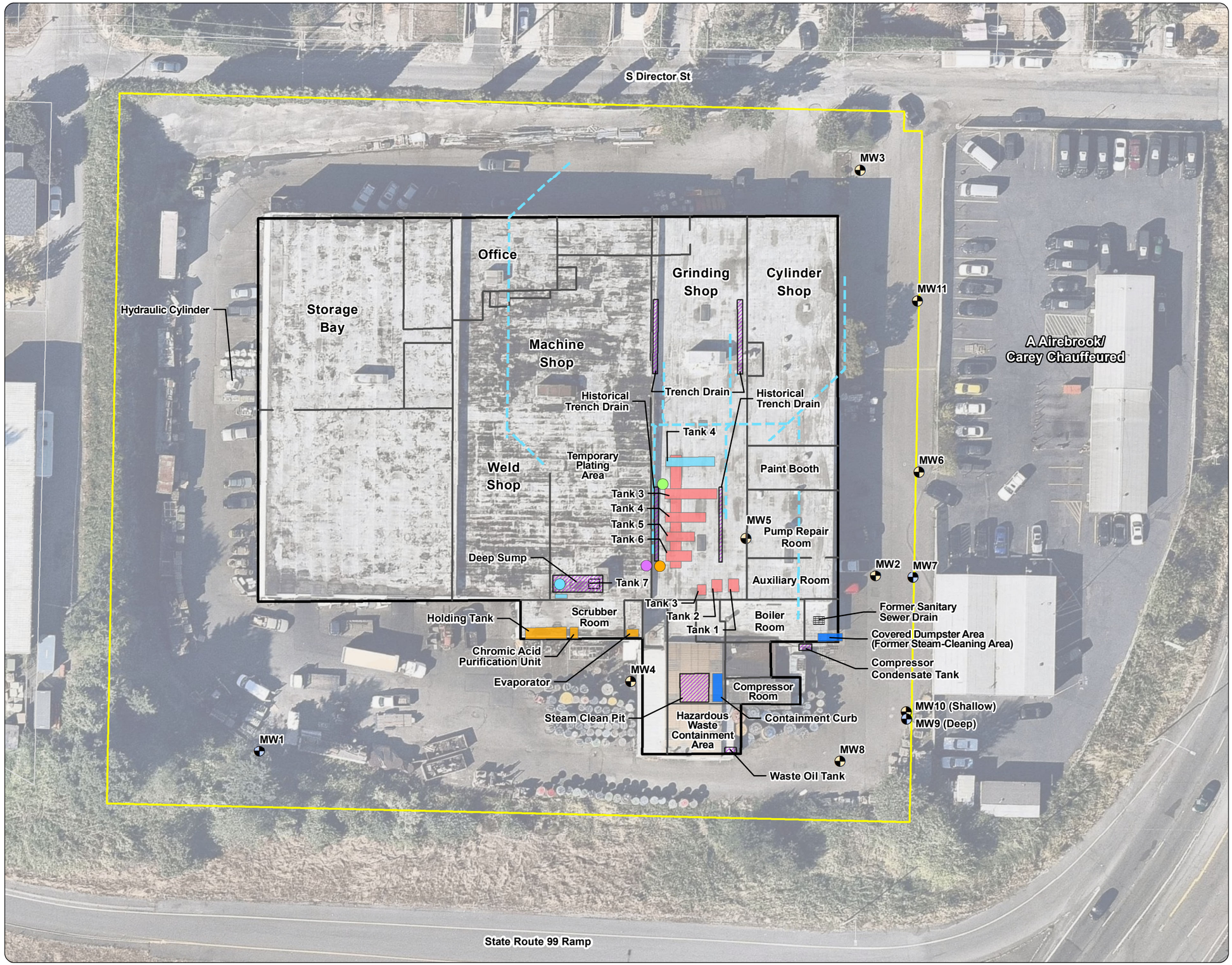
Produced By: mjosef
Project: 1803.01

# Figure 2
# Historical Site Features
Precision Engineering, Inc.
Seattle, Washington




## Legend

- Deep Monitoring Well
- Shallow Monitoring Well
- Sodium Hydroxide Tank
- Sodium Carbonate Tank
- Other Tanks Containing Chromic Acid
- Chromic Acid Plating Tank
- Trichloroethene Tank
- Hydrochloric Acid Tank
- Other Historical Feature
- Former Sanitary Sewer Piping (from July 1986 drawing by Precision Engineering, Inc.)
- King County Parcels
- Property Parcels

NOTES:
Deep monitoring wells are completed in the confined sand and gravel water-bearing zone.
Shallow monitoring wells are completed in the confined alluvial water-bearing zone.

0 25 50
Feet

Source: Aerial photograph obtained from Mapbox.
Well locations for MW01-MW08 obtained from survey conducted by Duncanson, Inc.

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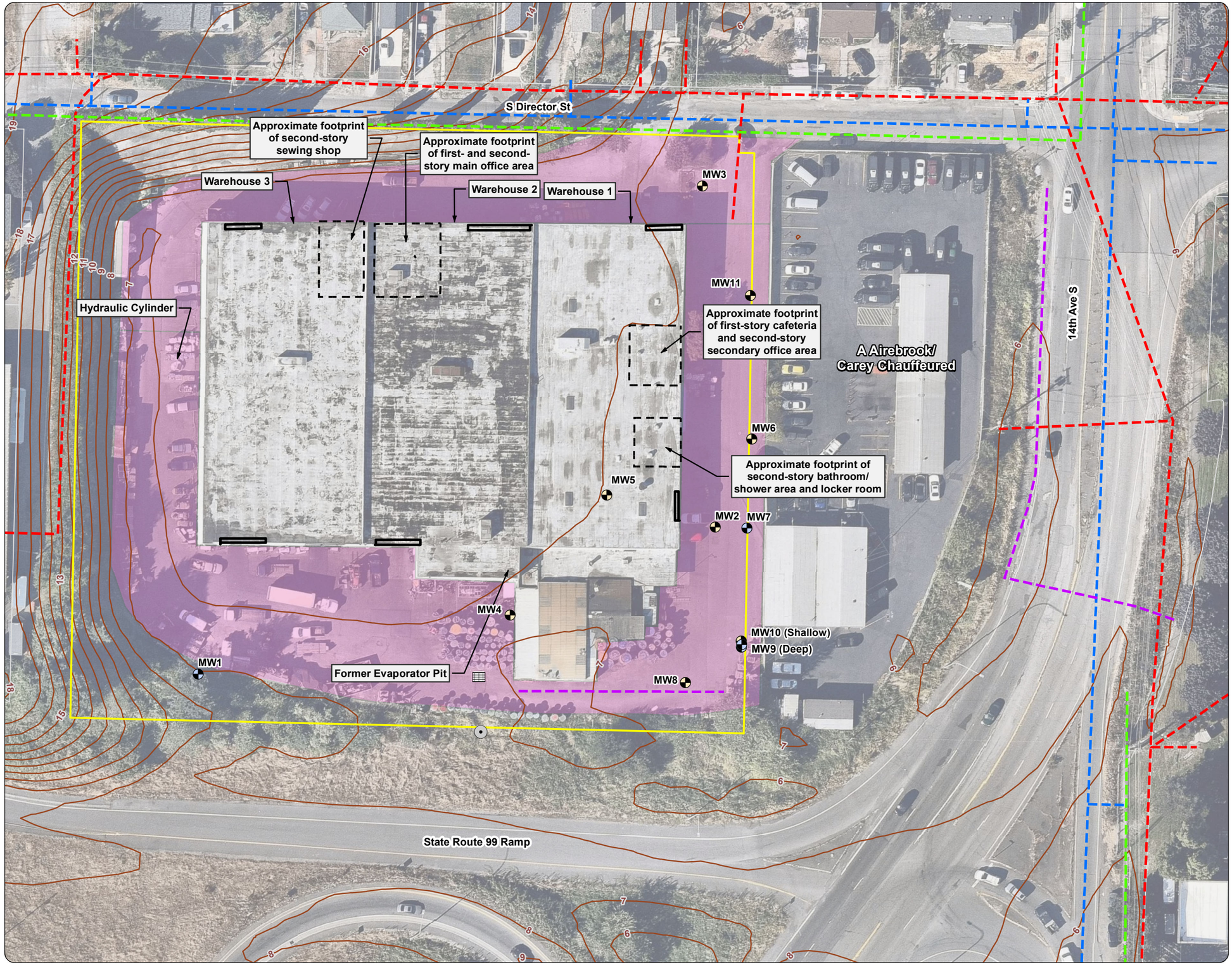
# Figure 3
# Current Site Features
Precision Engineering, Inc.
Seattle, Washington




## Legend

- Deep Monitoring Well
- Shallow Monitoring Well

**Utility Line**

- Electrical
- Puget Sound Energy Gas
- Sewer and Drainage
- Water
- Catch Basin
- Outfall to Drainage Ditch
- Elevation Contours (1ft interval)
- Overhead Door (approximate)
- Paved Area
- King County Parcels
- Property Parcels

NOTES:
Deep monitoring wells are completed in the confined sand and gravel water-bearing zone.
Monitoring well locations are based on previous surveys. All other feature locations are approximate.
Shallow monitoring wells are completed in the confined alluvial water-bearing zone.

0 30 60
Feet

Source: Aerial photograph obtained from Mapbox.
Well locations for MW01-MW08 obtained from survey conducted by Duncanson, Inc.

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# Figure 4
# TCE and Breakdown Product Detections - Soil and Groundwater

Precision Engineering, Inc.
Seattle, Washington

**GP11**
Soil (mg/kg)
Collection depth (ft bgs): 2.0
TCE: 0.0872
Collection depth (ft bgs): 6.5
cis-1,2-DCE: 0.0788
TCE: 0.281

**GP14**
Soil (mg/kg)
Collection depth (ft bgs): 3.0
TCE: 0.00449

**GP18**
Soil (mg/kg)
Collection depth (ft bgs): 1.0
TCE: 0.00343

**GP10**
Soil (mg/kg)
Collection depth (ft bgs): 1.5
1,1-DCE: 0.0237

**GP6**
Soil (mg/kg)
Collection depth (ft bgs): 1.0
TCE: 0.0405
Collection depth (ft bgs): 14.5
cis-1,2-DCE: 0.149
TCE: 1.16

**GP13**
Shallow Groundwater (ug/L)
Collection date: 12/14/2005
cis-1,2- DCE: 6.03
trans-1,2-DCE: 1.01
TCE: 0.22
VC: **16.5**

**MW3**
Shallow groundwater (ug/L)
Collection date: 12/29/2005
cis-1,2-DCE: 0.2

**GP16**
Soil (mg/kg)
Collection depth (ft bgs): 1.0
TCE: 0.00363

**MW5**
Shallow Groundwater (ug/L)
Collection date: 12/28/2005
cis-1,2- DCE: 2.42
TCE: **22.1**

**GP29**
Soil (mg/kg)
Collection depth (ft bgs): 1.0
cis-1,2-DCE: 0.00494
Collection depth (ft bgs): 6.0
cis-1,2-DCE: 0.00996

**MW8**
Shallow Groundwater (ug/L)
Collection date: 12/28/2005
VC: 0.56
Collection date: 4/18/2006
cis-1,2- DCE: 1.5

SB10, AMB-OUTDOOR, GP12, MW11, SB8, A Airebrook/ Carey Chauffeured, SB7, GP24, GP15, SB15, GP5, GP17, MW-6, GP32, GP19, SB6, SB16, SB14, GP23, GP3, GP2, GP20, GP9, GP7, GP1, MW2, GP4, GP8, GP22, GP21, GP26, GP28, SB5, GP30, GP31, SB17, SB13, GP25, MW4, GP27, MW10, SB4, SB1, SB3, SB18, SB12, SB11

| | Groundwater VI SL | Soil CUL |
|---|---|---|
| | ug/L | mg/kg |
| 1,1-DCE | 130 | 4,000 |
| cis-1,2-DCE | NV | 160 |
| trans-1,2-DCE | NV | 1,600 |
| TCE | 1.5 | 12 |
| VC | 0.35 | 0.67 |

## Legend

**TCE and Breakdown Product Detections**

- CUL or SL Exceedance
- Groundwater
- Soil

**Sample Location Type**

- Boring
- Shallow Monitoring Well
- King County Parcels
- Property Parcels

Notes:
Only detected concentrations are shown.
All compounds were non-detect in groundwater during the July 2019 event. Historical detections are shown for reference.
TCE and its breakdown products have not been detected in deep monitoring wells or hand auger and surface soil samples (locations not shown).
Bold values indicate SL or CUL exceedances.
SLs and CULs are provided only for detected compounds.
CUL = cleanup level.
DCE = dichloroethene.
ft bgs = feet below ground surface.
mg/kg = milligrams per kilogram.
NV = no value.
SL = screening level.
TCE = trichloroethene.
ug/L = micrograms per liter.
VC = vinyl chloride.
VI = vapor intrusion.

0 25 50
Feet

Source: Aerial photograph obtained from Mapbox.
Well locations for MW01-MW08 obtained from survey conducted by Duncanson, Inc.

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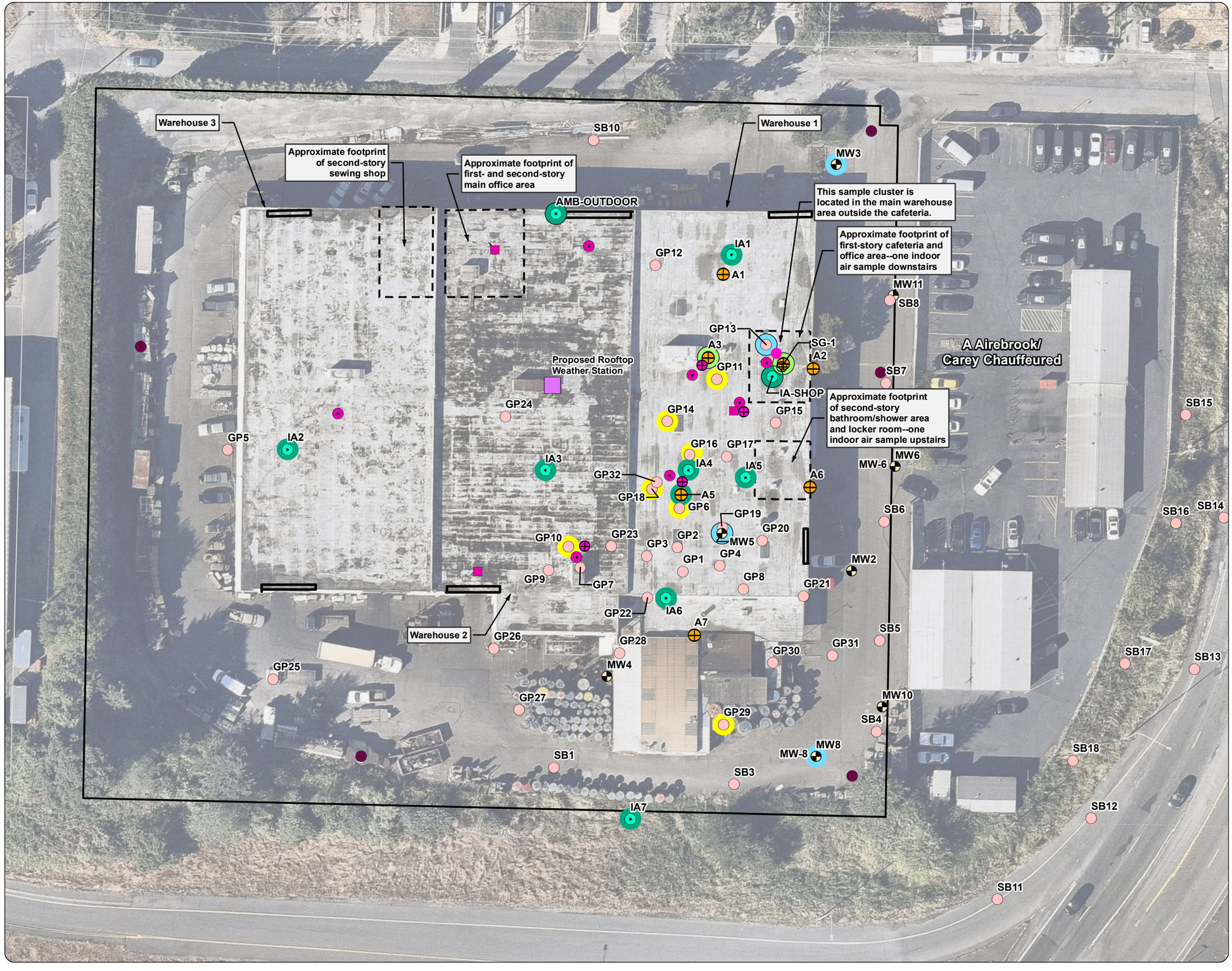
# Figure 5
# Proposed Soil Gas and Air Sample Locations

Precision Engineering, Inc.
Seattle, Washington

**DRAFT**




## Legend

**Proposed Sampling Location**

- Proposed Ambient Air
- Proposed Indoor Air
- Proposed Passive Sampler
- Proposed Sub-slab Soil Gas

**TCE and Breakdown Product Detections**

- CUL or SL Exceedance
- Indoor/Ambient Air
- Sub-slab Soil Gas
- Groundwater
- Soil
- Boring
- Indoor/Ambient Air
- Shallow Monitoring Well
- Sub-slab Soil Gas
- Overhead Door (approximate)
- King County Parcels
- Property Parcels

Notes:
All compounds were non-detect in groundwater during the July 2019 event. Historical detections are shown for reference.
All proposed indoor air sample locations shown are on the first story of the building. Second-story samples are indicated in the notes, but aren't shown on the map.
TCE and its breakdown products have not been detected in deep monitoring wells or hand auger and surface soil samples (locations not shown).
CUL = cleanup level.
SL = screening level.
TCE = trichloroethene.

0 25 50
Feet

Source: Aerial photograph obtained from Mapbox.
Well locations for MW01-MW08 obtained from survey conducted by Duncanson, Inc.

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# ATTACHMENT A

## RADIELLO® MANUAL

# USER MANUAL 2019

Istituti Clinici Scientifici Maugeri

radiello®


Centro di Ricerche Ambientali

*ENGLISH 01-2019*



# Index



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Edition 01/2019

# Subject index



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# how does the diffusive sampler work?

The diffusive sampler is a closed box, usually cylindrical. Of its two opposite sides, one is “transparent” to gaseous molecules which cross it, and are adsorbed onto the second side. The former side is named diffusive surface, the latter is the adsorbing surface (marked with ***S*** and ***A*** in the figure).

Driven by the concentration gradient ***dC/dl***, the gaseous molecules cross ***S*** and diffuse towards ***A*** along the path ***l***, parallel to the axis of the cylindrical box. The molecules, which can be trapped by the adsorbing material, are eventually adsorbed onto ***A*** according to the equation:

$$\frac{dm}{dt} = D\,S\,\frac{dC}{dl} \qquad [1]$$

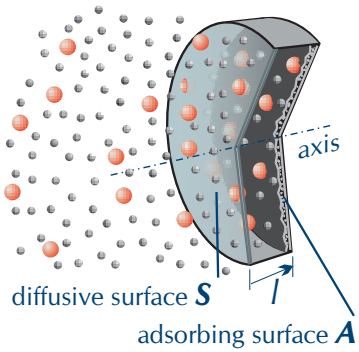
where ***dm*** is the adsorbed mass during time ***dt*** and ***D*** is the diffusion coefficient.

Let ***C*** be the concentration at the diffusive surface and $C_0$ the concentration at the adsorbing surface, the integral of [1] becomes

$$\frac{m}{t} = D\frac{S}{l}(C-C_0) \qquad [2]$$

If the concentration at the adsorbing surface is negligible, the equation can be approximated to

$$\frac{m}{t\,C} = D\frac{S}{l} = Q \quad \text{and then} \quad C = \frac{m}{t\,Q} \qquad [3]$$




*In the diffusive sampler, the adsorbing and the diffusive surfaces are two opposing plane of a closed box. Driven by the concentration gradient, the gaseus molecules (coloured in the figure) pass through the diffusive surface and are trapped from the adsorbing surface.*

***Q*** is the ***sampling rate*** and has the dimensions of a gaseous flow (if ***m*** is expressed in µg, ***t*** in minutes and ***C*** in $\mu g \cdot l^{-1}$, ***Q*** is expressed in $l \cdot min^{-1}$).

Therefore, if ***Q*** is constant and measured, to calculate the ambient air concentration you need only to quantify the mass of analyte trapped by the adsorbing material and to keep note of the time of exposure of the diffusive sampler.

To improve the analytical sensitivity the collected mass ***m*** should be increased by enlarging ***Q***. As ***D*** is a constant term, one can only try to improve the ***S/l*** ratio, namely the ***geometrical constant*** of the sampler. Unfortunately, in the common axial simmetry sampler, if ***S*** is enlarged, the adsorbing surface ***A*** must be enlarged too, in order to keep the two parallel surfaces at a fixed distance. Since the analytes can be recovered from the axial sampler only by solvent extraction, any increase of ***A*** lead to a proportional increase of the extraction solvent volume, thus the improvement of ***Q*** is canceled out by the effect of dilution.

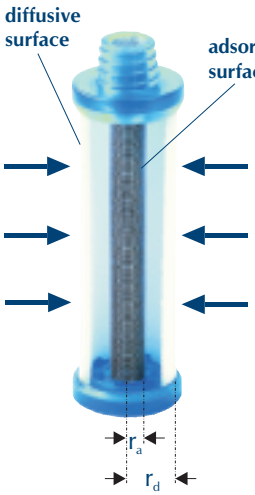
The value of distance ***l*** could also be reduced, but under the critical value of about 8 mm the diffusion law is no longer valid in the case of low air velocity values, since adsorption rate becomes higher than supplying rate of analyte molecules at the diffusive surface.

Cannot we improve ***Q*** then?

The answer is to improve the sampler geometry to a ***radial*** design.

From this idea the ***radiello*** sampler has been developed, its cylindrical outer surface acting as diffusive membrane: the gaseus molecules move axially parallel towards an adsorbent bed which is cylindrical too and coaxial to the diffusive surface.

When compared to the axial sampler, ***radiello*** shows a much higher diffusive surface without increase of the adsorbing material amount. Even if the adsorbing surface is quite smaller then the diffusive one, each point of the diffusive layer faces the diffusion barrier at the same distance.




*Section of **radiello**. Diffusive and adsorbing surfaces are cylindrical and coaxial: a large diffusive surface faces, at a fixed distance, the small surface of a little concentric cartridge.*

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As $S=2\pi rh$ (where $h$ is the height of the cylinder) and the diffusive path is as long as the radius $r$, we can then express equation [1] as follows

$$\frac{dm}{dt} = D\ 2\pi\ h\ r\ \frac{dC}{dr} \qquad [4]$$

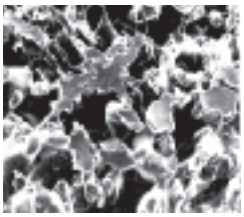
The integral of equation [4] from $r_d$ (radius of the diffusive cylindrical surface) to $r_a$ (radius of the adsorbing surface) becomes

$$\frac{m}{t\ C} = D\ \frac{2\pi\ h}{ln\ \frac{r_d}{r_a}} = Q \qquad [5]$$

the ratio

$$\frac{2\pi\ h}{ln\ \frac{r_d}{r_a}}$$

is the geometrical constant of **radiello**. The calculated uptake rate [5] is therefore proportional to the height of the diffusive cylinder and inversely proportional to the logarithm of the ratio of diffusive *vs* adsorbing cylinder radii.



*The microporous sintered polyethylene diffusive barrier of* **radiello** *photographed at the electron microscope; the path length is much longer than the membrane thickness due to the tortuosity of the pores.*

While $r_a$ can be easily measured, $r_d$ can only be calculated by exposure experiments. Actually the diffusive membrane has been designed with a thick tubular microporous layer. The actual diffusive path length is therefore much longer than the distance among the diffusive and adsorbing surfaces due to the tortuosity of the path through the pores. A diffusive cylinder of external diameter 8 mm, thickness 1.7 mm and average porosity of 25 µm, coupled to an adsorbing cartridge with radius 2.9 mm creates a diffusive path of 18 mm instead of the straight line path estimation of (8-2.9) = 5.1 mm.

The sampling rate $Q$ is function of diffusive coefficient $D$, which is a thermodynamic property of each chemical substance. $D$ varies with temperature ($T$) and pressure ($p$); therefore also the sampling rate is a function of those variables according to

$$Q = f\ (T,\ p)$$

$Q$ values that will be quoted in the following have been measured at 25 °C and 1013 hPa. As a consequence, they should be corrected so as to reflect the actual sampling conditions.

The correction of $Q$ for atmospheric pressure is usually negligible since its dependence is linear and very seldom we face variations of more than 30 hPa about the average value of 1013 hPa. In the worst case, if corrections for pressure are ignored you make an error of ±3%, usually it is within ±1.5%.

On the other hand, $Q$ depends exponentially on temperature variations, therefore more relevant errors can be introduced if average temperature is significantly different from 25 °C. Moreover, when chemiadsorbing cartridge are used kinetic effects (variations of reaction velocities between analyte and chemiadsorbing substrate) can be evident, apart from thermodynamic ones (variation of $D$).

**It is therefore very important to know the average temperature in order to ensure accuracy of experimental data. See how you can perform on-field temperature measurements on page B3.**

Even if some cartridges adsorb large quantities of water when exposed for a long time in wet atmosphere, generally this does not affect sampling by **radiello**. Some consequences, neverthless, can sometimes be felt on the analysis. As an example, a very wet graphitised charcoal cartridge could generate ice plugs during cryogenic focusing of thermally desorbed compounds or blow out a FID flame.

**It is therefore important to protect *radiello* from bad weather. See page B1 how this can be easily done.**



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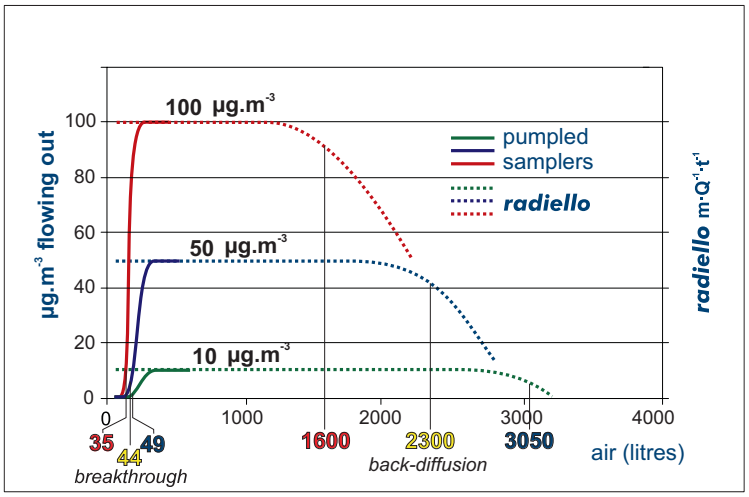
# why is radiello so *special?*

The diffusive sampling does not involve the use of heavy and encumbering pumping systems, does not have energy power supply problems, does not require supervision, is noiseless, is not flammable and does not represent an explosion hazard, can be performed by everybody everywhere and with very low costs.

Moreover, it is not subject to the breakthrough problem, which can be serious when active pumping is performed.

*In pumped sampling the adsorbed compound behaves as a chromatographic peak (top): air flow displaces it along the adsorbent bed and its concentration is distributed as a gaussian function. Eventually, the compound comes out from the opposite end. When its concentration in the outlet air is 10% of the concentration in the sampled air we say that the* ***breakthrough*** *has been reached or, with a misleading expression, that the tube has been saturated. Any further pumping leads to a loss of analyte and a consequent underestimation of the environmental concentration. The extent of this phenomenon depends weakly on the concentration of target compound but rather on the value of air flow, the overall sampling volume and the chemical compound involved.*




*In the graph the case of benzene is displayed, sampled at 25 °C onto an activated charcoal adsorbent bed of the same volume of a code 130* **radiello** *cartridge. The breakthrough is reached after 35, 44 or 49 liters of sampled air depending on benzene concentration in air (10, 50 or 100 µg·m$^{-3}$ respectively).*

*An apparently similar phenomenon is shown by* **radiello** *also. In this case, however, we cannot speak of breakthrough, since no actual air flow is involved, but rather of* ***backdiffusion****. This consists of a decrease of the value of m·Q$^{-1}$·t$^{-1}$ (which is equal to the measured concentration, see eqn. [3] on page A1). This term is constant and equal to the actual concentration until the adsorbed mass of analyte is far from the maximum amount allowed by the adsorbing medium capacity. The extent of backdiffusion depends on concentration and exposure time but a decrease of 10% in the m·Q$^{-1}$·t$^{-1}$ term is observed along with equivalent sampling volumes of magnitude bigger than those seen before: 1600, 2300 and 3050 liters at the concentration of 10, 50 and 100 µg·m$^{-3}$.*

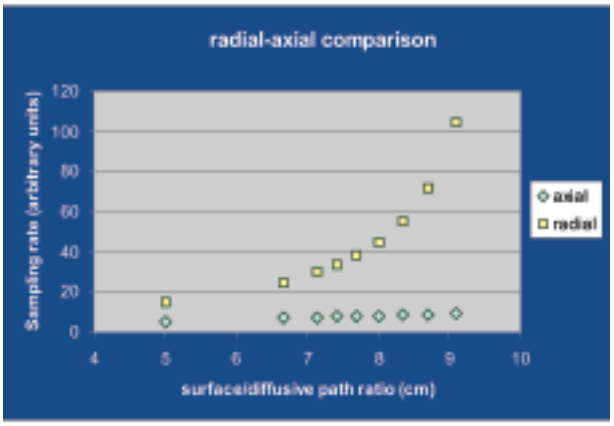
Why diffusive sampling has not been so extensively adopted up to now?

This is due to the fact that the traditional axial symmetry sampler has generally poor sensitivity and reproducibility because of the limits set by its geometry. On one side, uptake rate values are generally low, on the other, they often vary depending on environmental conditions.

These limitations have been overcome by **radiello**.

By virtue of radial simmetry, uptake rate is:

- ✓ **high**, since it does not vary linearly but exponentially with the ratio diffusive surface *vs* diffusive path length (see eqn. [5]). With the same dimensions, radiello's uptake rate is at least three times higher than that of any axial diffusive sampler;




*For a traditional axial simmetry sampler the uptake rate increases linearly with tha ratio of diffusive surface vs diffusive path length, while for the radial simmetry sampler, the corresponding increase is exponential. This means that, let the diffusive surface vs diffusive path length ratio be 8:1, for the axial sampler the uptake rate value is 8 (regardless of dimensions) while for the radial one it is 45.*

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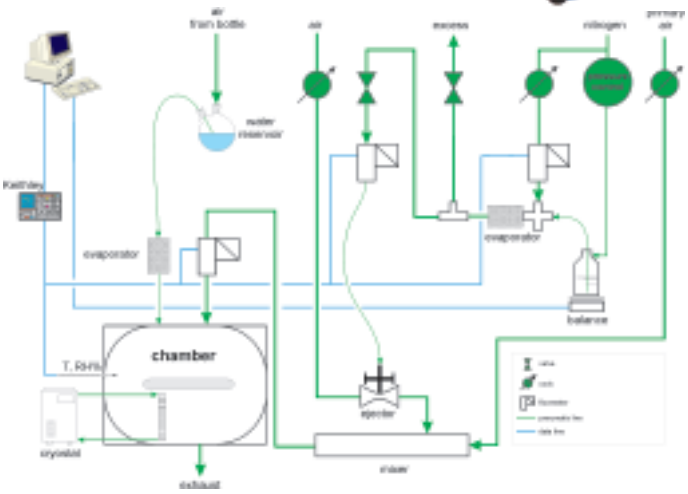
- ✓ **constant**, due to the great adsorbing capacity of the adsorbing substrates;
- ✓ **reproducible**, for the continuous control of the homogeneity of the materials used and of all the production lots of radiello;
- ✓ **precisely measured**, because the flow rate is not estimated but calculated experimentally, measured in dynamic atmosphere controlled chamber in a wide range of conditions of concentration, temperature, humidity, air velocity, presence of interfering




Moreover, ***radiello***

- is able to work properly also with bad weather conditions due to the water-repellent diffusive body
- has blank values lower than three times the instrumental noise due to the complex conditioning procedures of the bulk adsorbing (or chemiadsorbing) materials and to the repeated quality controls along the whole production
- has low detection limits and high adsorbing capacities that allow exposure time duration from 15 minutes to 30 days and concentration measurements from 1 ppb to over 1000 ppm
- offers high precision and accuracy over a wide range of exposure values

- allows thermal desorption and HRGC-MS analysis without interferents
- is suited to the sampling of a vast range of gaseous pollutants
- is though and chemically inert, being made of polycarbonate, microporous polyethylene and stainless steel
- is indefinitely reusable in all of its components apart from the adsorbing cartridge; the latter can be recovered if thermal desorption is employed
- it comes from the efforts of one of the main European scientific research institutions that produces it directly by high technology equipment and continuously submits it to severe tests and performs research and development in its laboratory in Padova

All the images in the manual concern the Environmental Research Center of the Istituti Clinici Scientifici Maugeri

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# the components of *radiello*

The essential parts of ***radiello*** are the adsorbing cartridge, the diffusive body, the supporting plate and the adhesive label with the bar code indication. Apart from the adsorbing cartridge, if not differently stated, all of the other components can be repeatedly used for several sampling experiments.

## The adsorbing cartridge

Depending on the polluting compound to be sampled, many different adsorbing or chemiadsorbing cartridges have been developed. Their dimensions are neverthless the same for all: 60 mm length and 4.8 or 5.8 mm diameter.

They are contained in glass or plastic tubes wrapped up in a transparent polyethylene thermowelded bag.

The code number, printed onto the bag along with the lot number and expiry date indicates the kind of cartridge.

Apart from the thermal desorption cartridges, all of the other kinds are for single use only.

**Available in 5 or 20 pieces per package.**

*The cartridge has to be introduced into the diffusive body.*


## The diffusive body

Four kinds of diffusive bodies are available, with like outer dimensions: 60 mm height and 16 mm diameter.

The **white** diffusive body, **code RAD120**, of general use, is made of microporous polyethylene 1.7 mm thick and average porosity 25 ± 5 µm. Diffusive path length is 18 mm.

The **blue** diffusive body, **code RAD1201**, has the same properties of the white one but is opaque to light: it is suited to the sampling of light-sensitive compounds.

The **yellow** diffusive body, **code RAD1202**, should be used whenever the sampling rate must be reduced; it is made of microporous polyethylene 5 mm thick and average porosity 10 ± 2 µm. Diffusive path length is 150 mm.

The **permeative** diffusive body, **code RAD1203**, is a 50 µm thick silicone membrane strengthened by a stainless steel net and a microporous polyethylene cylinder. It is employed for anaesthetic gases and vapours sampling.

**Available in 20 pieces per package only.**

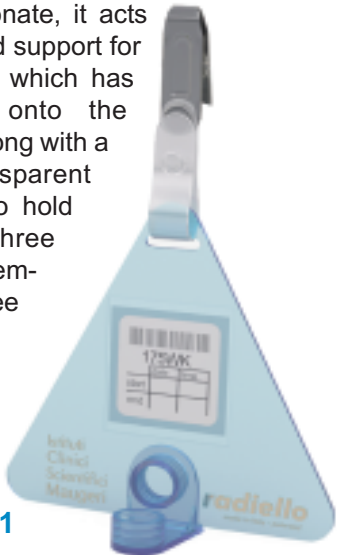
*The diffusive body has to be screwed onto the supporting plate.*

**RAD120** **RAD1201** **RAD1202** **RAD1203**

## The supporting plate

It is identified by the **code 121**. Made of polycarbonate, it acts both as closure and support for the diffusive body, which has to be screwed onto the thread. It comes along with a clip and a transparent adhesive pocket to hold the label. The three parts are to be assembled before use (see page A6).

**Available in 20 pieces per package only.**




**code RAD121**

## The label

**code RAD190**

Self-adhesive, with printed bar-code number. Since each bar-code number has been printed in only one copy, it allows an unmistakable identification of the sampling tube on field and in the laboratory for the subsequent analysis.

Each package of 20 adsorbing cartridges contains also 21 labels.

**If the labels are ordered separately, they are shipped in 198 pieces per package only.**

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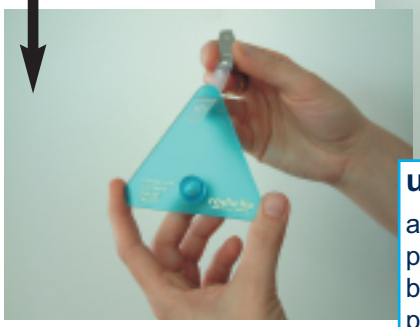
# how to use *radiello*

## before sampling

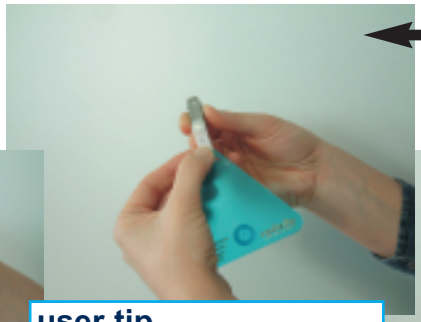
Before using ***radiello***, you have to assemble the supporting plate with the clip, necessary to suspend it, and the adhesive label pocket.

## assembling the supporting plate

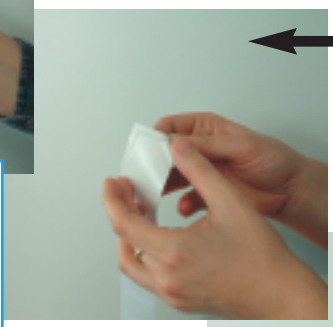
1 insert the clip strip in the slot, with the peg facing upwards



2 ply the strip and insert the peg into the hole



3 peel off the transparent pocket



**user tip**

assemble the supporting plate in your laboratory before the sampling campaign: on the field they are uselessly time-consuming.

4 and stick it onto the plate in a central position;

if you prefer, the pocket can be applied to the rear of the plate, but BE CAREFUL, always with the label insertion slot on the side (otherwise, if it starts raining the label can get wet)

## on-field

## to start the sampling

1 open the plastic bag, draw the cartridge out from the tube and put it in the diffusive body. ***Keep the glass or the plastic tube and stopper in the original plastic bag.***

The lower part of the diffusive body holds a seat for the central positioning of the cartridge. **A correctly centered cartridge should not stick out even by half a millimeter. If it is not so, the cartridge is not correctly positioned and is out of axis.**

As a consequence, when the diffusive body is screwed onto the supporting plate the cartridge is bent, the geometry of the sampler is disturbed and the results obtained become unreliable.

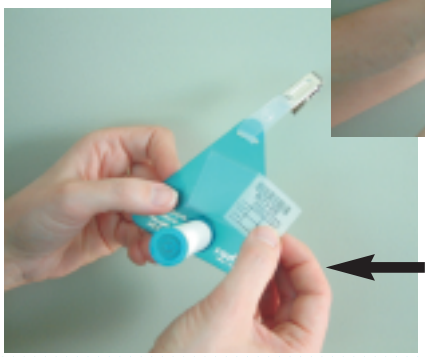
***To place the cartridge centrally you need only to tap on the diffusive body.***

2 keeping the diffusive body in a vertical position, screw it onto the supporting plate.

**BE CAREFUL: do not hold the diffusive body horizontally when you screw it onto the plate, otherwise the cartridge could come out from its seat and stick out.**

**user tip**

Do not touch the cartridge with your fingers if possible, particularly if it is impregnated with reactive



3 Insert a label in the pocket without peeling it off. Keep note of the date and time and expose ***radiello***. Sampling has started.

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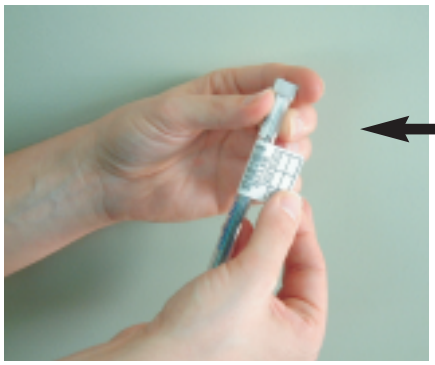
**user tip**

even if you can write date and time of the sampling start and end on the adhesive label, we suggest you to keep note of these parameters also separately: after a week exposure with bad weather conditions, your writings could become illegible!

**DO NOT USE MARKING PENS** to write on the label: they contain solvents that are sampled by ***radiello***!



## after the sampling

Keep note of the date and time of the end of exposure.

4 Place the cartridge into the tube, peel off the label and stick it onto the tube such that the barcode is parallel to the axis of the tube.

If you have performed the sampling of different polluting compounds at the same time, ***BE CAREFUL NOT TO MIX UP THE TUBES***: place the exposed cartridge in its original tube, identified by the code printed on the plastic bag.

**IMPORTANT**

Always stick the label such that the barcode is parallel to the axis of the tube: any other position will compromise the barcode automated reading by the optic reading device.

## maintenance

When exposed outdoors or in a workplace environment, the diffusive body may get dirty from airborne dust. Fine particles ($PM_{10}$) are especially harmful to yellow diffusive bodies since they can obstruct the pores. When the diffusive bodies are dirty you can wash them as follows.
Immerse the diffusive bodies in a beaker with a soapy solution (e.g. dish detergent) and sonicate them for 20 minutes. As the diffusive bodies float, you may make them sink by putting a smaller beaker on them, with water inside enough to dip it a few centimeters.

Rinse the diffusive bodies with plenty of water and then deionized water; let them finally dry in the air.

IMPORTANT: NEVER USE SOLVENTS TO CLEAN THE DIFFUSIVE BODIES!!!

After four or five washings, diffusive bodies need replacing: repeatedly adsorbed dust may have penetrated the pores such deeply to be undisturbed by washing.

The following table shows the advised washing schedule:

| $PM_{10}$ concentration ($\mu g \cdot m^{-3}$) | <30 | 40 | >50 |
|---|---|---|---|
| Washing after days of exposure | 45 | 30 | 15 |

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# radiello-ready-to-use

The ready-to-use version may be advantageous when you prefer not to assemble all of the components on field. It can be purchased as it is or in separate parts to be assembled by the customer.

In the ***as-it-is version*** the adsorbing cartridge is already contained in a diffusive body closed with a polycarbonate screw-thread cap. The whole is closed in a polypropylene airtight container. Just before use draw the diffusive body out of the container and fit it to the special snapping vertical adapter fixed to the supporting plate. After the end of exposure, the diffusive body with its content is placed again in the polypropylene airtight container to be shipped to the laboratory for analysis. The ***ready-to-use as-it-is radiello*** (polycarbonate cap, glass or plastic tube, special vertical adapter, barcode label and polypropylene container comprised for each type) is available for the sampling of the following compounds:

| code | sampling of | contains |
|---|---|---|
| **RAD1231** | BTEX and VOCs | white diffusive body and cartridge code RAD130 |
| **RAD1232** | BTEX and VOCs | yellow diffusive body and cartridge code RAD145 |
| **RAD1233** | $NO_2$, $SO_2$ and HF | blue diffusive body and cartridge code RAD166 |
| **RAD1233** | Aldehydes | blue diffusive body and cartridge code RAD165 |
| **RAD1235** | ozone | blue diffusive body and cartridge code RAD172 |
| **RAD1236** | hydrogen sulfide | white diffusive body and cartridge code RAD170 |
| **RAD1237** | ammonia | blue diffusive body and cartridge code RAD168 |
| **RAD1238** | HCl | white diffusive body and cartridge code RAD169 |

**on top**:
**to the right**, ***radiello-ready-to-use***
**to the left**, the diffusive body with the polycarbonate cap and the adsorbing cartridge inside

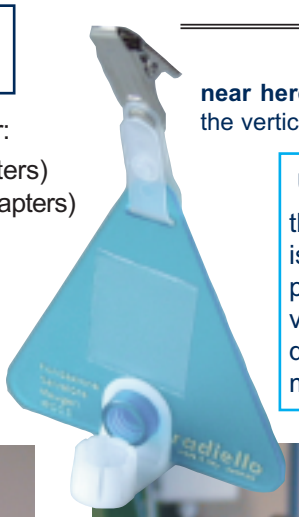
**in the center**: the special snapping adapter

**near here**: the supporting plate with the vertical snapping adapter

**IMPORTANT:** in the ready-to-use version ***the supporting plate is not provided***.

If you prefer ***to assemble it by yourselves***, you should order:

- ✓ diffusive bodies (of the required type, see following chapters)
- ✓ adsorbing cartridges (of the required type, see following chapters)
- ✓ polycarbonate caps, **code RAD1241**
- ✓ special snapping adapters, **code RAD1221**
- ✓ polypropylene containers, **code RAD1242**
- ✓ supporting plates, **code RAD121**



## user tip

the ***ready-to-use*** version of radiello is very useful in the workplace sampling campaigns but is not advised if very low concentrations in outdoor or domestic environments are to be measured



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# accessories

## vertical adapter

### code RAD122

**Available in 20 pieces per package only**

The diffusive body can be fitted to the supporting plate either in a vertical or horizontal position, the vertical one being more comfortable when ***radiello*** is used for personal sampling.

To assemble ***radiello*** in vertical position you have to screw it to the **vertical adapter code RAD122**, fitted to the supporting plate.

code RAD122

1 place the vertical adapter over the mounting point on the plate

2 press the adapter onto the plate with your thumbs till the ridge fits the edge of the plate.

The adapter can be removed from the plate by lifting the ridge

**IMPORTANT**

when mounting the diffusive body be careful to keep it vertical with the thread upside (see page A6).

## shelter

### code RAD196

For outdoor exposures a mountable polypropylene shelter is available which can be hanged to lamp posts.

**Available in 10 pieces per package only**

It has been designed to be mounted easily and without any tool on field, so that it is not cumbersome when you transport it from your laboratory. Once assembled, it ensures the best compromise between protection against bad weather and ventilation.

It can house up to four ***radiello*** and is able to fit a wide range of pole diameters.

Its colour is quite similar to that of the majority of lampposts: being less visible, it is less subject to acts of vandalism.

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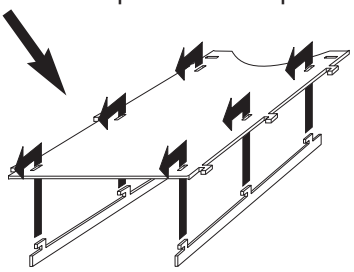
Il riparo è formato da:

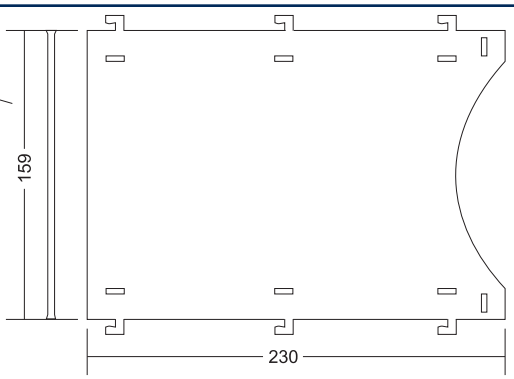
## how to assemble the shelter

All of the components are snap-on assembled.

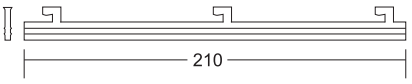
First of all, insert on this panel (the roof) the two supports that will be used to suspend the samplers.



One of the three equivalent panels will act as the roof of the shelter (quotes are in mm)

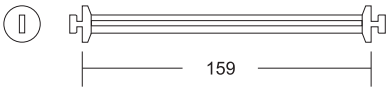


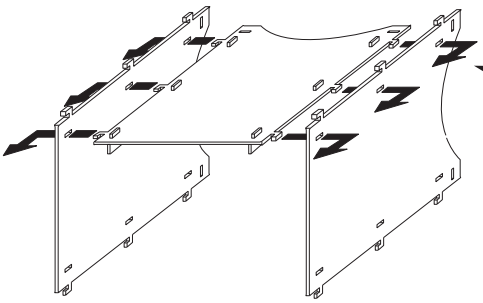

the two supports where to suspend *radiello*




two spacers

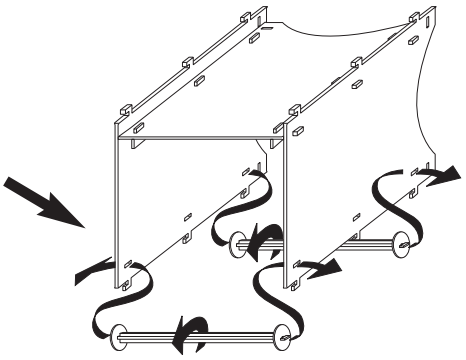
two strips

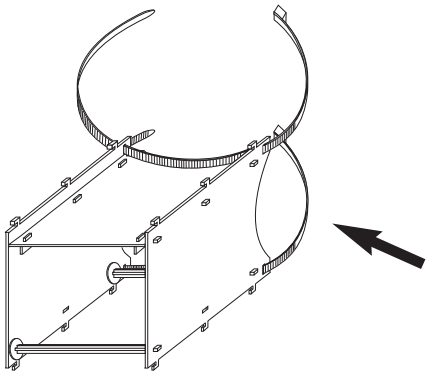


Then fix the two walls on the sides of the roof panel.

The whole becomes rigid by insertion of the two spacers. Fit them to the slots on bottom of the side panels and turn them by 90° (performing this rotation you may feel some resistance, but go on until you hear a clicking sound).





Finally, insert two plastic strips in the rear vertical slots of the side panels. The **strips** are also available as spare parts, in 100 pieces per package, identified by the **code RAD198**.

Suspend the shelter to the pole by closure of the strips, but ***DO NOT DRAW SO MUCH THAT THE SHELTER IS DEFORMED***. If the pole has diameter larger than 20 cm, the shelter leans on the curved edges on the rear of the sidewalls. If the pole has a smaller diameter, it leans against the curved edge of the roof panel and the rear spacer. If the diameter of the pole is very small the shelter bows down, the wind may make it go round, or the shelter may even slip down to ground. It is then advisable to choose another pole.

### user tip

If the pole diameter is larger than the strip length, you can put two or more strips together to extend the fastening system.

If the sampling site is very windy, do not introduce more than two ***radiello*** samplers in each shelter, otherwise rain could dampen the outermost samplers.

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# On-field temperature measurements

## codes RAD126 and RAD127

Since the uptake rate values of ***radiello*** depend on temperature, the concentration values obtained will be more accurate if precise temperature measurements are performed during the sampling.

To get reliable temperature data you may ask the local weather station, if there is one, and if the measurements are performed nearby your sampling sites. Bear in mind that you should take into the account the urban heat island: did you know that there can be a difference of even 4-5 °C between the center and the suburbs of a big town?

With ***radiello*** you can create your own temperature measurement station.

**thermometer code RAD126**
Available in 3 pieces per package only

A **thermometer** with precision ± 0,5 °C between -20 and 80 °C and equipped with a data logger capable of recording 2048 data points has been fixed to a vertical adapter (**code RAD126**). It is tiny enough (< 1 $cm^3$) to go perfectly unobserved.

It has no battery to replace, needs no maintenance and works properly even with bad weather conditions.

Its memory allows you to record one temperature value every 15 minutes for 22 days, or every 30 minutes for 43 days, or every 60 minutes for 85 days, or... it lasts ten years or a million readings!

The thermometer is fitted to the supporting plate of ***radiello***: use the sampler normally and measure temperature and pollution at the same time.

A very simple **reader** (**code RAD127**), connected to your PC by a serial port, allows you to program the temperature sensor for the measurements on field, to download the aquired data and to perform data statistical and graphic processing by a very user-friendly software.

One reader serves an unlimited number of thermometers. The *SmartButton Reader Solution* software needed to program the thermometers and download the data can be purchased from the parent company's website at the link:

http://www.acrsystems.com

**reader code RAD127**
single unit, serial port adapter included

### user tip

When performing urban monitoring install a thermometer every ten sampling sites. IIf this may help you, contact us to discuss sampling strategies.

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# calibration solution for $H_2S$

## code RAD171

Code RAD171 relieves you from the task of preparing the sodium sulfide standard solution for the calibration curve used for the determination of $H_2S$ by the cartridge code 170 (see page H1).

Since sodium sulfide is deliquescent, its weight is not a primary standard and sodium sulfide solution need titration once prepared. Moreover, titration must be repeated often due to the instability of diluted solution (one hour time is sufficient to decrease sulfide content by 10%).

Code RAD171 is a methylene blue concentrated solution that, once diluted 1:50, provides the same absorbance value at 665 nm of a sodium sulfide solution of with concentration 1.145 µg·ml$^{-1}$ sulfide ions.

This concentration value has been chosen to obtain the highest absorbance value within the linearity range of the spectrophotometer.

To obtain a complete calibration curve, just dilute the mother solution as shown in the table.

| Solution | ml of | ml of water | equivalent to µg.ml$^{-1}$ of $S^=$ |
|---|---|---|---|
| A | 2 di codice 171 | 98 | 1.145 |
| B | 25 di A | 25 | 0.572 |
| C | 10 di A | 40 | 0.229 |
| D | 5 di A | 45 | 0.115 |

Code RAD171 allows you to prepare as many as 50 calibration curves.

Kept closed at room temperature, code RAD171 solution is stable for at least one year.

# filtration kit

## code RAD174

Code RAD174 filtration kit is composed by 20 single use plastic syringes and 20 single use micropore hydrophilic polypropylene filters with diameter 13 mm and 0.45 µm porosity.

Both filter and syringe are suited to filtration of aqueous solutions with pH in the range of 0 to 12 with commonplace eluents for ion chromatography and reverse phase HPLC.

# calibration solutions for aldehydes

## code RAD302

Calibration curves for aldehydes are obtained with standard solutions of the corresponding 2,4-dinitrophenylhydrazones (see page C1). Although their synthesis is straightforward, their purification is tricky and time-consuming. Code RAD302 offers a certified and convenient choice: a solution of nine 2,4-dinitrophenylhydrazones in a solvent compatible with HPLC eluents and with concentrations suitable for the preparation of calibration curves in the range usually spanned by ***radiello*** samples.

Code RAD302 is delivered as 10 ml of acetonitrile solutions of the nine 2,4-dinitrophenylhydrazones formed by the aldehydes listed in the table, contained in a pierceable-septum crimped cap vial. The listed concentration values are indicative, actual ones are certified for each lot.

Kept tightly capped in a dark place at 4 °C, the solution is stable for at least four months.

| 2,4-DNPH of | µg·ml$^{-1}$ as aldehyde |
|---|---|
| formaldehyde | 50 |
| acetaldehyde | 50 |
| acrolein | 10 |
| propanal | 50 |
| butanal | 50 |
| isopentanal | 50 |
| pentanal | 50 |
| hexanal | 50 |
| benzaldehyde | 50 |

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# calibration solutions for BTEX ($CS_2$ desorption)

## code RAD405

Code RAD405 calibration kit has been conceived for the analysis of BTEX sampled in urban environments by the cartridge code RAD130 and chemically desorbed by carbon disulfide (see page D1).

The kit may be used both for routine calibration and for scheduled quality control of the calibration procedure described on page D4.

It is composed of 12 code RAD130 cartridges, three of which are blanks and nine, divided into three groups of three, preloaded with BTEX to simulate 7 days exposures (10,080 minutes) to the concentrations listed in the table. The values shown are indicative, actual ones are certified for each lot.

The mass of each analyte deposited onto the cartridge spans the whole range of concentrations usually found in urban environments, extreme values included.

BTEX loading is performed by injection of precisely known amounts of vaporized standard solutions in $CS_2$ of the five compounds under nitrogen flow.

Kept at 4 °C, the cartridges are stable for at least four months.

| code RAD405 | simulated concentrations in $\mu g \cdot m^{-3}$ (7 days exposure equivalent) | | |
|---|---|---|---|
| | Group 1 | Group 2 | Group 3 |
| benzene | 1 | 10 | 50 |
| toluene | 2 | 20 | 100 |
| ethylbenzene | 1 | 10 | 50 |
| m-xylene | 1 | 10 | 50 |
| p-xylene | 1 | 10 | 50 |
| o-xylene | 1 | 10 | 50 |

# calibration solutions for VOCs in workplace environments

## code RAD406

The code RAD406 kit has been conceived for scheduled quality control of the calibration procedure for the analysis of volatile organic compounds (VOCs) sampled by code RAD130 cartridges in workplace environments (see page D4).

It is composed of 12 code RAD130 cartridges, three of which are blanks and nine, divided into three groups of three, preloaded with VOCs to simulate 8 hours exposures (480 minutes) to the concentrations listed in the table. The values shown are indicative, actual ones are certified for each lot.

The composition of the mixture is simple but it includes compounds with different polarity. The loaded mass is calculated in order to represent exposures to 0.5, 1 and 2 times the TLV value for the mixture.

| code RAD406 | simulated concentrations in $mg \cdot m^{-3}$ (8 hours exposure equivalent) | | |
|---|---|---|---|
| | Group 1 | Group 2 | Group 3 |
| benzene | 0.1 | 0.2 | 0.4 |
| toluene | 19 | 38 | 76 |
| ethylbenzene | 12 | 24 | 48 |
| m-xylene | 12 | 24 | 48 |
| p-xylene | 12 | 24 | 48 |
| o-xylene | 12 | 24 | 48 |
| butanol | 15 | 30 | 60 |
| 2-etoxyiethyl acetate | 2.5 | 5 | 10 |

VOCs loading is performed by injection of precisely known amounts of calibrated mixtures of the eight compounds under nitrogen flow.

Kept at 4 °C, the cartridges are stable for at least four months.

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# calibration solutions for BTEX (thermal desorption)

| code RAD407 | simulated concentrations in µg·m$^{-3}$ (7 days exposure equivalent) | | |
|---|---|---|---|
| | Group 1 | Group 2 | Group 3 |
| benzene | 1 | 5 | 25 |
| toluene | 2 | 10 | 50 |
| ethylbenzene | 1 | 5 | 25 |
| m-xylene | 1 | 5 | 25 |
| p-xylene | 1 | 5 | 25 |
| o-xylene | 1 | 5 | 25 |

## code RAD407

Code RAD407 calibration kit has been conceived for the analysis of BTEX sampled in urban environments by the cartridge code RAD145 and thermally desorbed (see VOCs - thermal desorption).

The kit may be used both for routine calibration and for scheduled quality control of the calibration procedure described on page E5.It is composed of 12 code RAD145 cartridges, three of which are blanks and nine, divided into three groups of three, preloaded with BTEX to simulate 7 days exposures (10,080 minutes) to the concentrations listed in the table.

The values shown are indicative, actual ones are certified for each lot.

BTEX loading is performed by injection of precisely known amounts of vaporized standard solutions in methanol of the five compounds under nitrogen flow. During the analysis the chromatographic peak of methanol will be visible. Kept at 4 °C, the cartridges are stable for at least four months.

# the spare parts

## Empty cartridge

Can be loaded by the customer with the desired adsorbent.
It is delivered with the two end caps and the glass tube.
**Available in 20 pieces per package only.**

## Barcode adhesive label

**Codice RAD190**
**Available in 198 pieces per package only**

**codice RAD175**
stainless steel net, 100 mesh, 5.9 mm

**codice RAD176**
stainless steel net, 100 mesh, 4.9 mm diameter

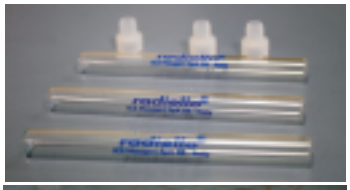
**codice RAD177**
stainless steel net, 3x8 µm, 4.9 mm diameter

## Clips

**Code RAD195**
**Available in 20 pieces per package only.**

## Tubes

**Available in 20 pieces per package only.**



**code RAD1991**
glass tube, working volume 2.8 ml

**code RAD1992**
polypropylene tube, working volume 12 ml

## Strip

**Code RAD198**
Useful for repositioning of *radiello* shelter.
Lenght 75 cm.
**Available in 100 pieces per package only.**

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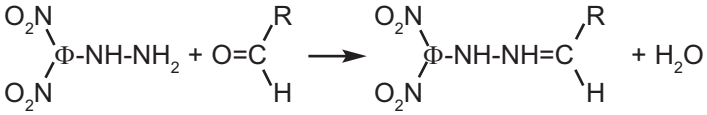
# Aldehydes

## what you need

**blue diffusive body code RAD1201**
**supporting plate code RAD121**
**vertical adapter code RAD122 (optional)**
**chemiadsorbing cartridge code RAD165**
**filtration kit code RAD174 (only for analysis)**

## Principle

Code 165 is a stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated Florisil®. Aldehydes react with 2,4-DNPH to give the corresponding 2,4-dinitrophenylhydrazones




2,4-DNPH aldehyde 2,4-DNPhydrazone

The 2,4-dinitrophenylhydrazones are then extracted with acetronitrile and analyzed by reverse phase HPLC and UV detection.

## Sampling rates

Sampling rates values at 298 K (25 °C) and 1013 hPa are listed below:

| | sampling rate ml·min$^{-1}$ | linearity range µg·m$^{-3}$·min | limit of quantitation[1] µg·m$^{-3}$ | uncertainty at 2σ % |
|---|---|---|---|---|
| acetaldehyde | 84 | 1,000÷12,000,000 | 0.1 | 15.9 |
| acrolein | 33 | 3,000÷3,000,000 | 0.3 | 16.5 |
| benzaldehyde | 92 | 1,000÷8,000,000 | 0.1 | 17.2 |
| butanal | 11 | 9,000÷10,000,000 | 0.9 | 23.5 |
| hexanal | 18 | 5,000÷15,000,000 | 0.6 | 20.2 |
| formaldehyde | 99 | 1,000÷4,000,000 | 0.1 | 13.8 |
| glutaric aldehyde | 90 | 1,000÷3,000,000 | 0.1 | 14.5 |
| isopentanal | 61 | 1,500÷12,000,000 | 0.2 | 17.0 |
| pentanal | 27 | 4,000÷12,000,000 | 0.4 | 22.9 |
| propanal | 39 | 3,000÷8,000,000 | 0.3 | 17.1 |

[1]after 7 days exposure

### Effect of temperature, humidity and wind speed

Sampling rate varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation:

$$Q_K = Q_{298} \left(\frac{K}{298}\right)^{0.35}$$

where $Q_K$ is the sampling rate at the temperature K and $Q_{298}$ is the reference value at 298 K. This produces a variation of ± 1% for 10 °C variation (upwards or downwards) from 25 °C.

Sampling rate is invariant with humidity in the range 15-90% and with wind speed between 0.1 and 10 m·s$^{-1}$.

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## Calculations

The average concentration ***C*** over the whole sampling time (in $\mu g \cdot m^{-3}$) is calculated according to the expression:

$$C\ [\mu g \cdot m^{-3}] = \frac{m\ [\mu g]}{Q\ [ml \cdot min^{-1}] \cdot t\ [min]}\ 1{,}000{,}000$$

where:
***m*** = mass of aldehyde in µg
***t*** = exposure time in minutes

## Exposure

The optimum exposure duration varies with the expected concentration. Taking formaldehyde as an example, concentration values of 5-30 $\mu g \cdot m^{-3}$ are usually found in outdoor urban measurements while 20-200 $\mu g \cdot m^{-3}$ are expected in workplace environments. In workplace environments concentrations may be as high as 2,000-3,000 $\mu g \cdot m^{-3}$ for short time intervals: it can therefore be interesting to evaluate the peak value (usually referred to by *STEL*). The corresponding advised exposure time is shown in the table below:

**Advised exposure times**

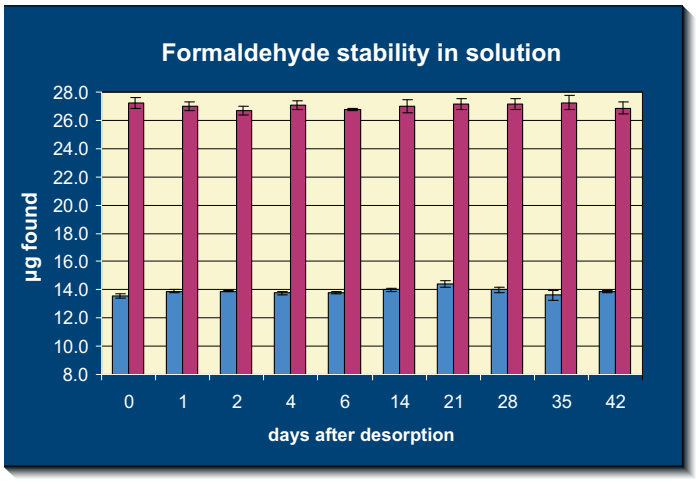
| | outdoor environment | indoor environment | workplace environment average conc. | workplace environment peak conc. |
|---|---|---|---|---|
| minimum | 8 h | 8 h | 2 h | 15 minutes |
| maximum | 7 days | 7 days | 8 h | 1 h |

Do not expose all of the cartridges belonging to the same lot: keep at least two cartridges as blanks.

## Storage

The cartridges need to be kept, properly sealed, in a dark place at 4 °C for ensuring a shelf life (according to EN 13528-2) of six months. If stored at -18 °C, the shelf life will be twelve months. Each lot is approved for use when the blank value of formaldehyde and acetaldehyde are less than 0.1 µg and 0.3 µg per cartridge, respectively, corresponding to a concentration in air less than 0.1 and 0.25 µg·m-3 over one week of exposure, respectively. The blank value may increase with time.

After exposure keep the cartridges well capped at 4 °C,




*Formaldehyde stability in the cartridge after the sampling (on top) and in solution (left). The stability tests were performed upon cartridges exposed for one week in a standard atmosphere chamber at 25 °C and with 50% relative humidity and at two different concentration levels. Each bar in the plot represents the average and error from the analysis of six samples.*

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they are stable for 60 days. After solvent desorption (see *Analysis*) discard the cartridge. The resulting solution, well capped and stored at 4 °C, is stable for at least 42 days.

## Analysis

### Desorption

Materials
- HPLC grade acetonitrile
- class A volumetric pipette, capacity 2 ml
- micropore filter membranes, porosity 0.45 µm, solvent resistant

Procedure
Introduce 2 ml acetonitrile directly in the cartridge tube, recap and stir from time to time for 30 minutes. Discard the cartridge. Filter the resulting solution and keep it well capped until analysis time. If analysis has to be delayed, store the solution at 4 °C.

**user tip**

For a reliable and rapid filtration employ the filtration kit **code RAD174**.

To obtain an accurate calibration curve we offer you the calibration solution **code RAD302**.

### Instrumental analysis

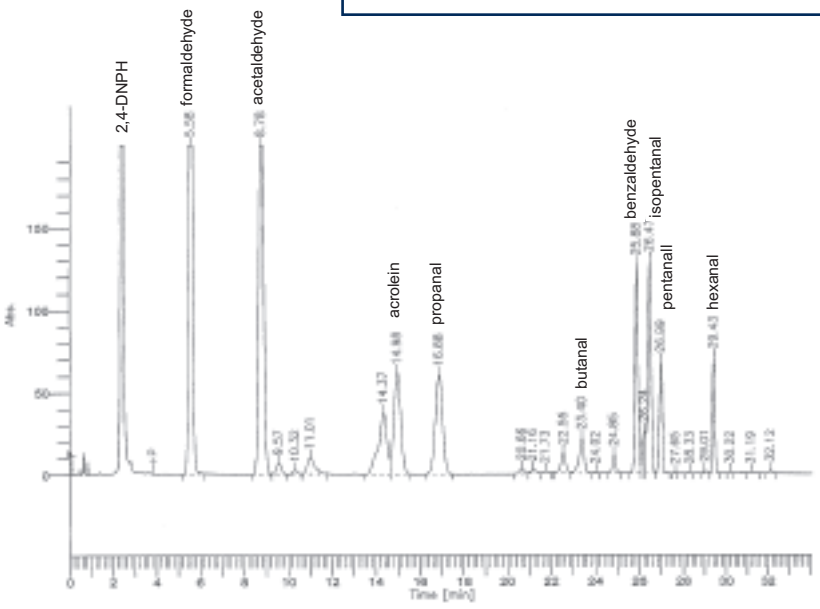
The method suggested below is only indicative; the analyst can choose an alternative method, on the basis of its personal experience.

**IMPORTANT:** verify the presence and the abundance of the 2,4-DNPH chromatographic peak: otherwise, the cartridge could be saturated.

Materials
- reverse phase $C_{18}$ HPLC column, length 150 mm, 4.6 mm diameter, 5 µm packing particle size
- HPLC apparatus capable of elution gradient and UV detection

Procedure
Set the detector at the wavelength of 365 nm. Inject between 10 and 50 µl of solution and elute as follow:
- flow: 1.9 ml·min$^{-1}$
- Isocratic elution with acetonitrile/water 38:62 v/v for 10 minutes, up to acetonitrile/water 75:25 v/v in 10 minutes, reverse gradient to acetonitrile/water 38:62 v/v in 5 minutes.

On the right: the chromatogram of a real sample analyzed under the described conditions.




*HPLC chromatogram of aldehydes sampled by* **radiello**

**IMPORTANT**

**Acrolein** gives place to three chromatographic peaks, two of them are unresolved. Calculate the concentration basing onto this most abundant peak and ignore the others.

**Isopentanal** appears as two unresolved peaks: its concentration should be obtained by integration of both peaks as a sum.

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**user tip**

If you perform several analyses, a barcode reader will greatly improve productivity in your laboratory and will also minimize the possibility of errors in the copying of sample labels.

Please contact us to help you in the implementation of the reader.

## Interferences

### Other carbonyl compounds

All carbonyl compounds, ketones included, react with 2,4-DNPH but do not interfere in the analysis if proper chromatographic parameters are selected.
In the described chromatographic conditions acetone-2,4-DNPH peak is well resolved from acrolein-2,4-DNPH. Neverthless, if acetone concentration is higher than 50,000 $\mu g \cdot m^{-3}$, acrolein-2,4-DNPH peak intensity is depressed by 25%.

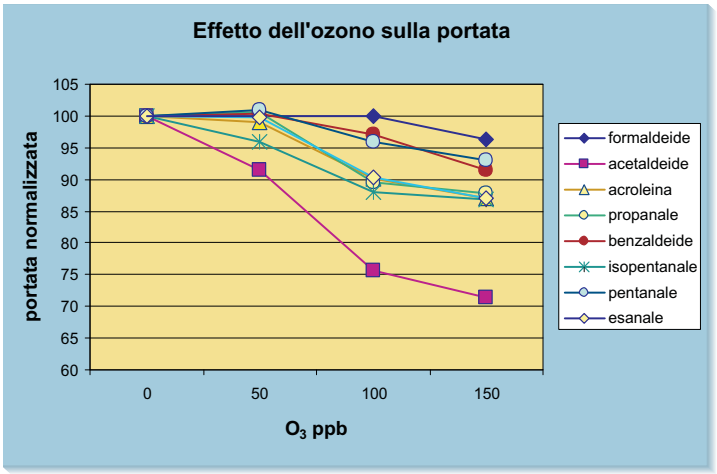
### Ozone

Examples of ozonolysis of dinitrophenylhydrazones on active supporting materials as silica gel are found in the literature.

On code 165 cartridge, packed with coated Florisil®, ozonolysis is much less important than on any other commercial aldehyde sampling device, either diffusive or pumped, and becomes appreciable only if ozone concentration, averaged over the whole exposure time interval, is higher than 100 ppb. Since this is not usually the case, generally no correction is needed to take into account ozone concentration. If there is firm evidence that ozone concentration is equal or higher than 100 ppb over the whole exposure time, make use of the corrected sampling rate values shown in the table below, where $[O_3]$ is ozone concentration in ppb.

The listed values are referred to the temperature of 298 K (25 °C), for deviations larger than ± 10 °C substitute the base value (e.g. 99 $ml \cdot min^{-1}$ for formaldehyde) with the corrected value calculated according to equation on page C1.

No experimental data is available for butanal and glutaric aldehyde.




*Portata di campionamento in funzione della concentrazione di ozono, posta uguale a 100 quella misurata a concentrazione zero di ozono. Con l'eccezione dell'acetaldeide, l'effetto dell'ozono diventa sensibile solo a concentrazione superiore a 100 ppb, intesa come valore medio dell'intero periodo di esposizione.*

| | corrected sampling rate $ml \cdot min^{-1}$ |
|---|---|
| acetaldehyde | 84-0.018$[O_3]$* |
| acrolein | 33-0.027$[O_3]$ |
| benzaldehyde | 92-0.05$[O_3]$ |
| hexanal | 18-0.02$[O_3]$ |
| formaldehyde | 99-0.02$[O_3]$ |
| isopentanal | 61-0.06$[O_3]$ |
| pentanal | 27-0.01$[O_3]$ |
| propanal | 39-0.03$[O_3]$ |

Sampling rate for ozone concentration $[O_3]$ in ppb (apply only if $[O_3]$ >100 ppb)

*applicare per concentrazioni di ozono pari o superiori a 50 ppb

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Edition 01/2019

# Volatile organic compounds (VOCs)

## chemically desorbed with $CS_2$

### what you need

**white diffusive body code RAD120**
**supporting plate code RAD121**
**vertical adapter code RAD122 (optional)**
**chemiadsorbing cartridge code RAD130**

**Or: radiello-ready-to-use code RAD1231**

### Principle

Code RAD130 cartridge is a stainless steel net cylinder, with 100 mesh grid opening and 5.8 mm diameter, packed with 530 ± 30 mg of activated charcoal, particle size is 35-50 mesh. Volatile organic compounds are trapped by adsorption and recovered by carbon disulfide displacementI, analysis is performed by FID gas chromatography.

### Sampling rates

The table on pages D2 and D3 lists sampling rate values at 298 K (25 °C) and 1013 hPa, experimentally measured in a standard atmosphere chamber. For other compounds whose diffusion coefficient[1] is known sampling rate can be calculated according to equation [5] on page working principle, taking into account that white diffusive body and code 130 cartridge give the geometric constant of radiello the value of 14.145 ± 0.110 cm. Several experiments performed in the standard atmosphere chamber demonstrate that the calculated sampling rates seldom deviate by more than ±10% from the experimentally measured values.

#### Effect of temperature, humidity and wind speed

Sampling rates varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation:

$$Q_K = Q_{298} \left(\frac{K}{298}\right)^{1,5}$$

where $\mathbf{Q_K}$ is the sampling rate at the temperature K and $\mathbf{Q_{298}}$ is the reference value at 298 K. This produces a variation of ±5% for 10 °C variation (upwards or downwards) from 25 °C.
Sampling rate is invariant with humidity in the range 15 ÷ 90% and with wind speed between 0.1 and 10 $m \cdot s^{-1}$.

[1]Lugg G.A.: Diffusion Coefficients of Some Organic and Other Vapors in Air. *Anal. Chem*. **40-7**:1072-1077 (1968).

### Calculations

The listed sampling rate values already take into account for the desorption efficiency with carbon disulfide. The average concentration over the exposure time interval is therefore calculated from the mass of analyte found onto the cartridge and exposure time without introducing any corrective factor, apart from corrections due to average temperature different from 25 °C.

Average concentration (in $\mu g \cdot m^{-3}$) over the whole exposure time is calculated according to the following expression:

$$C\ [\mu g \cdot m^{-3}] = \frac{m\ [\mu g]}{Q_K\ [ml \cdot min^{-1}] \cdot t\ [min]}\ 1{,}000{,}000$$

where:
**m** = mass of analyte in µg
**t** = exposure time in minutes

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# D2

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**Sampling rate values at 25°C (298 K)**

| | sampling rate $ml \cdot min^{-1}$ | linearity range $\mu g \cdot m^{-3} \cdot min$ | uncertainty at 2σ % | notes |
|---|---|---|---|---|
| acetone | 77 | $10{,}000\text{-}600 \cdot 10^6$ | 7.0 | **a** |
| acetonitrile | 73 | $10{,}000\text{-}6 \cdot 10^6$ | 8.2 | **b** |
| acrylonitrile | 75 | $1{,}000\text{-}50 \cdot 10^6$ | 2.2 | |
| benzyl alcohol | 37 | $1{,}000\text{-}800 \cdot 10^6$ | 6.5 | |
| amyl acetate | 52 | $1{,}000\text{-}800 \cdot 10^6$ | 3.4 | |
| benzene | 80 | $500\text{-}500 \cdot 10^6$ | 1.8 | |
| bromochloromethane | 70 | $50{,}000\text{-}1{,}000 \cdot 10^6$ | 1.4 | |
| butanol | 74 | $1{,}000\text{-}500 \cdot 10^6$ | 5.0 | |
| *sec*-butanol | 64 | $1{,}000\text{-}300 \cdot 10^6$ | 5.2 | |
| *tert*-butanol | 62 | $1{,}000\text{-}300 \cdot 10^6$ | 5.5 | |
| butyl acetate | 60 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 3.0 | |
| 2-butoxyethanol | 56 | $1{,}000\text{-}100 \cdot 10^6$ | 5.7 | |
| 2-butoxyethyl acetate | 41 | $1{,}000\text{-}100 \cdot 10^6$ | 5.5 | |
| carbon tetrachloride | 67 | $100{,}000\text{-}60 \cdot 10^6$ | 9.0 | |
| cyclohexane | 54 | $500\text{-}500 \cdot 10^6$ | 4.5 | |
| cyclohexanone | 68 | $5{,}000\text{-}120 \cdot 10^6$ | 4.2 | |
| cyclohexanol | 54 | $5{,}000\text{-}120 \cdot 10^6$ | 4.5 | |
| chlorobenzene | 68 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 3.6 | |
| chloroform | 75 | $100{,}000\text{-}60 \cdot 10^6$ | 9.7 | **a** |
| n-decane | 43 | $500\text{-}1{,}000 \cdot 10^6$ | 1.1 | |
| diaceton alcohol | 43 | $500\text{-}1{,}000 \cdot 10^6$ | 4.5 | |
| 1,4-dichlorobenzene | 51 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 7.7 | |
| 1,2-dichloroethane | 77 | $1{,}000\text{-}500 \cdot 10^6$ | 8.2 | |
| 1,2-dichloropropane | 66 | $500\text{-}250 \cdot 10^6$ | 4.5 | |
| dichloromethane | 90 | $500\text{-}60 \cdot 10^6$ | 8.7 | |
| N,N-dimetylformamide | 82 | $1{,}000\text{-}200 \cdot 10^6$ | 14.5 | **c** |
| 1,4-dioxane | 68 | $1{,}000\text{-}600 \cdot 10^6$ | 5.5 | |
| n-dodecane | 8 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 4.7 | |
| n-heptane | 58 | $5{,}000\text{-}1{,}500 \cdot 10^6$ | 3.0 | |
| n-hexane | 66 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 2.5 | |
| 1-hexanol | 52 | $5{,}000\text{-}120 \cdot 10^6$ | 5.5 | |
| ethanol | 102 | $10{,}000\text{-}500 \cdot 10^6$ | 7.5 | **a-b** |
| diethyl ether | 78 | $5{,}000\text{-}500 \cdot 10^6$ | 12.0 | **a** |
| ethyl acetate | 78 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 1.5 | |
| ethylbenzene | 68 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 2.4 | |
| 2-ethyl-1-hexanol | 43 | $5{,}000\text{-}500 \cdot 10^6$ | 10.1 | |
| 2-ethoxyethanol | 55 | $500\text{-}50 \cdot 10^6$ | 6.7 | **b** |
| 2-ethoxyethyl acetate | 54 | $10{,}000\text{-}100 \cdot 10^6$ | 2.5 | |
| ethyl-*tert*-butyl ether (ETBE) | 61 | $500\text{-}200 \cdot 10^6$ | 3.0 | |
| isobutanol | 77 | $1{,}000\text{-}300 \cdot 10^6$ | 2.5 | |
| isobutyl acetate | 63 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 5.2 | |
| isooctane | 55 | $500\text{-}1{,}000 \cdot 10^6$ | 3.2 | |
| isopropanol | 52 | $10{,}000\text{-}400 \cdot 10^6$ | 12.0 | **b** |
| isopropyl acetate | 66 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 9.9 | |
| isopropylbenzene | 58 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 2.7 | |
| limonene | 43 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 10.0 | |
| methanol | 125 | $10{,}000\text{-}250 \cdot 10^6$ | 9.2 | **a-b** |
| methyl acetate | 80 | $1{,}000\text{-}1{,}000 \cdot 10^6$ | 12.0 | |
| methyl-*ter*-butyl ether (MTBE) | 65 | $500\text{-}200 \cdot 10^6$ | 2.5 | |

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| | sampling rate ml·min$^{-1}$ | linearity range µg·m$^{-3}$·min | uncertainty at 2σ % | notes |
|---|---|---|---|---|
| methylcyclohexane | 66 | 1,000-1,000·10$^6$ | 6.5 | |
| methylcyclopentane | 70 | 1,000-1,000·10$^6$ | 2.5 | |
| methylethylketone | 79 | 1,000-500·10$^6$ | 1.6 | |
| methylisobutylketone | 67 | 1,000-250·10$^6$ | 8.7 | |
| methyl metacrylate | 68 | 1,000-500·10$^6$ | 2.5 | |
| 2-methylpentane | 70 | 1,000-1,000·10$^6$ | 2.5 | |
| 3-methylpentane | 70 | 1,000-1,000·10$^6$ | 2.5 | |
| 2-methoxyethanol | 35 | 5,000-100·10$^6$ | 11.0 | **b** |
| 2-methoxyethyl acetate | 56 | 2,000-100·10$^6$ | 3.0 | |
| 1-methoxy-2-propanol | 55 | 1,000-350·10$^6$ | 6.0 | |
| 1-methoxy-2-propyl acetate | 60 | 2,000-350·10$^6$ | 6.2 | |
| naphtalene | 25 | 1,000-1,000·10$^6$ | 7.0 | |
| n-nonane | 48 | 1,000-1,000·10$^6$ | 5.4 | |
| n-octane | 53 | 500-1,000·10$^6$ | 3.2 | |
| pentane | 74 | 1,000-1,000·10$^6$ | 1.9 | |
| α-pinene | 53 | 1,000-1,000·10$^6$ | 7.0 | |
| propyl acetate | 65 | 500-1,000·10$^6$ | 7.5 | |
| propylbenzene | 57 | 1,000-1,000·10$^6$ | 2.9 | |
| styrene | 61 | 1,000-500·10$^6$ | 3.0 | |
| tetrachloroethylene | 59 | 10,000-500·10$^6$ | 2.5 | |
| tetrahydrofuran | 74 | 2,000-250·10$^6$ | 11.0 | **b** |
| toluene | 74 | 500-1,000·10$^6$ | 1.5 | |
| 1,1,1-trichloroethane | 62 | 5,000-1,000·10$^6$ | 5.5 | |
| trichloroethylene | 69 | 5,000-1,000·10$^6$ | 2.4 | |
| 1,2,4-trimethylbenzene | 50 | 500-1,000·10$^6$ | 6.6 | |
| n-undecane | 24 | 1,000-1,000·10$^6$ | 10.0 | |
| m-xylene | 70 | 500-1,000·10$^6$ | 2.5 | |
| o-xylene | 65 | 500-1,000·10$^6$ | 2.5 | |
| p-xylene | 70 | 500-1,000·10$^6$ | 2.5 | |

Notes:

**a** = weakly adsorbed compound. If its concentration is higher than the TLV for the workplace environments it may be partially displaced by other compounds that are more strongly trapped if their concentration is also high. If this is the case, it is advisable to reduce sampling time under 8 hours.

**b** = prolonged exposure of charcoal cartridges at relative average humidity higher than 80% causes adsorption of up to 100 mg of water. Water does not interfere with adsorption mechanisms but is displaced by carbon disulfide and gives raise to a separate layer. Some very water soluble polar compounds will distribute between the two solvents, thus provoking an underestimation of the actual air concentration since only the carbon disulfide is injected in the gas chromatograph. When the concentration of polar compounds has to be determined, the calibration curve should be prepared by spiking 50 µl of water in each tube containing the cartridge and the 2 ml of carbon disulfide standard solution (see Analysis).

**c** = better reproducibility obtained by use of methanol as extraction solvent instead of carbon disulfide.

## Limit of quantitation

The limit of quantitation depends on the instrumentation and on the analytical conditions. The minimum revealable environmental concentration can be estimated on the basis of the equation on chapter Calculations, where m is the minimum revealable mass, experimentally measured for each compound. Under the analytical conditions described on the following chapter Analysis, the limit of quantitation for 7 days exposure usually ranges from 0.05 and 1 µg·m$^{-3}$, depending on the compound.

In any case, the limit of quantitation can never be lower than the inferior limit of the linearity range indicated in the previous table.

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# D4

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## Exposure

Code RAD130 cartridge has a very large loading capacity: about 80 mg, corresponding to an overall VOCs concentration of 3,000 - 3,500 mg·m$^{-3}$ sampled for 8 hours or 70,000 - 80,000 µg·m$^{-3}$ sampled for 14 days. Neverthless, if the quantified overall adsorbed mass should be near 80 mg, sampling rate could have deviated from linearity. If this is the case, it is advisable to repeat the sampling experiment reducing exposure time.

### Workplace environment

In workplace environments complex mixtures of airborne solvent vapours are often found at concentrations 2,000-3,000 mg·m$^{-3}$. The outstanding adsorbing capacity of code RAD130 cartridges allows you to sample them for the whole working shift of 8 hours. On the other hand, the very high values of sampling rates for a variety of compounds allow you to perform accurate concentration measurements even after very short exposures. For example, 15 minutes are enough to measure 0.1 mg·m$^{-3}$ of benzene.

radiello can therefore be employed to evaluate both **TWA** and **STEL** concentrations.

### Other indoor sampling experiments and outdoor campaigns

High sampling rates of radiello ensure very low limits of detection also for short exposure time intervals. For example, you may measure benzene concentrations as low as 2 µg·m$^{-3}$ with an error not exceeding 4% after 8 hours of exposure. If radiello is exposed for 7 days, limit of quantitation becomes 0.1 µg·m$^{-3}$.

Generally speaking, we suggest exposure time duration ranging from 8 hours to 30 days, the ideal value being 7 days.

## Storage

The activated charcoal cartridges have undergone a complex conditioning process that ensures an outstanding chromatographic blank level, never exceeding three times the instrumental noise of a FID detector at the lowest attenuation.

Kept in a cool place and away from volatile organic compounds, the cartridges mantain unchanging blank level and adsorbing capacity for at least two years. Expiry day and lot number are printed onto the plastic bag wrapping each cartridge: its integrity stands as warranty seal.

After exposure the cartridges, well capped and kept in a cool and solvent-free place, maintain their content unalterated for at least six months

## Analysis

### Extraction

Introduce 2 ml of $CS_2$ and 100 µl of internal standard solution (see next) directly in the radiello glass tube without drawing out the cartridge. Always use class A volumetric pipettes or dispensers. Stir from time to time for 30 minutes. If analysis is not performed soon after, draw out the cartridge and discard it.

**IMPORTANT**

always use high purity grade CS2, for example Honeywell cod. 342270.

**BE CAREFUL**

even refrigerated, $CS_2$ permeates the tube plastic cap: its volume decreases by 4-5% a day. If the internal standard has been added, it is only matter of unpleasant odour...

## Calibration

### outdoor environment sampling

If benzene, toluene, ethylbenzene and xylenes (BTEX) have to be analyzed, prepare three or four standard solutions in $CS_2$ having decreasing concentrations of the analytes in the following ranges (in mg·l$^{-1}$):

| | | | |
|---|---|---|---|
| benzene | 0.04 ÷ 17.6 | etilbenzene | 0.04 ÷ 17.7 |
| toluene | 0.09 ÷ 34.8 | m-xilene | 0.04 ÷ 17.2 |
| o-xilene | 0.04 ÷ 17.6 | p-xilene | 0.04 ÷ 17.2 |

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## Analysis of unknown samples

Identify the sample that has been exposed for the longest time or at the highest expected concentration. Introduce 2 ml of $CS_2$ but do not add the internal standard, stir and let the sample stand for 30 minutes. Without discarding the cartridge, inject the $CS_2$ solution in the gas chromatograph with FID detector (see below), identify the compounds appearing in the chromatogram and make an estimation of the order of magnitude of their concentrations.

**user tip**

For a very accurate calibration we offer the preloaded cartridges code 405 (outdoor environment) and code 406 (workplace environment).

Prepare a $CS_2$ solution of the identified compounds with doubled concentration with respect to the sample. Dilute this solution in order to obtain standard solutions of concentration respectively about 0.1, 0.5 and 1 times the concentration estimated in the sample. Introduce 2 ml of each standard solution onto a blank code RAD130 cartridge in its glass tube, along with the chosen internal standard solution.

The chosen **internal standard** should have a retention time that does not cause interference with other compounds in the chromatogram. Compatibly with this requirements, we suggest to employ a solution of 2-fluorotoluene (e.g. Aldrich F 1,532-3) in $CS_2$ with concentration of 100 $\mu l \cdot l^{-1}$ for outdoor samples and 2 $ml \cdot l^{-1}$ for workplace samples.

Add 2 ml of $CS_2$ and the internal standard to all of the samples, stir, let the samples stand for 30 minutes and discard the cartridges prior to the analysis.

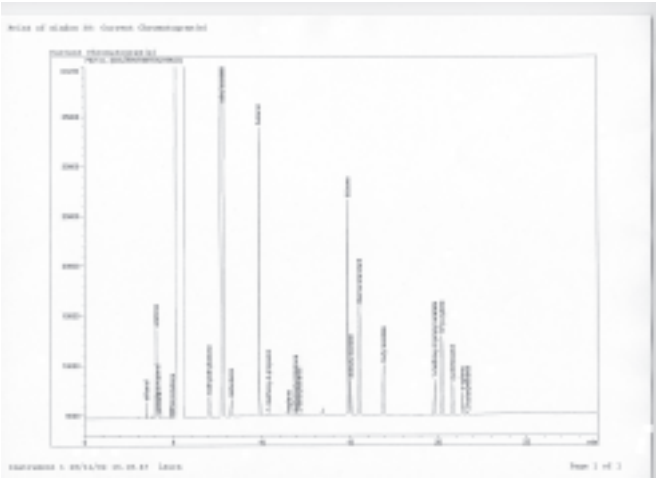
## Instrumental analysis (advised)

**Capillary gas chromatography with FID detection**

***outdoor environment samples:*** 100% dimethylpolysiloxane column 0.2 mm·50 m, film thickness 0.5 µm; split injection of 2 µl; split ratio 25:1; nitrogen carrier gas at constant pressure of 20 psi; injector temperature 240 °C; oven initial temperature 35 °C for 5 minutes, 5 $°C \cdot min^{-1}$ up to 90 °C, maintain for 3 minutes, 10 $°C \cdot min^{-1}$ up to 220 °C, final isotherm for 5 minutes.

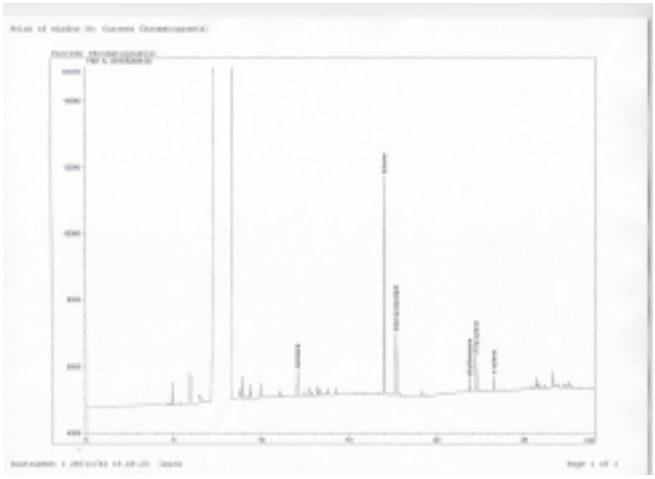
***workplace samples:*** 100% dimethylpolysiloxane column 0.2 mm·50 m, film 0.5 µm; split injection of 3 µl, split ratio 100:1; carrier $N_2$ at constant pressure of 20 psi; injector temperature 240 °C; oven initial temperature 50 °C for 5 minutes, 5 $°C \cdot min^{-1}$ up to 80 °C, 15 $°C \cdot min^{-1}$ up to 135 °C, 20 $°C \cdot min^{-1}$ up to 220 °C, final isotherm 10 minutes. Total time: 29 minutes.

The retention times for several compounds analyzed under the described conditions are listed in the table on next page.



**On top:** *FID chromatogram of a real workplace sample*

**on the left:** *chromatogram of a real urban outdoor sample*



**USER TIP**

If you perform several analyses, a barcode reader will greatly improve productivity in your laboratory and will also minimize the possibility of errors in the copying of sample labels.

Please contact us to help you in the implementation of the reader.

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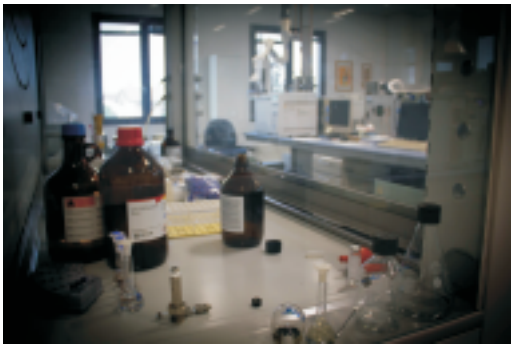
## Perchè la cartuccia codice 130 non ha eguali?

| | retention time (minutes) |
|---|---|
| methanol | 4.834 |
| ethanol | 5.340 |
| acetone | 5.712 |
| isopropanol | 5.835 |
| pentane | 6.121 |
| methyl acetate | 6.346 |
| dichloromethane | 6.405 |
| 2-methylpentane | 7.559 |
| methylethylketone | 7.719 |
| 3-methylpentane | 7.941 |
| ethyl acetate | 8.331 |
| n-hexane | 8.402 |
| isobutanol | 8.763 |
| methylcyclopentane | 9.350 |
| 1,1,1-trichloroethane | 9.636 |
| butanol | 9.956 |
| isopropyl acetate | 9.978 |
| benzene | 10.203 |
| 1-methoxy-2-propanol | 10.424 |
| cyclohexane | 10.580 |
| 1,2-dichloropropane | 11.285 |
| trichloroethylene | 11.625 |
| isooctane | 11.667 |
| 2-ethoxyethanol | 11.831 |
| propyl acetate | 11.868 |
| n-eptane | 12.068 |
| 1-ethoxy-2-propanol | 12.775 |
| methylcyclohexane | 12.912 |
| methylisobutylketone | 13.258 |
| isobutyl acetate | 14.005 |
| toluene | 14.055 |
| butyl acetate | 15.279 |
| n-octane | 15.435 |
| tetrachloroethylene | 15.601 |
| diaceton alcohol | 15.915 |
| 1-methoxy-2-propyl acetate | 16.609 |
| ethylbenzene | 16.997 |
| m+p-xylene | 17.241 |
| cyclohexanone | 17.436 |
| cyclohexanol | 17.436 |
| styrene | 17.716 |
| o-xylene | 17.832 |
| 2-buthoxyethanol | 17.880 |
| n-nonane | 18.186 |
| α-pinene | 19.129 |
| n-decane | 20.334 |
| n-undecane | 22.142 |

### the container

The container is realised by stainless steel cloth AISI 316 with 100 mesh opening. It is electric welded with no supply of foreign materials. It has tolerance of ±0.05 mm diameter and of ±0.1 mm length.

### the contents



The cartridge is packed with vegetal activated charcoal with a very large adsorbing surface. Its exceptionally low blank is obtained by conditioning it in a nitrogen stream fluidised bed at 450 °C for 16 hours.

The fluidised bed technique does not only guarantee the thorough purification of adsorbing material but also performs an accurate selection of its granulometry, by ventilation separations of the fraction under 50 mesh and over 35 mesh.

### the production

The cartridge is filled up with charcoal by a very complex automated apparatus that was designed and realised in our laboratory. It avoids any contamination of the adsorbing material during the delicate process of cartridge production and ensures a very accurate dosing of the material itself, providing a variability of less than 2% of the weight of the activated charcoal among the cartridges.

### the quality controls

Each cartridge batch undergoes statistical quality control of the blank level. If amounts higher than 20 ng of each of the BTEX compounds are found, the entire lot is discarded.

### sampling rate measurements

The sampling rate is measured in a standard atmosphere chamber unique in Italy and one of the few found all over Europe.

It allows the dynamic generation of high flows of controlled concentration gas mixtures from 1 $\mu g \cdot m^{-3}$ to 1,000 $mg \cdot m^{-3}$ (dynamic range from 1 to 106) of each investigated compound alone or mixed with others. The chamber allows temperature control from -20 to 60 °C, relative humidity control from 5% to 100% and air speed variation from 0.1 to 10 $m \cdot s^{-1}$.

All of the gas flows are measured as mass flows and have therefore the properties of primary standards. All of the operating parameters (gas flows, temperature, relative humidity, ...) are recorded and the records are available along with the certification documents.

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# Volatile organic compounds (VOCs)

## thermally desorbed

### what you need

**yellow diffusive body code RAD1202**
**supporting plate code RAD121**
**vertical adapter code RAD122 (optional)**
**chemiadsorbing cartridge code RAD145**

### Principle

Code RAD145 is a stainless steel net cylinder, with 3x8 µm mesh opening and 4.8 mm diameter, packed with 350 ± 10 mg of graphitised charcoal (Carbograph 4), particle size is 35-50 mesh.

Volatile organic compounds are trapped by adsorption and recovered by thermal desorption, analysis is performed by capillary gas chromatography and FID or MS detection.

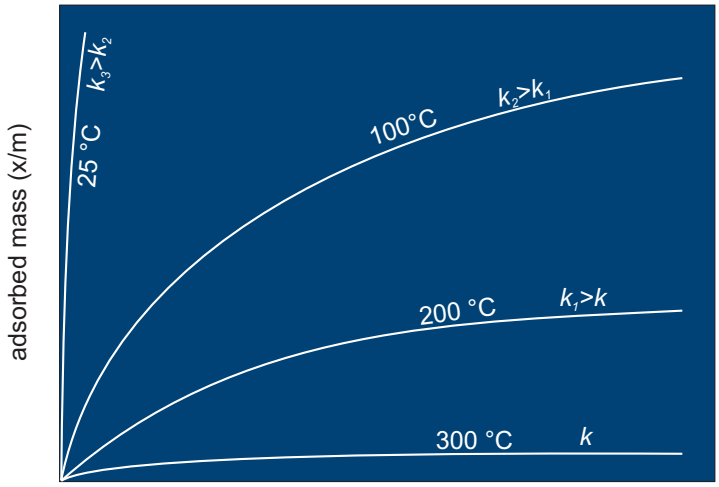
### General considerations

Thermal desorption is an easy-to-use technique, but it implies some precautions and is of less general use than chemical desorption.

The recovery of adsorbed compounds is based onto the different shape of adsorption isotherms at different temperatures. Since quantitative desorption of trapped molecules should ideally be accomplished at moderate temperatures, only weak adsorbing media are employed, with active adsorbing surface between 10 and 50 times smaller than that of activated charcoal.

Use of thermal desorption requires therefore an accurate preliminary investigation about the adsorbed compound - adsorbing medium pair. Stronger adsorbents are suitable for very volatile compounds, but will yield only partial desorption of heavier compounds.

Anyway, *backdiffusion* (see page A3) is always lying in wait: due to the adsorbing medium weakness heavier compounds will eventually displace the more volatile ones. Once you have made an accurate choice of the adsorbing material, therefore, you should bear in mind that a real atmosphere is composed by a variety of compounds apart from those you are analyzing at unpredictable concentrations. As a consequence, sampling times can not be as long as those allowed by activated charcoal, otherwise lighter compounds will be lost. With the purpose of allowing reasonable sampling times (up to two weeks) the sampling rate has been dramatically reduced by changing the diffusive body from the white type (code RAD120) to the yellow one (code RAD1202). Smaller average pore size and thicker diffusive membrane make the diffusive path longer and, as a consequence,




concentration in gaseous phase (C)

*When in contact with a solid adsorbing medium, a gaseous compound will be adsorbed following the* Freundlich isotherm*, that is to say the adsorbed mass will be* $x/m=kC^{1/n}$*, where* x *is the mass of gaseous compound adsorbed by the mass m of the solid adsorbent and C is the concentration of the gaseous compound at the equilibrium in the gas phase. K and n depend on temperature and on the adsorbate - adsorbing medium pair. K increases with decreasing temperature and n is the closer to 1 the stronger the adsorbent.*

*At low temperatures,* x/m *depends almost linearly on the concentration in air (see the curve at 25 °C): this allows diffusive sampling. At high temperatures, the adsorbent mass is very low whatever the concentration in the gas phase: this allows the recovery of adsorbed compounds by heating (see the curve at 300 °C).*

*To ensure the best possible recovery yields, k and n have to be small. This, however, will compromise sampling efficiency. In other words, compounds strongly adsorbed at room temperature will be only partially recovered by thermal desorption. On the other hand, compounds that are easily desorbed by heating will be sampled at room temperature with low efficiency.*

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sampling rates are reduced to less than one third compared to those obtained with white diffusive bodies.

Some compounds, moreover, are thermally unstable. Thermal degradation of such compounds will cause an underestimation of their concentration or the appearance of ghost peaks.

Thermal desorption is neverthless an outstanding analytical technique because it is easy to perform, it does not require the use of toxic solvents as carbon disulfide, it ensures very low limits of detection, is suited to mass spectrometric detection and allows the recovery of the adsorbing cartridges. Basing on our experience, we have chosen Carbograph 4 as the best compromise between sampling efficiency and recovery yields for a wide range of organic compounds.

## Sampling rates

Sampling rate values at 298 K (25 °C) and 1013 hPa are listed in table on page ***E3***. All of the values shown have been experimentally measured. Exposure tests have been performed up to the levels shown (in $\mu g \cdot m^{-3} \cdot min$) and sampling rates are guaranteed to be linear up to the limit values and for overall concentration of volatile organic compounds in air not exceeding 2,000 $\mu g \cdot m^{-3}$.

### Effect of temperature, humidity and wind speed

Sampling rates varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation

$$Q_K = Q_{298} \left(\frac{K}{298}\right)^{1,5}$$

where $Q_K$ is the sampling rate at the temperature **K** and $Q_{298}$ is the reference value at 298 K. This produces a variation of ± 5% for 10 °C variation (upwards or downwards) from 25 °C.

Sampling rate is invariant with humidity in the range 15-90% and with wind speed between 0.1 and 10 $m \cdot s^{-1}$.
Do not expose directly ***radiello*** to rain: even if small amounts of water are adsorbed by Carbograph 4, they can neverthless interfere with analysis.

## Calculations

The listed sampling rate values take already into account the recovery yields of adsorbed compounds. The average concentration over the sampling period is therefore calculated from sampled mass of analyte and exposure time without introducing any other corrective factor**,** apart from temperature variations of Q.

Average concentration ***C*** in $\mu g \cdot m^{-3}$ over the whole exposure time is calculated according to the following expression:

$$C\ [\mu g \cdot m^{-3}] = \frac{m\ [\mu g]}{Q_K\ [ml \cdot min^{-1}] \cdot t\ [min]}\ 1{,}000{,}000$$

where:
***m*** = mass of analyte in µg
***t*** = exposure time in minutes

## Exposure

### Workplace environment

The use of ligth adsorbing media is not recommended in the workplace environment.

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## Other indoor sampling experiments and outdoor campaigns

Thermal desorption is exceptionally suited for long exposure times at low concentrations, as in outdoor campaigns and some indoor environments (e.g. homes, schools, etc...), particularly if the subsequent analysis is performed by HRGC-MS.

The recommended exposure times range from 8 hours to the upper limits shown in the table below. It is advisable to reduce sampling time if the estimated overall VOCs concentration is higher than 2,000 $\mu g \cdot m^{-3}$.

**Sampling rate values at 25°C (298 K)**

| | sampling rate $ml \cdot min^{-1}$ | exposure time upper limit | linear up to $\mu g \cdot m^{-3} \cdot min$ | uncertainty (2σ) % | limit of detection[1] $\mu g \cdot m^{-3}$ |
|---|---|---|---|---|---|
| benzene | 27.8 | 7 | 410,000 | 8.3 | 0.05 |
| benzene | 26.8 | 14 | 410,000[2] | 7.5 | 0.05 |
| butyl acetate | 24.5 | 14 | 580,000 | 12.4 | 0.05 |
| 2-butoxyethanol | 19.4 | 14 | 550,000 | 9.7 | 0.1 |
| cyclohexane | 27.6 | 7 | 470,000 | 14.7 | 0.1 |
| n-decane | 22.3 | 14 | 450,000 | 22.4 | 0.1 |
| 1,4-dichlorobenzene | 22.0 | 14 | 650,000 | 9.5 | 0.1 |
| dimethyl disulfide | 23.7 | 7 | 500,000 | 9.1 | 0.04 |
| n-heptane | 25.3 | 14 | 420,000 | 7.6 | 0.05 |
| n-hexane | 25.5 | 7 | 420,000 | 10.9 | 0.05 |
| ethylbenzene | 25.7 | 14 | 550,000 | 9.1 | 0.01 |
| ethyl-tert-butyl ether (ETBE) | 30.0 | 7 | 600,000 | - | 0.1 |
| 2-ethyl-1-hexanol | 14.3 | 14 | 550,000 | 17.4 | 0.07 |
| 2-ethoxyethanol | 26.0 | 14 | 570,000 | 7.7 | 0.05 |
| 2-ethoxyethyl acetate | 20.9 | 14 | 600,000 | 8.0 | 0.05 |
| isopropyl acetate | 25.8 | 7 | 540,000 | 9.6 | 0.1 |
| limonene | 12.8 | 14 | 550,000 | 24.8 | 0.2 |
| methyl-tert-butyl ether (MTBE) | 30.0 | 7 | 600,000 | - | 0.2 |
| 2-methoxyethanol | 4.0 | 7 | 1,000,000 | -- | 1.0 |
| 2-metoxyethyl acetate | 21.0 | 7 | 1,000,000 | -- | 0.1 |
| 1-methoxy-2-propanol | 26.6 | 7 | 600,000 | 11.6 | 0.2 |
| n-nonane | 21.0 | 14 | 440,000 | 11.8 | 0.07 |
| n-octane | 24.1 | 14 | 440,000 | 13.4 | 0.07 |
| α-pinene | 6.4 | 14 | 550,000 | 29.5 | 0.2 |
| styrene | 27.1 | 14 | 550,000 | 24.0 | 0.01 |
| tetrachloroethylene | 25.4 | 7 | 1,000,000 | 8.9 | 0.02 |
| toluene | 30.0 | 14 | 550,000 | 8.3 | 0.01 |
| 1,1,1-trichloroethane | 20.0 | 7 | 300,000 | 13.0 | 0.1 |
| trichloroethylene | 27.1 | 7 | 800,000 | 9.5 | 0.02 |
| 1,2,4-trimethylbenzene | 21.9 | 14 | 550,000 | 9.6 | 0.05 |
| n-undecane | 12.0 | 14 | 520,000 | 32.7 | 0.05 |
| m-xylene | 26.6 | 14 | 550,000 | 11.3 | 0.01 |
| o-xylene | 24.6 | 14 | 550,000 | 9.1 | 0.01 |
| p-xylene | 26.6 | 14 | 550,000 | 11.3 | 0.01 |

[1]after 7 days exposure and with MS detection; analytical conditions as described in the Analysis paragraph
[2]for overall VOCs concentrations not exceeding 500 $\mu g \cdot m^{-3}$

## Storage

The cartridges are thermally conditioned in a high temperature stove with an inert atmosphere, with an oxygen content lower than 10 ppm. The duration of the adsorbent capacity of graphitized carbon is virtually unlimited and has been tested six months after production. Cartridges should be stored in a clean and solvent-free environment, in the refrigerator or at room temperature. The expiry date and the lot number are printed on the transparent plastic casing, whose integrity acts as a guarantee seal

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## Analysis

The methods proposed here have been elaborated with the Perkin-Elmer Turbomatrix thermal desorber coupled to the Agilent 6890 gas chromatograph and Agilent 5973 mass spectrometer. They can naturally be transferred to other instruments.

A method for BTEX and one for VOC are proposed here. The first refers to samples from urban air monitoring where research is usually limited to benzene, toluene, ethylbenzene and xylene isomers. The second is more suitable for indoor investigations, allowing the quantification of all the compounds listed in the table above and the more general qualitative research, which also includes analytes with medium polarity.

### Desorption

The thermal desorber is equipped with 1/4" s.s. sample tubes, they have to be hollow and free: discard the stainless steel gauze disk which is fitted to the groove and discard also the springs if present.

Code RAD145 cartridge has been dimensioned to fit the diameter of Turbomatrix thermal desorption tubes. Its length is such that, when the cartridge is introduced into the tube and is stopped by the groove, it is positioned exactly centrally with respect to the tube length. The same considerations apply to the Markes Unity thermal desorber.

Once capped, the Turbomatrix steel tube has to be positioned in the carousel with the grooves on the bottom.

The described conditions have been optimized for seven days exposures to typical concentrations of urban atmospheres and indoor environments. Shorter exposure times or considerably higher concentrations would require different settings of split flows.

*Usually, the cartridge enters into the Turbomatrix tube by simple pouring. If it does not occur, use a pushing tool to press the cartridge till the nick on the tube.*

### BTEX – detector FID

Temperatures and timing

- Desorption: 320 °C for 10 minutes, nitrogen flow through the tube 85 ml·min$^{-1}$, of which 35 ml·min$^{-1}$ sent to the cryofocalization trap and 50 ml·min$^{-1}$ to the inlet split
- Cryofocusing trap (Tenax TA): adsorption 2 °C, desorption 99 °C·sec$^{-1}$ up to 290 °C, 1 minute at 290 °C, trap desorption in nitrogen flow at 22.8 ml·min$^{-1}$, of which 22 ml·min$^{-1}$ at the split outlet
- Six port valve: 150 °C
- Transfer line: 200 °C

Flows

- Carrier gas: helium, 24 psi
- Desorption flow: 100 ml·min$^{-1}$
- Inlet split: 90 ml·min$^{-1}$
- Outlet split: 30 ml·min$^{-1}$

### Instrumental analysis

Column

J&W PONA, length 50 m, d.i. 0.2 mm, film thickness 0.5 µm; the column head can be connected directly to the Turbomatrix six-way valve.

Temperatures

GC oven: 36 °C for 1 minute, 6 °C·min$^{-1}$ up to 110 °C, mantain for 1 minute, 20 °C·min$^{-1}$ up to 250 °C, final isotherm 5 minutes.

Flows

Carrier gas: nitrogen at 0.8 ml·min$^{-1}$

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## COV – detector MSD

Temperatures and timing

- Desorption: 350 °C for 10 minutes, helium flow through the tube 120 ml·min$^{-1}$, of which 20 ml·min$^{-1}$ sent to the cryofocalization trap and 100 ml·min$^{-1}$ to the inlet split
- Cryofocalization trap (Tenax TA): in adsorption 2 °C, in desorption 99 °C·sec$^{-1}$ up to 290 °C, 1 minute at 290 °C, trap desorption in helium flow at 31 ml·min$^{-1}$, of which 30 ml·min$^{-1}$ at the split outlet
- Six port valve: 150 °C
- Transfer line: 200 °C

**user tip**

If you perform several analyses, a barcode reader greatly improve productivity in your lab and will also minimize the possibility of errors in the copying of sample labels.

Please contact us to help you in the implementation of the reader.

### Instrumental analysis

Column

J&W HP-5MS Ultra Inert or equivalent, length 60 m, d.i. 0.25 mm, film thickness 0.25 µm; the column head can be connected directly to the Turbomatrix six-way valve.

Temperatures

- GC oven: 45 °C for 10 minute, 5 °C·min$^{-1}$ up to 115 °C, 10 °C·min$^{-1}$ up to 175 °C, 30 °C·min$^{-1}$ up to 295 °C, final isotherm 6 minutes.

Flows

Carrier gas: helium at 1.0 ml·min$^{-1}$

**user tip**

For a very accurate BTEX calibration we offer the preloaded cartridges **code RAD407**

Here, below, we display two total ion current chromatograms from an outdoor urban site and an indoor sampling respectively.

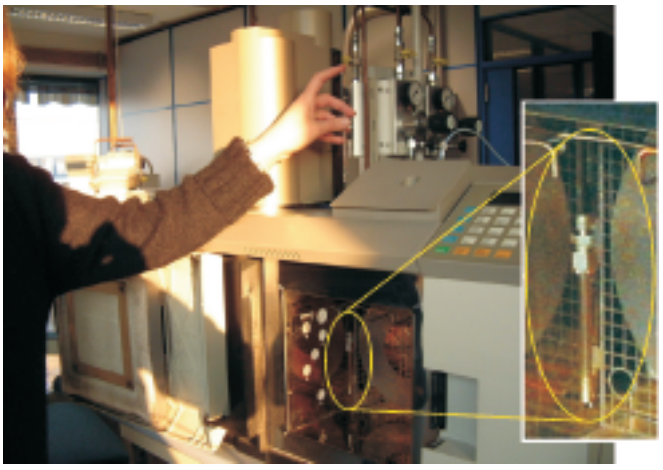
In the first case, the benzene peak corresponds to an average concentration of 2.2 µg·m$^{-3}$ ; in the second the concentration of 1,4-dichlorobenzene was 14 µg·m$^{-3}$.

### Calibration

Calibration curves are obtained by gas-phase injection of methanol solutions of the target compounds onto blank cartridges. Injections are performed through a GC injector, where a short piece (10 cm) of wide-bore (0.25 mm i.d.) deactivated uncoated column is installed. The other end bears a Swagelock reducing connection (1/16”-1/4”).

The 1/4” Swagelock nut has to be equipped with a PTFE ferrule instead of the original steel one (use PTFE ferrules that come along with the Turbomatrix caps).

Introduce a blank cartridge in a Turbomatrix tube and fit the tube to the Swagelock nut. Mantain the injector at 170 °C but do not heat the oven. Inject slowly 1 µl of each calibration solution under nitrogen flow (40 ml·min$^{-1}$) and let the system purge for 2 minutes. Analyze the cartridge as you would do with a sample. We suggest you to prepare a complete set of calibration solutions by subsequent dilutions such as they contain, for example, 8, 4, 2, 1, 0.04, 0.02 and 0.01 µg·µl$^{-1}$ of each compound.



*To prepare the calibration standards fit a 1/16”-1/4” Swagelock reducing connection to the GC injector by a short piece (10 cm) of wide-bore deactivated uncoated column.*

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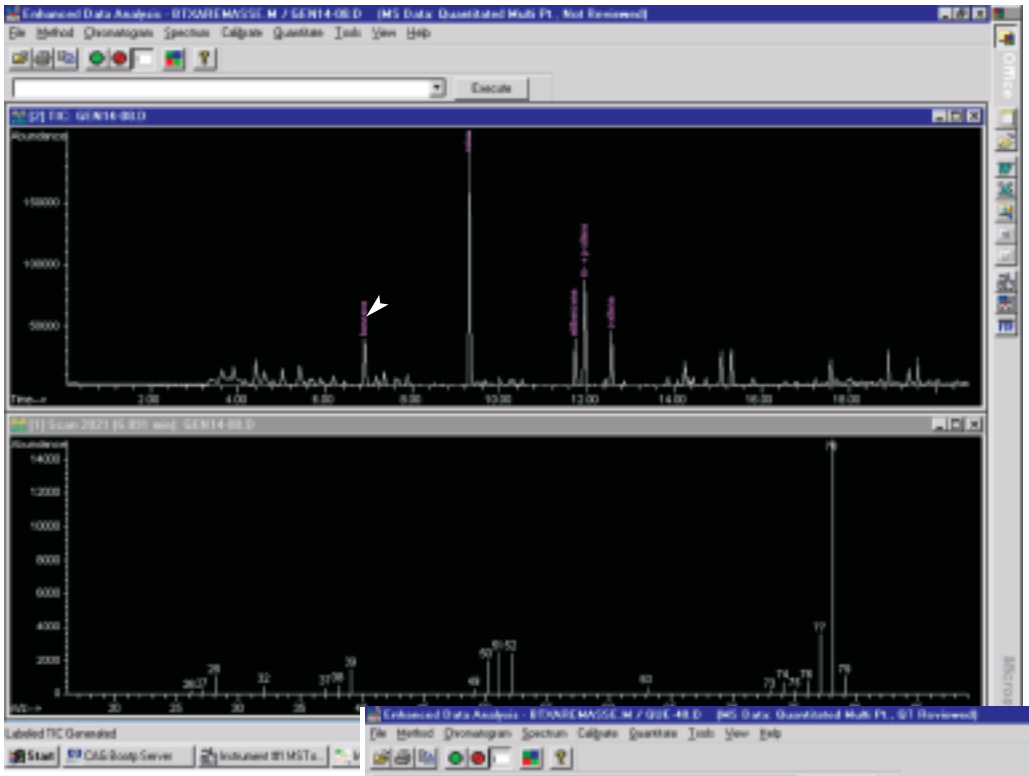
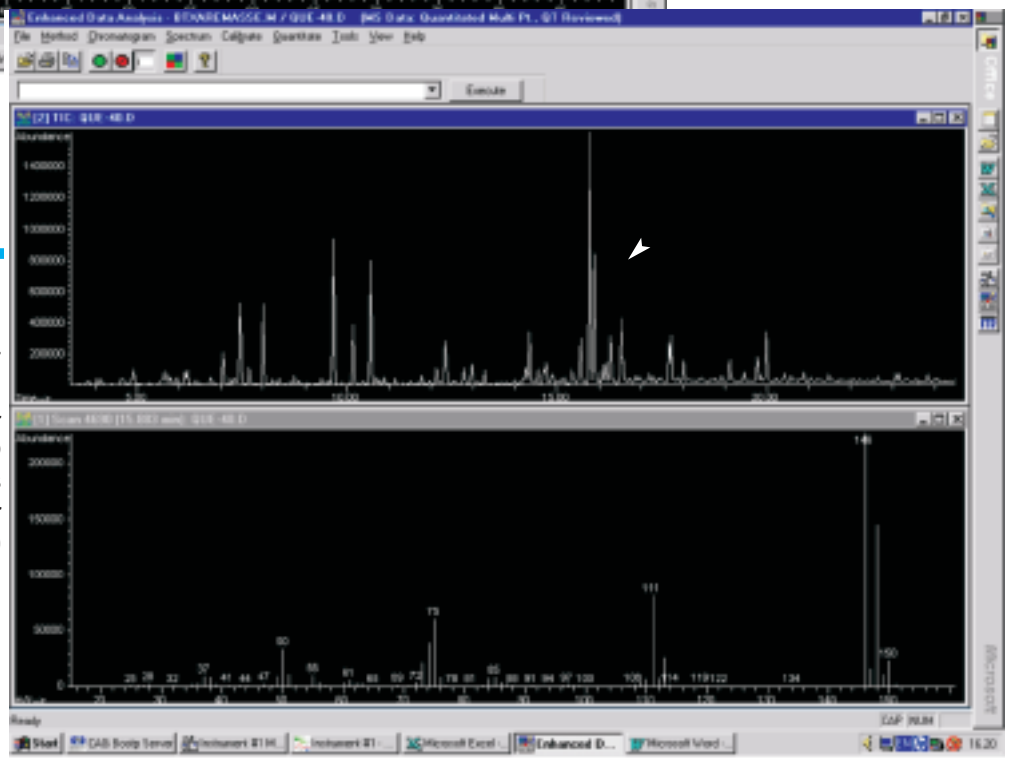


*TIC chromatograms of an outdoor urban sampling (left) and of indoor air (bottom). Mass spectra of benzene and of 1,4-dichlorobenzene are shown on bottom of each picture, at concentrations of 2.2 and 14 µg·m-3 respectively. Despite the low concentration values, the signal-to-noise ratio is very high in both cases. As a consequence, very reliable mass spectral identification is possible by comparison with mass spectral data libreries with no need of further processing.*



## Cartridge recovery

The cartridges can be reconditioned using the thermal desorber in "*tube conditioning*" mode, heating them to 350 °C for at least 20 minutes in an inert gas flow (helium or nitrogen at a flow of 50 ÷ 100 ml·min$^{-1}$).

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# Nitrogen and sulfur dioxides ($NO_2$ and $SO_2$)

## what you need

**blue diffusive body code RAD1201**
**supporting plate code RAD121**
**vertical adapter code RAD122 (optional)**
**chemiadsorbing cartridge code RAD166**

## Principle

The cartridge code RAD166 is made of mycroporous polyethylene coated with triethanolamine (TEA). Nitrogen ($NO_2$) and sulfur ($SO_2$) dioxide is chemiadsorbed onto TEA as nitrite and sulphite or sulphate ions respectively. Nitrite is quantified by visible spectrophotometry while sulphite and sulphate are analysed by ion chromatography ($NO_2$ and $SO_2$ can be analysed together by ion chromatography).

Sampling is selective for gaseous molecules: any airborne nitrite, sulphite or suplhate will not cross the diffusive membrane.

## Sampling rates

### $NO_2$

The sampling rate value $\mathbf{Q_{298}}$ at 298 K (25°C) and 1013 hPa is **0.141 ± 0.007 ng·ppb$^{-1}$·min$^{-1}$**.

### $SO_2$

The sampling rate value $\mathbf{Q_{298}}$ at 298 K (25°C) and 1013 hPa is **0.466 ± 0.022 ng·ppb$^{-1}$·min$^{-1}$.**

### Effetto della temperatura, dell'umidità e della velocità dell'aria

Sampling rate of $NO_2$ varies from the value at 298 K on the effect of temperature (in Kelvin) following the equation:

$$Q_K = Q_{298} \cdot \left(\frac{K}{298}\right)^{7,0}$$

where $\mathbf{Q_K}$ is the sampling rate at the temperature **K** ranging from 263 to 313 K (from -10 to 40 °C) and $\mathbf{Q_{298}}$ is the reference value at 298 K.
Sampling rate for $SO_2$ does not vary with temperature between 263 and 313 K (from -10 to 40 °C).
Sampling rate is invariant with humidity in the range 15 - 90% and with wind speed between 0.1 and 10 m·s$^{-1}$ for both gases.

## Calculations

### $NO_2$

The concentration $\mathbf{C_{NO_2}}$ is calculated according to the equation:

$$C_{NO2} = \frac{m_{NO2}}{Q_K \cdot t}$$

where $\mathbf{m_{NO_2}}$ is nitrite mass in **ng** found on the cartridge, **t** is exposure time in **minutes** and $\mathbf{Q_K}$ is the sampling rate value at the temperature **K** in Kelvin.

### $SO_2$

Convert the sulphite found onto the cartridge into sulphate by multiplying its mass by 1.2, then sum the obtained value to the sulphate found in the cartridge. The concentration in ppb is calculated according to the equation:

$$C_{SO2} = \frac{m_{SO4}}{0.466 \cdot t}$$

where $\mathbf{m_{SO_4}}$ is the overall sulphate mass in ng found in the cartridge (sulphate itself and sulphite converted into sulphate) and **t** is exposure time in minutes.

**user tip**
It is advisable to measure the sampling temperature by the thermometer **code RAD126**.

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## Exposure

Exposure up to 15 days is feasible but if relative humidity is higher than 70% for the entire sampling duration it is not advisable to sample for more than 7 days. Due to the fact that TEA is very hygroscopic in fact, even if water does not actually interfere with sampling or analysis, the excess water adsorbed by the cartridge could cause some loss of adsorbing medium by percolation.

**WARNING:** $NO_2$ results may differ from those produced by automatic chemiluminescent instrumentation due to exponential variation of the sampling rate of radiello with temperature. This phenomenon is characteristic of all $NO_2$ samplers that use TEA as an absorbent medium. The reason is not yet completely clear, but it is assumed that it depends in part on the balance in the air between the species $NO_2$ and $N_2O_4$, whose ratio is strongly linked to temperature: the TEA captures only the species $NO_2$.

## Limit of quantitation and uncertainty

Sampling rate of $NO_2$ and $SO_2$ is linear ranging from 10,000 to 5,000,000 ppb·min. Limit of quantitation after 7 days exposure is 1 ppb for both gases. The uncertainty at $2\sigma$ is 11.9% for $NO_2$ and 9.2% for $SO_2$.

## Storage

The cartridges are stable for at least 12 months before and 4 months after the sampling, if kept in the dark at 4 °C. Expiry date is printed on the plastic bag.

Do not expose all of the cartridges belonging to the same lot, keep at least two of them as blanks.

## Analysis

Add **5 ml** of water in the plastic tube with the cartridge and stir vigorously by a vortexer for 1 minute. Do the same with two-three unexposed cartridges.

### Colorimetric determination of nitrite ion

Nitrogen dioxide is quantitatively converted to nitrite ion. Prepare the following reactives:

- *sulphanilamide*: dissolve 10 g of sulphanilamide in 100 ml concentrated HCl and dilute to 1,000 ml with water
- *NEDA*: dissolve 250 mg of N-(1-naphthyl)ethylendiamine dihydrochloride in 250 ml of water (discard the solution when it turns brown).

Transfer 0.5 ml (or a different volume, see the table below) of the cartridge extraction solution to a plastic or glass 10 ml tube along with 5 ml of *sulphanilamide* reactive. Cap tigthly, stir and wait for 5 minutes. Add 1 ml of *NEDA* reactive, stir and wait for 10 minutes. Do the same with unexposed cartridges.

Measure the absorbance of samples at 537 nm using water to zero the spectrophotometer, then subtract the blank value from unexposed cartridges. Prepare the calibration standards in the same way from sodium nitrite solutions of concentration ranging from 0.1 to 20 $mg \cdot l^{-1}$ expressed as $NO_2^-$.

When nitrite ion concentration is higher than 20 $\mu g \cdot ml^{-1}$ (corresponding to 7 days of exposure to 70 ppb) the absorbance value is no longer comprised in the calibration curve. To analyse the samples, draw smaller amounts of the extraction solution as shown in the table. In order to mantain the overall volume unaltered, add the listed volume of water.

| average expected concentration for 7 days exposure in ppb | sample volume ml | water volume to be added ml |
|---|---|---|
| up to 70 | 0.5 | 0 |
| from 70 to 150 | 0.25 | 0.25 |
| higher than 150 | 0.1 | 0.4 |

### Determination of the sulphite and sulphate ions

Though $SO_2$ is converted into sulphite and sulphate ions with variable ratios, the sum of the two ion equivalents is linear with exposure to $SO_2$. To obtain calibration curves, prepare solutions containing both ions at concentrations ranging from 5 to 50 $mg \cdot l^{-1}$. Perform the ion chromatography analysis of the standard solutions and the extraction solutions from ***radiello*** cartridges in the same way according to your usual laboratory practice.

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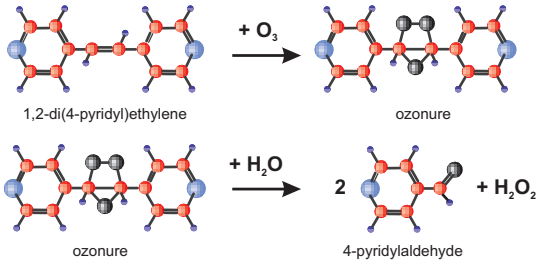
# Ozone ($O_3$)

## What you need

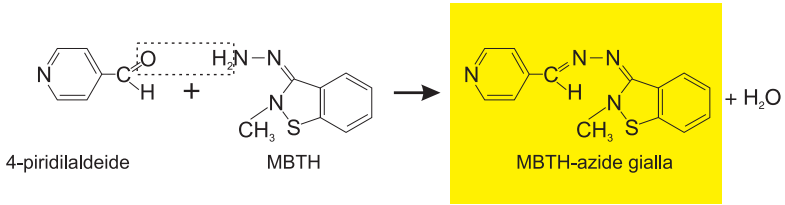
**blue diffusive body code RAD1201**
**supporting plate code RAD121**
**vertical adapter code RAD122 (optional)**
**chemiadsorbing cartridge code RAD172**

## Principle

The adsorbing cartridge is formed by a micropore polyethylene tube filled with silica gel coated with 4,4'-dipyridylethylene and closed, at one end, by a PTFE cap. Upon exposure, acid-catalysed ozonolysis of 4,4'-dipyridylethylene leads to 4-pyridylaldehyde. Silica gel ensures the presence of water, necessary to complete ozonolysis reactions.




In the laboratory, 4-pyridylaldheyde is condensed with 3-methyl-2-benzothiazolinone hydrazone (MTBH) to yield the corresponding azide, yellow coloured.




The absorbance of the solution is measured at 430 nm. Production of 4-pyridylaldehyde is a specific reaction of ozone; neither nitrogen oxides nor organic compounds, if present, do interfere.

## Sampling rate

The sampling rate value $\mathbf{Q_{298}}$ at 298 K (25°C) and 1013 hPa is **24.6 ml·min$^{-1}$**.
Sampling is linear in the exposure range from 10,000 to 4,000,000 µg·m$^{-3}$·min$^{-1}$.

### Effect of temperature, humidity and wind speed

Sampling rate varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation:

$$\mathbf{Q_K = Q_{298}} \left( \frac{\mathbf{K}}{\mathbf{298}} \right)^{1.5}$$

where $\mathbf{Q_K}$ is the sampling rate at the temperature K and $\boldsymbol{Q_{298}}$ is the reference value at 298 K.
Sampling rate is not influenced by humidity or wind speed.

## Calculations

The average concentration over the whole exposure time is calculated according to the equation

$$\boldsymbol{C}\ [\mu g \cdot m^{-3}] = \frac{\boldsymbol{m}\ [\mu g]}{24.6\ \boldsymbol{t}\ [min]}\ 1{,}000{,}000$$

where ***m*** is ozone mass in µg sampled by *radiello* and **t** is exposure time in minutes.

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## Exposure

Introduce the cartridge in the diffusive body and make sure that the PTFE cap is positioned at the same end of the screw.

In outdoor environments, where typical ozone concentrations range from 2 to 400 $\mu g \cdot m^{-3}$, we suggest exposure time from 24 hours to 14 days. The ideal range is from 3 to 7 days.

In workplace environments it is advisable to sample over the entire 8 hours shift.

## Limit of detection and uncertainty

The limit of detection is 2 $\mu g \cdot m^{-3}$ for 7 days exposures. The cartridge is saturated after 14 days exposure at 400 $\mu g \cdot m^{-3}$. The uncertainty at $2\sigma$ is 14.5% over the whole sampling rate linearity range.

## Storage

The cartridges need only protection from direct sunlight: keep them in a drawer or a cupboard at room temperature. In these conditions, the blank level does not exceed 0.015 absorbance units for up to six months.

Expiry date is printed onto the plastic bag wrapping each cartridge.

Generally, an increase of blank level does not imply that the cartridge must be discarded. The only consequence is a corresponding increase of the analytical limit of quantification.

After exposure the samples have to be stored in the dark as before, along with three unused cartridges to be analysed as blanks. Analyse them within a week.

## Analysis

### Reactives and materials

- 3-methyl-2-benzothiazolinone hydrazone hydrocloride (MBTH): dissolve 5 g per litre in water and add 5 ml of concentrated sulphuric acid; this solution is to be freshly prepared.
- 4-pyridylaldehyde
- micropore filter membrane 0.45 µm

**user tip**

For a simple and accurate filtration make use of the filtration kit **code RAD174**.

### Procedure

Draw the cartridge out from the plastic tube, discard the PTFE cap and pour the silica gel into the tube. Add 5 ml of MBTH solution, recap the tube and stir vigorously. Let the tube stand for at least one hour to react, stirring from time to time. Filter through the micropore filter (if you make use of the code 174, act as follows: fit the filter to the syringe, transfer the solution from the tube to the syringe and filter it into a second tube or directly into the spectrophotometer measure cell).

**IMPORTANT**

If the absorbance value is higher than the calibration curve upper limit dilute the sample with the MBTH solution: **never use water to dilute!** Water alters the pH of the solution with unpredictable variations in the linearity of absorbance values vs concentration.

Measure absorbance at 430 nm using water to zero the spectrophotometer. The yellow colour is stable for several days if the solution is kept well capped in its tube.

Treat in the same manner three unused cartridges of the same lot and subtract the average blank value from the absorbance values of the samples.

## Calibration

Dissolve 100 µl (112.2 mg at 20° C) of 4-pyridylaldehyde in 1 litre of water and dilute this solution (e.g. 1:2, 1:5, 1:10) to obtain calibration solutions. Transfer 0.5 ml of each calibration solution in a plastic tube together with 4.5 ml of MTBH solution. Stir and let stand for one hour, then read the absorbance at 430 nm (filtration is not needed). Plot the calibration curve for ozone mass *vs* measured absorbance, taking into account that:

1 µg of 4-pyridylaldehyde = 0.224 µg of ozone.

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Edition 01/2019

# Hydrogen sulfide ($H_2S$)

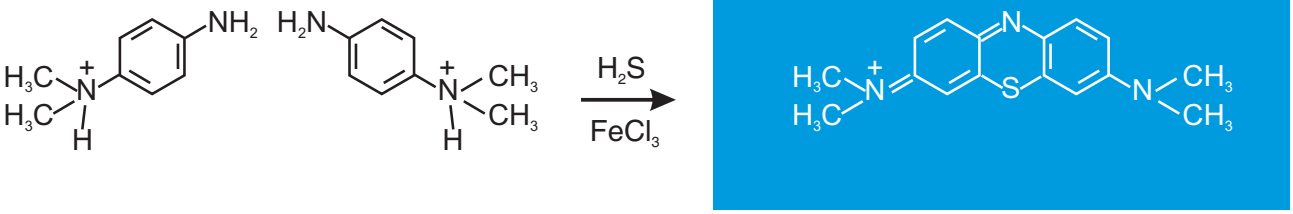
## What you need

**blue diffusive body code RAD1201 or white code RAD120**
**supporting plate code RAD121**
**vertical adapter code RAD122 (optional)**
**chemiadsorbing cartridge code RAD170**

## Principle

The cartridge code RAD170 is made of microporous polyethylene and impregnated with zinc acetate. Hydrogen sulphide is chemiadsorbed by zinc acetate and transformed into stable zinc sulfide.

The sulfide is recovered by extraction with water. In contact with an oxidizing agent as ferric chloride in a strongly acid solution it reacts with the N,N-dimethyl-p-phenylendiammonium ion to yield methylene blue.




N,N-dimethyl-p-phenylendiammonium

Methylene blue

Methylene blue is quantified by visible spectrometry.

## Sampling rate

Sampling rate $\mathbf{Q_{298}}$ at 298 K (25°C) and 1013 hPa is **0.096 ± 0.005 ng·ppb$^{-1}$·min$^{-1}$**.

### Effect of temperature, humidity and wind speed

Sampling rate varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation:

$$\mathbf{Q_K = 0{,}096 \left(\frac{K}{298}\right)^{3,8}}$$

where $\mathbf{Q_K}$ is the sampling rate at the temperature K ranging from 268 to 313 K (from -5 to 40 °C).

Sampling rate is invariant with humidity in the range 10 - 90% and with wind speed between 0.1 and 10 m·s$^{-1}$.

## Calculations

Once $Q_K$ at the sampling temperature has been calculated, the concentration **C** is obtained according to the equation:

$$\mathbf{C = \frac{m}{Q_K \cdot t}\ 1{,}000}$$

where **m** is the mass of sulphide ion in **µg** found onto the cartridge and **t** is exposure time in **minutes**.

## Exposure

Exposure duration may vary from 1 hour to 15 days. Sampling is linear from 2,000 to 50,000,000 ppb·min of $H_2S$.

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## Limit of detection and uncertainty

The limit of detection is 30 ppb for 1 hour exposure or 1 ppb for 24 hour exposure. The uncertainty at 2σ is 8.7% over the whole exposure range.

## Storage

The cartridges are stable at least for 12 months before and 6 months after exposure. Do not expose all of the cartridges of the same lot: keep at least two of them as blanks.

## Analysis

### Reactives and materials

- *sulphuric acid*: slowly add 25 ml of concentrated sulphuric acid to 10 ml water and let the solution cool;
- *amine*: dissolve 6.75 g of N,N-dimethyl-p-phenylendiammonium oxalate in the *sulphuric acid* solution. Dilute this solution to 1 litre with sulphuric acid - water 1:1 v/v. Kept in a dark bottle and well capped, this solution is stable for at least four weeks. **CAUTION**: this solution is very poisonous.
- *ferric chloride*: dissolve 100 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in 40 ml of water.
- *ferric chloride-amine*: mix 10 ml of *ferric chloride* solution with 50 ml of *amine* solution. This solution has to be freshly prepared;
- *sulphuric acid for dilution*: slowly dissolve 40 ml of concentrated sulphuric acid in 900 ml of water, let the solution cool and make up to 1,000 ml.

### Procedure

Add 10 ml of water to the plastic tube containing the cartridge, recap and stir vigorously, preferably by a VORTEX stirrer.

Add 0.5 ml of *ferric chloride* - *amine* solution, recap **immediately** and stir. The tube must be capped immediately in order to avoid that the developed hydrogen sulfide can escape from the tube before reacting.

Wait for 30 minutes and measure absorbance at 665 nm using water to zero the spectrophotometer. The colour is stable for several weeks.

Do the same with two or three unexposed cartridges of the same lot and obtain the average blank value, then subtract it to the samples.

**IMPORTANT**

Absorbance is linear up to 1,200 absorbance units, corresponding to an exposure value of about 80,000 ppb·min. If higher absorbance values are obtained, dilute the samples with the sulphuric acid for dilution.

Be careful to apply the same dilution ratio to the samples and the blanks.

NEVER USE WATER TO DILUTE.

## Calibration

Calibration curves may be prepared by sodium sulfide standard solutions, which have to be titrated just before use. As diluted sodium sulfide solutions are very unstable (the sulfide content can diminish as much as the 10% in an hour) it is strongly recommended to make use of the calibration solution code RAD171, following the instructions included.

**user tip**

**Code RAD171** calibration solution relieves you from the task of preparation and titration of the sodium sulfide solutions.

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# Ammonia ($NH_3$)

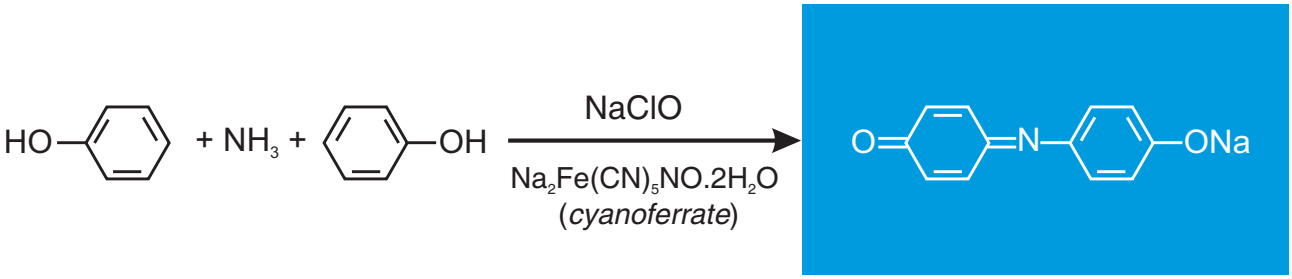
## What you need

**blue diffusive body code RAD1201 or white code RAD120**
**supporting plate code RAD121**
**vertical adapter code RAD122 (optional)**
**chemiadsorbing cartridge code RAD168**

## Principle

The cartridge code RAD168 is made of microporous polyethylene and impregnated with phosphoric acid. Ammonia is adsorbed as ammonium ion. Airborne ammonium salts dispersed as particulate matter do not cross the diffusive membrane of radiello.

Ammonium ion is quantified by visible spectrometry as indophenol: at basic buffered pH ammonium ion reacts with phenol and sodium hypochlorite, with pentacyanonitrosylferrate catalysis (in the following *cyanoferrate*), to form indophenol. The reaction product is intensely coloured in blue, and its absorbance measured at 635 nm.




indophenol

## Sampling rate

Sampling rate $\mathbf{Q_{298}}$ at 298 K (25°C) and 1013 hPa is **235 ml·min$^{-1}$**.

### Effect of temperature, humidity and wind speed

The effect of temperature on sampling rate is negligible (<0.1%/°C) in the range from 275 ÷ 312 K (2 ÷ 39 °C). Sampling rate is invariant with humidity in the range 10 - 90% and with wind speed between 0.1 and 10 m·s$^{-1}$.

## Calculations

The concentration **C** in µg·m$^{-3}$ is obtained according to the equation:

$$\mathbf{C} = 0.944 \frac{\mathbf{m}}{\mathbf{235 \cdot t}} 1{,}000{,}000$$

where **m** is the mass of ammonium ion in **µg** found onto the cartridge and **t** is exposure time in **minutes**.

0.944 is the numerical factor necessary to convert ammonium ion into ammonia (see Analysis)

## Exposure

Introduce the cartridge in the diffusive body and make sure that the PTFE cap is positioned at the same end of the screw.

Ammonia is sampled linearly in the range from 2,000 - 20,000,000 µg·m$^{-3}$·min. Exposure time is allowed to range from 1 hour to 14 days.

**IMPORTANT**

Do not touch the microporous portion of the cartridge with your fingers: sweat contains ammonium ions.

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## Limit of detection and uncertainty

The limit of detection is 1 $\mu g \cdot m^{-3}$ for 24 hour exposure. The uncertainty at $2\sigma$ is 6.5% over the whole allowed exposure range.

## Storage

The cartridges are stable at least for 12 months before and after exposure if kept at room temperature in an ammonia-free environment. Do not expose all of the cartridges of the same lot: keep at least two of them as blanks.

## Analysis

### Materials

- plastic or glass tube, volume 12 ml, with cap
- micropipet with variable volume from 0.1 to 1.0 ml
- 5 ml glass pipet

### Reactives

- *buffer* solution (pH 10.6): dissolve 1.1 g of NaOH and 3.04 g of $NaHCO_3$ in one litre of water
- *phenol*: dissolve 10 g of phenol in 100 ml of ethanol
- *cyanoferrate*: dissolve 0.5 g of sodium pentacyanonitrosylferrate dihydrate ($Na_2Fe(CN)_5NO \cdot 2H_2O$) in 100 ml of water and add a few drops of 10% NaOH. Keep this solution in a dark bottle and prepare it freshly.
- *oxidising* solution: sodium hypochlorite with 1% of active chlorine in 0.2 M NaOH. Keep cool in a dark bottle.

### Ammonium ion quantification

Open ***radiello*** tube and cautiously discard the cartridge PTFE cap (it may have been contaminated with handling). Help yourself with a pair of pliers.

Add 10 ml of deionised water to the cartridge in its tube (make sure that no trace of ammonium ion is found in the water you use). Recap the tube and stir vigorously by a VORTEX stirrer for at least 15 seconds.

Transfer 1 ml of the solution into another tube along with 0.4 ml of *phenol*, 0.4 ml of *cyanoferrate*, 5 ml of *buffer* solution and 1 ml of *oxidising* solution.

Wait for 1 hour and then measure the absorbance of the solution at 635 nm using water to zero the spectrophotometer.

Do the same with two unexposed cartridges and subtract their absorbance value to the samples. Generally, the blank value does not exceed 0.040 absorbance units.

For exposure value higher than 500,000 $\mu g \cdot m^{-3} \cdot min$ the absorbance value is no longer linear: **diluite a known fraction of the coloured solution with the *buffer*.**

Calibration curves are conveniently prepared with ammonium chloride solutions in the range from 0.5 to 10 $mg \cdot l^{-1}$ as ammonium ion.

**IMPORTANT**

If sample is too concentrated (absorbance no longer linear) DO NOT DILUTE WITH WATER: the pH value is critical in the determination of the colour intensity.

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Edition 01/2019

# Hydrochloric acid (HCl)

## What you need

**blue diffusive body code RAD1201 or white code RAD120**
**supporting plate code RAD121**
**vertical adapter code RAD122 (optional)**
**chemiadsorbing cartridge code RAD169**

## Principle

Code RAD169 cartridge is made of stainless steel net loaded with silica gel (0.1 to 0.4 mm particle size). Gaseous hydrochloric acid is adsorbed by silica gel and subsequently extracted with water to be quantified by ion chromatography as chloride ion.

Sampling is selective for the gaseous molecules: any airborne chloride salt will not cross the diffusive membrane of *radiello*.

## Sampling rate

Sampling rate ($\mathbf{Q_{298}}$) at 25 °C (298 K) and 1013 hPa is **103 cm$^3$·min$^{-1}$**.

### Effect of temperature, humidity and wind speed

Sampling rate varies from the value at 298 K (25 °C) on the effect of temperature (in Kelvin) as expressed by the following equation:

$$Q_K = 103 \left(\frac{K}{298}\right)^{1,5}$$

where $Q_K$ is the sampling rate at temperature **K** and $\mathbf{Q_{298}}$ is the sampling rate value at the reference temperature of 298 K. This yields a ± 5% variation of Q for a 10 °C variation (upwards or downwards) from 25 °C.

Sampling rate is invariant with humidity in the range 15 - 90% for short exposure time (see *Exposure*) and with wind speed between 0.1 and 10 m·s$^{-1}$.

## Calculations

Let ***m*** be the mass of chloride ion in µg found onto the cartridge and ***t*** the exposure time in minutes, the environmental concentration ***C*** of hydrochloric acid in µg·m$^{-3}$ is obtained according to the equation:

$$C = \frac{1.028\ m}{Q_K\ t} 1{,}000{,}000$$

where $Q_K$ is the sampling rate at temperature K (in Kelvin) and 1.028 is the ratio between molecular masses of HCl and $Cl^-$(see *Analysis*).

## Exposure

Hydrochloric acid is sampled linearly in the range from 20,000 ÷ 20,000,000 µg·m$^{-3}$·min.

### Workplace environment

In workplace environment we recommend exposure time from 15 minutes to 8 hours: the *ceiling* values can be measured.

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### Outdoor environment

We recommend exposure time from 2 hours to 2 days. Exposure time as long as 7 days is allowed if average relative humidity does not exceed 50%, taking into account the water absorbing properties of silica gel.

We also recommend to protect ***radiello*** from rain by the mountable shelter code RAD196.

## Limit of detection and uncertainty

The limit of detection is 10 $\mu g \cdot m^{-3}$ for 24 hour exposure. The uncertainty at $2\sigma$ is 3.5% over the whole allowed exposure range.

## Interferences

Gaseous chlorine is adsorbed by silica gel and is revealed as 0.02 ng of chloride ion for 1 $\mu g \cdot m^{-3} \cdot min$ of chlorine.

## Storage

Kept in a clean environment free from gaseous hydrochloric acid, the cartridges code 169 are stable for at least 24 months before and after sampling.

If more than six months have passed since you received the cartridges, before environmental sampling campaigns, it is advisable to analyse some cartridges to check for contamination from the background. Discard the cartridges if they contain more than 5 µg of chloride ion.

## Analysis

Add 2 ml of deionised water to the cartridge in its tube (make sure that no trace of chloride ion is found in the water you use). Recap the tube and stir vigorously by a VORTEX stirrer for 1-2 minutes. Analyse the solution by ion chromatography. Subtract the blank value obtained from two unexposed cartridges.

Prepare the calibration solutions with sodium or potassium chloride concentrations ranging from 0.5 to 25 mg/litre as $Cl^-$.

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Edition 01/2019

# Hydrofluoric acid (HF)

## What you need

**blue diffusive body code RAD1201 or white code RAD120**
**supporting plate code RAD121**
**vertical adapter code RAD122 (optional)**
**chemiadsorbing cartridge code RAD166**

## Principle

The cartridge code RAD166 is made of microporous polyethylene coated with triethanolamine (TEA). Gaseous hydrofluoric acid is adsorbed by TEA and subsequently extracted with water to be quantified by ion chromatography or by ion selective electrode as fluoride ion.

Sampling is selective for the gaseous molecules: any airborne fluoride salt will not cross the diffusive membrane of *radiello*.

## Sampling rate

Sampling rate at 25 °C and 1013 hPa is **187 $cm^3 \cdot min^{-1}$**.

### Effect of temperature, humidity and wind speed

Sampling rate is invariant with humidity in the range 10 - 90% for short exposure time (see Exposure) and with wind speed between 0.1 and 10 $m \cdot s^{-1}$. The effect of temperature is under investigation.

## Calculations

Let ***m*** be the mass of fluoride ion in µg found onto the cartridge and ***t*** the exposure time in minutes, the environmental concentration ***C*** of HF in $\mu g \cdot m^{-3}$ is obtained according to the equation:

$$C = \frac{1.053\ m}{187\ t}\ 1{,}000{,}000$$

where 1.053 is the ratio between molecular masses of HF and $F^-$(see *Analysis*).

## Exposure

Hydrofluoric acid is sampled linearly in the range from 10,000 to 50,000,000 $\mu g \cdot m^{-3} \cdot min$.

### Workplace environment

In workplace environments we recommend exposure time from 15 minutes to 8 hours: the *ceiling* values can be measured.

### Outdoor environment

We recommend exposure time from 2 hours to 14 days.

Protect *radiello* from rain by the mountable shelter code RAD196.

## Limit of detection and uncertainty

The limit of detection is 7 $\mu g \cdot m^{-3}$ for 24 hour exposure. The uncertainty at $2\sigma$ is 4.5% over the whole exposure range.

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## Storage

Kept in a dark place at 4 °C, the cartridges stay unaltered for at least 12 months before exposure and 4 months after sampling. Expiry date is printed on the plastic bag wrapping each cartridge.

If more than six months have passed since you received the cartridges, before environmental sampling campaigns, it is advisable to analyse some cartridges to measure any contamination from the background. Discard the cartridges if they contain more than 2 µg of fluoride ion.

Keep at least two unexposed cartridges for each lot and analyse them as blanks.

## Analysis

### Ion chromatography

Add 5 ml of the eluent solution to the ***radiello*** tube. Stir vigorously by a VORTEX stirrer for 1-2 minutes. Let the tube stand for 10 minutes, then stir manually and inject the solution in the ion chromatographic apparatus without further treatment.

Analyse 1-2 unexposed cartridges and subtract the average blank value to the samples.

### Ion Selective Electrode

Prepare an ionic strength buffer as follows. Dissolve 57 ml of acetic acid in 500 ml water and add 50 g of sodium chloride and 0.3 g of sodium citrate. When complete solubilisation has been achieved, adjust the pH value to 5-5.5 (ideal value is 5.3) by adding drops of 10 M sodium hydroxide. Make up to 1 litre with water.

Add 5 ml water to ***radiello*** tube and stir vigorously by a vortexer for 1-2 minutes, then let stand for 10 minutes. Introduce a magnetic stirring bar in a 20 ml beaker, add 10 ml of ionic strength buffer and 1 ml of the extraction solution of the cartridge. Start the magnetic stirrer and make the potentiometric measurement by an ion selective electrode for fluorides. In the described analytical conditions, the electrode response should be linear in the range from 1 to 1,000 $mg \cdot l^{-1}$ of $F^-$ with slope close to 59 ± 0.5 (if potential is expressed in mV).

**IMPORTANT**

Always use water with fluoride content lower than 0.5 $mg \cdot l^{-1}$.

Analyse 1-2 unexposed cartridges and subtract the average blank value to the samples.

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# Anaesthetic gases and vapours
# $N_2O$, isoflurane, ethrane, halothane and sevorane

## What you need

**Sampling kit code RAD125, containing 20 single packages each composed of:**
**1 permeative body (code RAD1203)**
**1 supporting plate (code RAD121)**
**1 vertical adapter (code RAD122)**
**1 adsorbing cartridge (code RAD132)**

the listed components are contained in a closed aluminum envelope, which is wrapped by a thermowelded paper-polyethylene bag.

The whole is sterilized by γ-rays.

The single components are also available non-sterilized in 20 pieces per package.

## Principle

Code RAD132 cartridge is made of stainless steel net loaded with a mixture of molecular sieve and activated charcoal 35-50 mesh.

Nitrous oxide and halogenated anaesthetic gases permeate the silicone membrane and are sampled by the molecular sieve and by activated charcoal respectively.

The sampled compounds are displaced by a water-methanol mixture and are quantified by capillary gas chromatography and a headspace sampler.

$N_2O$, isoflurane, ethrane and halothane are detected by the Electron Capture Detector (ECD) with very good sensitivity; sevorane can not be quantified by ECD detection and has to be analyzed by mass spectrometry.

## Sampling rate

Sampling rate values at 25 °C (298 K) and 1013 hPa are listed in the table on the right.

| | sampling rate ($ml \cdot min^{-1}$) |
|---|---|
| $N_2O$ | 1.01 |
| isoflurane | 2.25 |
| ethrane | 3.39 |
| halothane | 4.93 |
| sevorane | 0.92 |

### Effect of temperature, humidity and wind speed

Sampling rate varies from the values at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation:

$$Q_K = Q_{298} \left(\frac{K}{298}\right)^{1.5}$$

where $Q_K$ is the sampling rate at temperature **K** and $Q_{298}$ is the sampling rate value at reference temperature of 298 K. This yields a ± 5% variation of Q for a 10 °C variation (upwards or downwards) from 25 °C.
Sampling rate is invariant with humidity in the range 10 ÷ 90% for exposure time not exceeding 8 hours and with wind speed between 0.1 and 10 $m \cdot s^{-1}$.

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## Calculations

Concentration in air is obtained by the following equation:

$$C = \frac{m \cdot}{Q_K \cdot t} 1{,}000$$

where:
$C$ = concentration in $mg \cdot m^{-3}$
$m$ = mass of analyte found on the cartridge in µg
$Q_K$ = sampling rate in $ml \cdot min^{-1}$
$t$ = exposure time in minutes

## Exposure

Sampling rate is constant for exposure time up to 8 hours at relative humidity up to 80% with $N_2O$ concentration up to 500 ppm and overall halogenated anaesthetic compounds concentration up to 100 ppm.

Exposure time longer than 8 hours in presence of relative humidity higher than 80% leads to the loss of the nitrous oxide already sampled by the effect of competing water vapour adsorption on the molecular sieve sites.

## Limit of detection and uncertainty

The cartridges are conditioned to ensure a chromatographic blank level lower than three times the instrumental noise at the minimum attenuation.

If a well conditioned ECD is employed, 4 hours of exposure ensure the following analytical sensitivities: 0.5 ppm of $N_2O$, 0.002 ppm of isoflurane, 0.01 ppm of ethrane and 0.002 ppm of halothane. Sevorane is not detected by ECD. The Flame Ionisation Detector (FID) can be employed instead with acceptable sensitivity, but if nitrous oxide and the other halogenated compounds have to be quantified at the same time, a mass spectrometry detector must be used. Acquiring by the SIM (Single Ion Monitoring) technique detection limits close to the ECD performances can be achieved for $N_2O$, isoflurane, ethrane and halothane. For sevorane, 1 hour exposure allows to detect 0.1 ppm.

The uncertainty at $2\sigma$ is: 5.5% for $N_2O$, 4.7 - 5.6% for isoflurane, ethrane and halothane with ECD detection, 6.2% for $N_2O$ and 5.5 - 6.2% for isoflurane, ethrane, halothane and sevorane with MS detection.

## Storage

**IMPORTANT**

DO NOT STERILIZE THE SAMPLER BY AUTOCLAVING. Autoclaving treatment permanently damages the silicone permeative membrane.

The sampling kit code RAD125 is sterilized by γ-rays. Use of the sampler makes it no longer sterile. With the exception of the adsorbing cartridge, the sampler is indefinitely re-usable. After the first sampling, if you can arrange for sterilization by yourselves you only need to re-order code RAD132 cartridges to perform other sampling campaigns. Adsorbing cartridges need not to be sterile.

If kept in a dry place free from chemical contamination, the cartridges are stable for at least 12 months.

After the sampling, the cartridges are stable for 30 days if stored with the same precautions.

## Analysis

### Materials needed for the analysis

- 20 ml headspace glass vials with open-top aluminum crimp caps and rubber/PTFE septa
- water/methanol mixture 60/40 v/v
- usual laboratory glassware

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## Materials needed for the calibration curve

- pure $N_2O$ in a gas cylinder
- halogenated anaesthetic compounds
- gastight syringe (volume 500 µl) and other syringes (volume 100 and 10 µl)
- 1 litre glass bottle with threaded neck, equipped with open-top screw cap and rubber/PTFE septum *(the volume of the bottle must be precisely measured and the bottle must be rinsed with dry nitrogen before use*)
- magnetic stirrer with large magnetic stirring bar (about 30-40 mm long)
- usual laboratory glassware

## Extraction

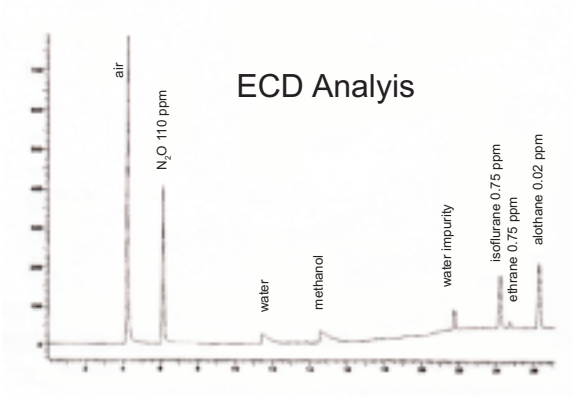
Introduce 10 ml of water/methanol mixture in a headspace vial by a volumetric pipette. Add the ***radiello*** cartridge and cap immediately. Stir and let equilibrate, place the vial in the headspace bath and let equilibrate for one hour at 45 °C.

## Instrumental analysis

## ECD detection (sevorane is not detected)

- vial pressurization gas: $N_2$ at 1.2 atm
- loop volume: 1 ml
- gas chromatographic column: polystyrene-divinylbenzene PLOT, 30 m long, 0.32 mm inner diameter, 20 µm film thickness (allows quantification of nitrous oxide and other anaesthetic gases in one chromatographic run)
- carrier gas: $N_2$ at 1.0 atm
- split ratio: 10/1
- make-up gas: Ar-$CH_4$ ($CH_4$ 10% v/v) at 30 ml·min$^{-1}$
- GC oven: 40° C for 2 min, 10° C·min$^{-1}$ up to 150° C, 6° C·min$^{-1}$ up to 200° C, final isotherm for 5 minutes
- injector temperature: 150° C
- detector temperature: 300° C

In the described analytical conditions chromatogram similar to the one in the figure are obtained. In the example shown, exposure time was 4 hours at the concentration values indicated and with relative humidity of 70%.




## MS detection

The instrumental conditions are as described above, with the exception of the carrier gas (helium has to be used instead) and the make-up gas, which is not employed. Acquire by SIM (Single Ion Monitoring) focussing the detector on the following signals (the base peak is underlined):

**$N_2O$**: 44; **isoflurane** and **ethrane**: 51, 67, 117; h**alothane**: 117, 198, 179; **sevorane**: 33, 131, 181

If high concentrations of $CO_2$ interfere (it gives a strong signal at m/z 44), $N_2O$ can be quantified basing on the signal at m/z 30. On page L4 a typical GC-MS chromatogram (as total ion current) is displayed. It can be observed that, as an effect of the vacuum applied on the detector end of the column, retention times are shorter with respect to those obtained with ECD detection.

## Calibration

Calibration curves for $N_2O$ and halogenated anaesthetics can be prepared simultaneously.

Draw pure $N_2O$ in a gas sampling bulb. Transfer 20 ml of pure $N_2O$ in the 1 litre bottle through the septum by a gastight syringe. Switch on the magnetic stirrer and let the mixture equilibrate for 30 minutes.

Standard solutions of the halogenated compounds must be prepared in water/methanol 60/40 v/v in order to con-

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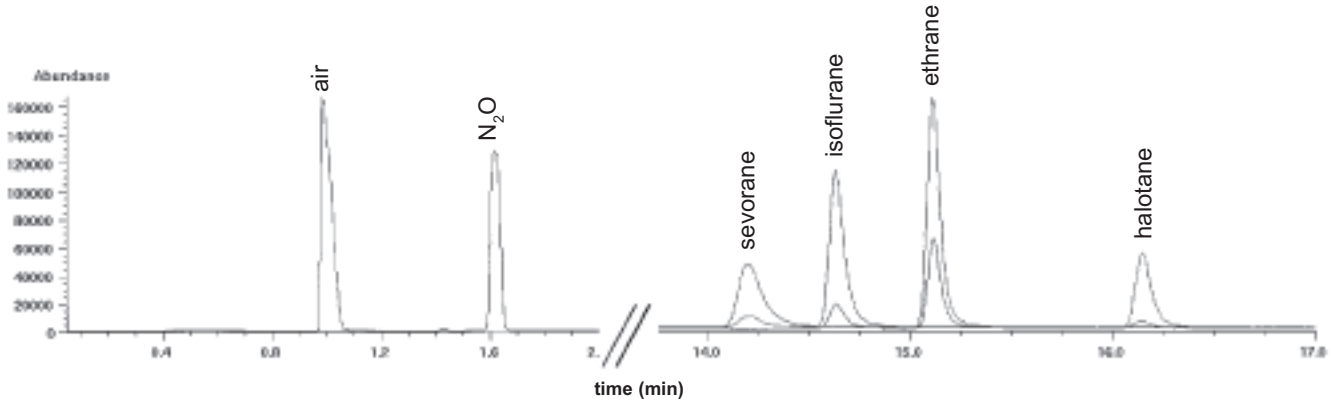
MSD Analysis




tain from 0.05 to 3.0 mg/l of each compound; five calibration levels are recommended.
For each level pipet 10 ml of calibration solution in an empty vial, add a blank code 132 cartridge and cap immediately.
Add also a precisely measured volume of diluted $N_2O$ drawn from the bottle by a gastight syringe (usually added volume ranges from 50 to 1,000 µl), stir and let equilibrate at 45 °C for 1 hour.

The values above generally comprise the usual conditions of operating theatres. The analyst may choose different values if needed, but equivalent exposure values should not exceed 400,000 $mg \cdot m^{-3} \cdot min$ for nitrous oxide and 50,000 $mg \cdot m^{-3} \cdot min$ for each of the halogenated compounds.

Pay attention: the ECD and/or MSD response may not be linear. If this should be the case, use a second order calibration curve.

**Useful data**

| name | chemical formula | molecular weight | 1 $mg \cdot m^{-3}$ at 25°C = ppm |
|---|---|---|---|
| nitrous oxide | $N_2O$ | 44 | 0.556 |
| forane | $CHF_2$-O-CHCl-$CF_3$ | 184.5 | 0.133 |
| ethrane | $CHF_2$-O-$CF_2$-CHClF | 184.5 | 0.133 |
| halothane | $CF_3$-CHBrCl | 197.4 | 0.124 |
| sevorane | $CH_2F$-O-CH$(CF_3)_2$ | 200 | 0.123 |

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Edizione 01/2019

# phenol, methylphenol and dimethylphenol

## (thermally desorbed)

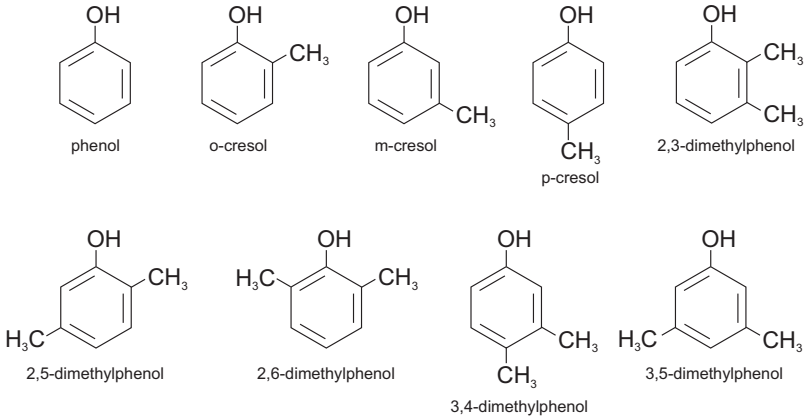
## What you need

**white diffusive body code RAD120**
**supporting plate code RAD121**
**vertical adapter code RAD122 (optional)**
**chemiadsorbing cartridge code RAD147**

## Principle

Code RAD147 cartridge is a stainless steel net cylinder with 100 mesh opening and 4.8 mm diameter, packed with 250 ± 10 mg of Tenax-TA, particle size 20-35 mesh. Phenols are trapped by adsorption and recovered by thermal desorption, analysis is performed by capillary gas chromatography and MS detection.

The method has been optimized for the following compounds:




## Sampling rates

Sampling rate values (in ml·min$^{-1}$) at 298 K (25 °C) and 1013 hPa are listed in the table on the right. All of the values shown have been experimentally measured.

### Effect of temperature, humidity and wind speed

Sampling rates varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation

$$Q_K = Q_{298} \left(\frac{K}{298}\right)^{1.5}$$

where $Q_K$ is the sampling rate at the temperature K and $Q_{298}$ is the reference value at 298 K.

This produces a variation of ±5% for 10 °C variation (upwards or downwards) from 25 °C.

Sampling rate is invariant with humidity in the range 15 ÷ 90% and with wind speed between 0.1 and 10 m·s$^{-1}$.

| | sampling rate ml·min$^{-1}$ | limit of detection[1] µg·m$^{-3}$ | uncer-tainty at 2σ % |
|---|---|---|---|
| phenol | 38 | 0.3 | 24.1 |
| o-chresol | 45 | 0.4 | 17.5 |
| m-chresol | 48 | 0.4 | 8.0 |
| p-chresol | 48 | 0.4 | 8.0 |
| 2,3-dimethylphenol | 53 | 0.4 | 26.0 |
| 2,5-dimethylphenol | 51 | 0.3 | 25.2 |
| 2,6-dimethylphenol | 46 | 0.4 | 7.6 |
| 3,4-dimethylphenol | 60 | 0.4 | 22.1 |
| 3,5-dimethylphenol | 61 | 0.4 | 22.2 |

[1]riferita ad esposizione di 24 ore e misurata con rivelatore a spettrometro di massa nelle condizioni di desorbimento descritte in Analisi

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## Calculations

The listed sampling rate values take already into account the recovery yields of adsorbed compounds. The average concentration over the sampling period is therefore calculated from sampled mass of analyte and exposure time without introducing any other corrective factor, apart from temperature variations of Q.

Average concentration ***C*** in $\mu g \cdot m^{-3}$ over the whole exposure time is calculated according to the following expression:

$$C\ [\mu g \cdot m^{-3}] = \frac{m\ [\mu g]}{Q_K\ [ml \cdot min^{-1}] \cdot t\ [min]}\ 1.000.000$$

where:
***m*** = mass of analyte in µg
***t*** = exposure time in minutes

## Exposure

### Workplace environment

Exposure time can range from 2 to 8 hours.

### Other indoor sampling experiments and outdoor campaigns

The recommended exposure times range from 8 hours to 7 days.

## Storage

The duration of Tenax adsorbent capacity is virtually unlimited. If kept in a cool place not contaminated by phenols, white and adsorbent capacity remain unchanged for at least twenty-four months. The expiry date and the lot number are printed on the transparent plastic casing, whose integrity acts as a guarantee seal.

After exposure the cartridges, well capped and kept in a cool and solvent-free place, maintain their content unaltered for at least three months.

## Analysis

The analytical method hereafter described have been set up by the Perkin-Elmer Turbomatrix thermal desorber and Agilent 5973 MSD mass spectrometer detector. They may be implemented on other instruments by introducing minor adjustements.

### Desorption

The thermal desorber is equipped with 1/4” s.s. sample tubes, they have to be hollow and free: discard the stainless steel gauze disk which is fitted to the groove and discard also the springs if present.

Code 147 cartridge has been dimensioned to fit the diameter of Turbomatrix thermal desorption tubes. Its length is such that, when the cartridge is introduced into the tube and is stopped by the groove, it is positioned exactly centrally with respect to the tube length. The same considerations apply to the Markes Unity thermal desorber.

Once capped, the Turbomatrix steel tube has to be positioned in the carousel with the grooves on the bottom.

The desorption conditions described below have been developed to obtain the best results from cartridges exposed for seven days to the usual concentrations of urban and indoor pollution. Shorter exposure times or much higher concentrations than usual may make it necessary to readjust the splits.

Temperatures and timing

- Desorption: 280°C for 10 minutes
- Cryofocusing trap (Tenax TA): during primary desorption maintain at 2 °C, secondary desorption at 99 $°C \cdot sec^{-1}$ up to 290 °C, maintain at 290 °C for 1 minute
- Six port valve: 150 °C
- Transfer line: 200 °C

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Flows

- Carrier gas: helium, 24 psi
- Desorption flow: 100 ml·min$^{-1}$
- Flow from tube to cryofocusing trap: 20 ml·min$^{-1}$
- Outlet split: 25 ml·min$^{-1}$

## Instrumental analysis

Column

J&W HP-5MS Ultra Inert or equivalent, length 60 m, internal diameter 0.25 mm, film thickness 0.25 µm; the column is directly fitted to the six-port valve of Turbomatrix apparatus

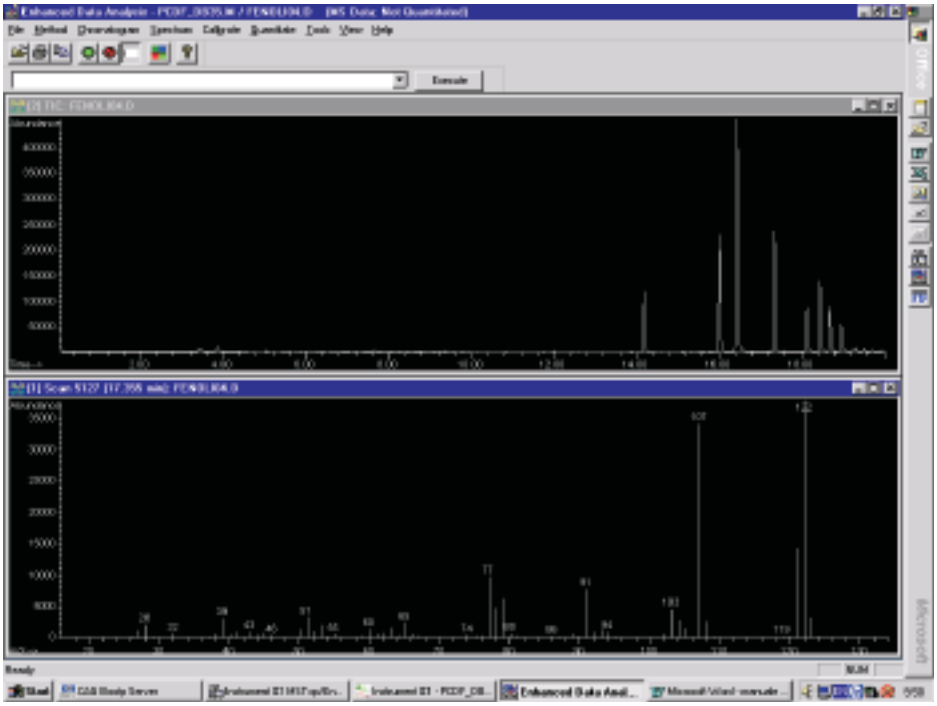
Temperatures

- GC oven: 40 °C for 5 minutes, 5 °C·min$^{-1}$ up to 115°C, 10 °C·min$^{-1}$ up to 165 °C, 30 °C·min$^{-1}$ up to 285 °C, final isotherm 3 minutes
- GC-MS interface: 260 °C
-

Flows

- helium carrier gas: 1.6 ml·min$^{-1}$
-

*In the figure on the right a typical chromatogram (as total ion current) is shown.*



## Calibration

Calibration curves are obtained by gas-phase injection of methanol solutions of the target compounds onto blank cartridges. Injections are performed through a GC injector, where a short piece of wide-bore (0.53 mm i.d.) deactivated uncoated column is installed. The other end bears a Swagelock reducing connection (1/16”-1/4”).

The 1/4” Swagelock nut has to be equipped with a PTFE ferrule instead of the original steel one (use PTFE ferrules that come along with the Turbomatrix caps).

Introduce a blank code RAD147 cartridge in a Turbomatrix tube and fit the tube to the Swagelock nut. Keep the injector at 170 °C but do not heat the oven. Inject slowly 1 µl of each calibration solution under nitrogen flow (40 ml·min$^{-1}$) and let the system purge for 2 minutes. Analyze the cartridge as you would do with a sample. We suggest you to prepare a complete set of calibration solutions by subsequent dilutions such as they contain, for example, 4, 2, 1, 0.05, 0.025 and 0.01 µg·µl$^{-1}$ of each compound.

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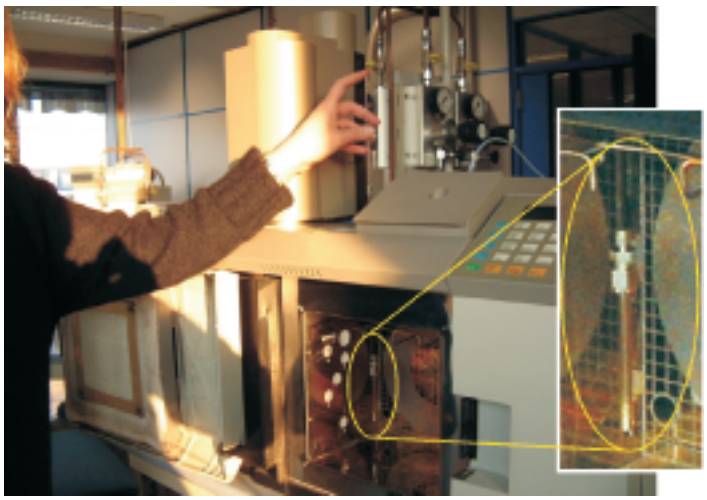
## Recupero delle cartucce

The cartridges can be reconditioned using the thermal desorber in tube conditioning mode, heating them at 280 ° C for at least 20 minutes in an inert gas flow (helium or nitrogen at a flow of 50 ÷ 100 ml·min$^{-1}$).



*To prepare the calibration standards fit a 1/16”-1/4” Swagelock reducing connection to the GC injector by a short piece of wide-bore deactivated uncoated column.*

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# 1,3-butadiene and isoprene

## What you need

**yellow diffusive body code RAD1202**
**supporting plate code RAD121**
**vertical adapter code RAD122 (optional)**
**chemiadsorbing cartridge code RAD141**

## Principle

Cartridge code RAD141 is a 4.8 mm diameter stainless steel mesh tube with a mesh size of 3x8 µm, filled with approximately 480 mg of graphite carbon (Carbopack X) 40/60 mesh.

1,3-butadiene and isoprene are trapped by adsorption, recovered by thermal desorption and analysed by capillary gas chromatography with MS detector.

## Sampling rates

Sampling rate values were measured experimentally at 20°C (273 K) and 1013 hPa in a dynamic controlled atmosphere chamber.

The sampling rate for 1,3-butadiene in the workplace is **30.5 ± 0.3** ml·min$^{-1}$ (nominal value at a concentration between 114 and 226 µg·m$^{-3}$ for 8-hour exposures). For the longer term (7 days) sampling the value is **4.7** ml·min$^{-1}$ [Strandberg et al. (1), (2)].

For isoprene the sampling rate is **41.2 ± 4.9** ml·min$^{-1}$ (in the range 2 ÷ 6,680 µg·m$^{-3}$ for exposures of 30 to 480 min).

### Effect of temperature, humidity and wind speed

Both temperature and relative humidity affect the sampling rate of 1,3-butadiene. If the temperature drops to 5 °C, the bias is + 12.9% at 20% RH or -2.4% at 80% RH, compared to 20 °C and 50% RH. Avoid sampling at temperatures close to 40 °C, as the sampling rate shows a significant decrease.

The effect of temperature and relative humidity on the isoprene sampling rate is lower: at low temperature and humidity (5°C, 21% RH) the sampling rate is 10% higher, while at high temperature and humidity (41°C, 77% RH) there is a 23% decrease.

Do not expose the sampler directly to rain. Always use the weather box code RAD196 for outdoor sampling to prevent water from entering the membrane and bathing the absorbent.

## Calculations

The average concentration C over the exposure time interval is calculated from the mass of the analyte found on the cartridge (corrected for the white, if any) and from the exposure time, using the absorption values above, as follows:

$$C\ [\mu g \cdot m^{-3}] = \frac{m\ [\mu g]}{Q_K\ [ml \cdot min^{-1}] \cdot t\ [min]}\ 1{,}000{,}000$$

where:
***m*** = mass of analyte in µg
***t*** = exposure time in minutes

(1) Strandberg et al. Atmos. Environ., 2006. **39**(22), 4101-4110.
(2) Strandberg et al. Atmos. Environ., 2006. **40**(40), 7686-7695.

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## Limit of detection

The blank response, the limit of detection (LOD) and the limit of quantification (LOQ) depend on the instrumentation and the analytical conditions.

Under the analytical conditions specified below, the blank value is not detectable, i.e. it is less than 0.5 ng for both compounds.

The LOQ for 8-hour workplace exposure is 0.1 $\mu g \cdot m^{-3}$. For a 7-day exposure to ambient air, the LOQ is 0.03 $\mu g \cdot m^{-3}$; see also Strandberg et al. (2).

## Measurements uncertainty

The following table shows the values of uncertainty in 1,3-butadiene measurements in the workplace, evaluated with two different approaches. Uncertainties were first determined under laboratory conditions, following the methods of the ISO GUM (*Guide to Expression of Uncertainty in Measurement*, International Organization for Standardization) and ISO 5725 (*Accuracy (trueness and precision)* of measurement methods and results General principles and definitions) standards. In this case, the uncertainty takes into account all the contributions involved in the whole measurement process (time, T, RH on the sampling rate, uncertainty of the measured mass and so on), contributions which were determined according to EN 838. Subsequently, the uncertainty was determined by a field comparison with OSHA 56 (as a reference method), according to ISO 13752.

***Uncertainty of measurement for an 8-hour sampling of 1,3-butadiene in working environment***

| Relative combined expanded uncertainty ($2 \cdot u_c$) | 200 $\mu g \cdot m^{-3}$ | 442 $\mu g \cdot m^{-3}$ (0.1 TLV) | 2210 $\mu g \cdot m^{-3}$ (0.5 TLV) | 4420 $\mu g \cdot m^{-3}$ (TLV-TWA ACGIH) |
|---|---|---|---|---|
| Laboratory tests at 20 °C, 50% RH (EN 838, calculations by ISO GUM) | 48.4% | | | |
| Field comparison (ISO 13752) | 37.0% | 25.0% | 11.1% | 7.9% |

## Storage

After the exposure, the samples, well capped in their glass tubes, have to be stored in the freezer, because 1,3-butadiene and isoprene are reactive compounds. Laboratory tests according to EN 838 showed for both compounds a loss of analyte of 7-8% after 14-day storage. The samples shall therefore be analysed within 14 days from the end of exposure, in order to ensure the maximum loss of analyte remain within 10%.

## Analysis

The method proposed here was developed with the Perkin-Elmer Turbomatrix thermal desorber coupled to the Agilent 6890 gas chromatograph and Agilent 5973 mass spectrometer. It can of course be transferred to other instruments.

### Desorption

The 1/4 "pipe supplied with the Turbomatrix must be empty and free: remove the stainless steel disk placed inside it in correspondence with the circular incision and, if present, also the springs.

The code 141 cartridge has been sized so that its outer diameter coincides with the inner diameter of the Turbomatrix tube. Moreover, its length is such that, when the cartridge is introduced into the tube and is stopped by the groove, it is positioned exactly centrally with respect to the tube length. The same considerations apply to the Markes Unity thermal desorber.

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Once capped, the Turbomatrix steel tube has to be positioned in the carousel with the grooves on the bottom.

The described conditions have been optimized for seven days exposures to typical concentrations of urban atmospheres and indoor environments. Shorter exposure times or considerably higher concentrations would require different settings of split flows.

Temperatures and timing

- Desorption: 350 °C for 6 minutes, nitrogen flow through the tube 100 ml·min$^{-1}$, of which 20 ml·min$^{-1}$ sent to the cryofocalization trap and 80 ml·min$^{-1}$ to the inlet split:
- Cryofocusing trap (Tenax TA): adsorption -20 °C, desorption 99 °C·sec$^{-1}$ up to 290 °C, 1 minute at 290 °C, trap desorption in nitrogen flow at 26.8 ml·min$^{-1}$, of which 25 ml·min$^{-1}$ at the split outlet;
- Six port valve: 150 °C
- Transfer line: 200 °C

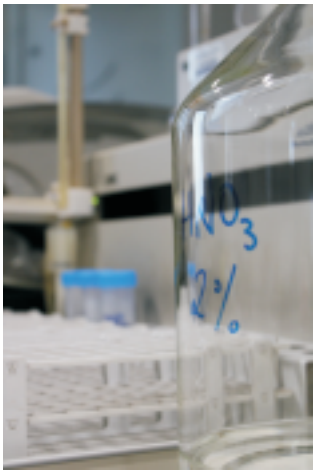
## Instrumental analysis

Column

J&W GS-GASPRO, length 60 m, i.d. 0.32 mm; the column is directly fitted to the six-port valve of Turbomatrix apparatus.

Temperatures

- GC oven: 80 °C for 1 minute, 25 °C·min$^{-1}$ up to 175 °C, mantain for 8 minutes, 25 °C·min$^{-1}$ up to 250 °C, final isotherm 11.2 minutes
- Interface GC-MS: 290 °C
- Ionic source: 230 °C, quadrupole 150 °C



Flows

- Carrier gas: helium at 1.8 ml·min$^{-1}$

## Calibration

The calibration curve is performed by injecting known aliquots of a gaseous mixture certified as 1,3-butadiene in nitrogen onto virgin cartridges. The operation is carried out with the injector of a gas chromatograph whose output is grafted with a short piece (10 cm) of a deactivated capillary column (0.25 mm id) connected to a Swagelock reducer 1/16 "-1/4" .

Instead of the 1/4 ”steel ferrule of the reducer, one of those in PTFE used for closing the Turbomatrix tubes is used

Introduced a virgin cartridge in the Turbomatrix tube and inserted the tube in the Swagelock reducer, keeping the injector at 50 °C and the oven cold, injecting different volumes of the gas mixture under a flow of nitrogen of 30 ml·min$^{-1}$, leaving flow the gas for 2 minutes.

It is recommended to use a mixture of 1,000 ppm of 1,3-butadiene in nitrogen and to inject aliquots of 20, 40, 60, 80 and 100 µl of mixture (with a 100 µl gas-tight syringe) or 100 aliquots , 200, 300, 400 and 500 µl of mixture (with a 500 µl gas-tight syringe) according to the desired calibration range.

## Cartridges conditioning

The cartridges can be reconditioned using the thermal desorber in "*tube conditioning*" mode, heating them to 350 °C for at least 20 minutes in an inert gas flow (helium or nitrogen at a flow of 50 ÷ 100 ml·min$^{-1}$).

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## Index by code



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# ATTACHMENT B

## STANDARD OPERATING PROCEDURE, SUB-SLAB SOIL GAS SAMPLING

# STANDARD OPERATING PROCEDURE SUB-SLAB SOIL GAS SAMPLING

MFA will install sub-slab soil-gas sampling points using the Cox-Colvin & Associates, Inc. (Cox-Colvin) Vapor Pin™ system. The procedures developed by Cox-Colvin for installing and removing the Vapor Pin™ system, including the secure cover, are attached.

According to the California Department of Toxic Substances Control (DTSC), the collection of sub-slab samples should follow the procedures in the California Environmental Protection Agency (Cal/EPA) active soil gas investigation advisory, which recommends purging, leak testing, and shut-in testing (Cal/EPA, 2015). Specific procedures are taken from the New Jersey Department of Environmental Protection Vapor Intrusion Technical Guidance (NJDEP, 2012). The following procedures will be followed in collecting sub-slab vapor samples from the sub-slab soil gas sampling points:

- To avoid air breakthrough from nearby foundation cracks in the slab, DTSC recommends using sampling containers with volumes less than or equal to one liter. Subsequently, sub-slab soil vapor samples will be collected using laboratory-supplied, depressurized, 1-liter Summa® canisters.
- MFA will connect the sampling equipment as shown in the attached figure such that the equipment can be purged, leak tested, shut-in tested, and sampled in the field. The vapor probe installed in the cement slab will be connected to the ¼ turn Swagelok® ball valve (Valve #1—sampling valve), using appurtenant stainless steel or Teflon®-lined tubing. The sampling valve is connected to a vacuum gauge, which is attached to the flow controller. At the flow controller, a Swagelok tee connection will be fitted to the 1-liter Summa canister and to a second ¼ turn Swagelok ball valve (Valve #2—purge valve) used to isolate the purging equipment during actual sampling. The Summa canister has a built-in valve that allows the canister to be isolated during purging and leak-checking activities. On the other side of the purge valve (#2), a vacuum pump will be connected in order to induce vacuum for purging and shut-in testing.
- Helium will be contained around the sampling apparatus and sampling probe to serve as a leak-check compound. Helium will be released into a small structure that is placed over the sampling probe and sampling train. With the Summa canister valve closed, a sample of the soil gas collected during purging (described below) will be contained in a Tedlar® bag. A field helium detector will be used to sample the air purged through the sampling train to verify the presence or absence of helium. A helium concentration greater than 10 percent of the concentration in the containment structure indicates that a leak is occurring (NJDEP, 2012). If a leak is detected, the sampling and purging train fittings will be tightened and the leak check will be repeated. The absence of helium during the purging process verifies the integrity of the sampling system before the sample is collected. The Summa canister will also be analyzed for helium by the analytical laboratory as a quality assurance measure.

- A shut-in test of the sampling train will be conducted independent of the leak check on the soil gas probe described in the Cox-Colvin procedure. To perform a shut-in test, the assembled aboveground apparatus (valves, lines, and fittings downstream of the top of the probe) will be evacuated to a measured vacuum of approximately 15 inches-mercury. The sample train will then be closed off (by closing valves #1 and #2) and the vacuum gauge observed for at least one minute. If there is any observable loss of vacuum, the fittings will be adjusted as needed until the vacuum in the aboveground portion of the sample train does not noticeably dissipate (McAlary et al., 2009).

- A vacuum pump will be used to purge the connecting tubing and the sampling train. Purging will take place with the Sample Valve (#1) open, and with the helium containment structure in place as described above. During purging, the generally established maximum flow rate of 200 milliliters per minute will not be exceeded (DTSC, 2011; NJDEP, 2012). A target maximum flow rate of 150 milliliters per minute will be established at each sample location during each sampling event by collecting purge gas in a sealed container with a known volume such as a 1-liter Tedlar bag. The target purge volume is equal to three volumes, which include the probe and entire sampling train (excluding the Summa canister). The necessary purge volume is determined by the following equation (NJDEP, 2012):

  $$Purge\ Volume\ (milliliters) = 3\ (\pi\ r^2\ h)\ (10^{-3})$$

  Where:
  $3$ = number of required purge volumes.
  $\pi$ = 3.14159.
  $r$ = inner radius of the probe and connecting tubing (millimeters).
  $h$ = length of probe and entire sampling train (millimeters).
  $10^{-3}$ = conversion factor between cubic millimeters and milliliters.

- After the sampling train is purged and no leaks are detected in the sampling train, MFA will close the valve leading to the vacuum pump (Valve #2—purge valve), open the valve leading to the sampling probe (Valve #1—sample valve), and then open the valve on the 1-liter Summa canister to collect the sample over a 30-minute period. MFA will record field data during the sampling, including the sampling start and stop times, the initial and final canister vacuum readings, and weather conditions. The sample will be rejected if the initial canister pressure is not at least -25 inch of mercury or if the final canister pressure is greater than -0.1 inch of mercury.

- Upon completion of all sampling events, the sub-slab probes will be properly decommissioned consistent with the attached Cox-Colvin procedure. The borehole will be filled with grout and/or concrete patch material. Surface restoration may include a followup visit for final sanding and finish work to restore the floor slab, and associated coverings, to their original condition as required.

## REFERENCES

Cal/EPA. 2015. Advisory—active soil gas investigation. Jointly issued by the Los Angeles Regional Water Quality Control Board, San Francisco Regional Water Quality Control Board, and the California Environmental Protection Agency Department of Toxic Substances Control. July.

McAlary, T. A., P. Nicholson, H. Groenevelt, and D. Bertrand. 2009. A case study of soil-gas sampling in silt and clay-rich (low permeability) soils. Ground Water Monitoring & Remediation 29: 144-152.

NJDEP. 2012. Vapor intrusion technical guidance. Vers. 2.0. New Jersey Department of Environmental Protection, Site Remediation Program. January.

USEPA. 2006. Assessment of vapor intrusion in homes near the Raymark Superfund site using basement and sub-slab air samples. Document No. EPA/600/R-05/147. U.S. Environmental Protection Agency, Office of Research and Development. March.

# Standard Operating Procedure Installation and Extraction of the Vapor Pin™

May 20, 2011

Scope:

This standard operating procedure describes the installation and extraction of the Vapor Pin™[1] for use in sub-slab soil-gas sampling.

Purpose:

The purpose of this procedure is to assure good quality control in field operations and uniformity between field personnel in the use of the Vapor Pin™ for the collection of sub-slab soil-gas samples.

Equipment Needed:

- Assembled Vapor Pin™ [Vapor Pin™ and silicone sleeve (Figure 1)];
- Hammer drill;
- 5/8-inch diameter hammer bit (Hilti™ TE-YX 5/8" x 22" #00206514 or equivalent);
- 1½-inch diameter hammer bit (Hilti™ TE-YX 1½" x 23" #00293032 or equivalent) for flush mount applications;
- ¾-inch diameter bottle brush;
- Wet/dry vacuum with HEPA filter (optional);
- Vapor Pin™ installation/extraction tool;
- Dead blow hammer;
- Vapor Pin™ flush mount cover, as necessary;
- Vapor Pin™ protective cap; and
- VOC-free hole patching material (hydraulic cement) and putty knife or trowel.

[1]Cox-Colvin & Associates, Inc., designed and developed the Vapor Pin™; a patent is pending.

**Figure 1**. Assembled Vapor Pin™.

Installation Procedure:

1) Check for buried obstacles (pipes, electrical lines, etc.) prior to proceeding.

2) Set up wet/dry vacuum to collect drill cuttings.

3) If a flush mount installation is required, drill a 1½-inch diameter hole at least 1¾-inches into the slab.

4) Drill a 5/8-inch diameter hole through the slab and approximately 1-inch into the underlying soil to form a void.

5) Remove the drill bit, brush the hole with the bottle brush, and remove the loose cuttings with the vacuum.

6) Place the lower end of Vapor Pin™ assembly into the drilled hole. Place the small hole located in the handle of the extraction/installation tool over the Vapor Pin™ to protect the barb fitting and cap, and tap the Vapor Pin™ into place using a

dead blow hammer (Figure 2). Make sure the extraction/installation tool is aligned parallel to the Vapor Pin™ to avoid damaging the barb fitting.

**Figure 2**. Installing the Vapor Pin™.

For flush mount installations, unscrew the threaded coupling from the installation/extraction handle and use the hole in the end of the tool to assist with the installation (Figure 3).

**Figure 3**. Flush-mount installation.

During installation, the silicone sleeve will form a slight bulge between the slab and the Vapor Pin™ shoulder. Place the protective cap on Vapor Pin™ to prevent vapor loss prior to sampling (Figure 4).

**Figure 4**. Installed Vapor Pin™.

7) For flush mount installations, cover the Vapor Pin™ with a flush mount cover.

8) Allow 20 minutes or more (consult applicable guidance for your situation) for the sub-slab soil-gas conditions to equilibrate prior to sampling.

9) Remove protective cap and connect sample tubing to the barb fitting of the Vapor Pin™ (Figure 5).

**Figure 5**. Vapor Pin™ sample connection.

10) Conduct leak tests [(e.g., real-time monitoring of oxygen levels on extracted sub-slab soil gas, or placement of a water

dam around the Vapor Pin™) Figure 6]. Consult your local guidance for possible tests.

**Figure 6**. Water dam used for leak detection.

11) Collect sub-slab soil gas sample. When finished sampling, replace the protective cap and flush mount cover until the next sampling event. If the sampling is complete, extract the Vapor Pin™.

Extraction Procedure:

1) Remove the protective cap, and thread the installation/extraction tool onto the barrel of the Vapor Pin™ (Figure 7). Continue turning the tool to assist in extraction, then pull the Vapor Pin™ from the hole (Figure 8).

**Figure 7**. Removing the Vapor Pin™.

**Figure 8**. Extracted Vapor Pin™.

2) Fill the void with hydraulic cement and smooth with the trowel or putty knife.

3) Prior to reuse, remove the silicone sleeve and discard. Decontaminate the Vapor Pin™ in a hot water and Alconox® wash, then heat in an oven to a temperature of 130° C.

The Vapor Pin™ to designed be used repeatedly; however, replacement parts and supplies will be required periodically. These parts are available on-line at www.CoxColvin.com.

Replacement Parts:

Vapor Pin™ Kit Case - VPC001
Vapor Pins™ - VPIN0522
Silicone Sleeves - VPTS077
Installation/Extraction Tool - VPIE023
Protective Caps - VPPC010
Flush Mount Covers - VPFM050
Water Dam - VPWD004
Brush - VPB026

# Standard Operating Procedure Use of the Vapor Pin™ Drilling Guide and Secure Cover

July 16, 2012

Scope:

This standard operating procedure (SOP) describes the methodology to use the Vapor Pin™ Drilling Guide and Secure Cover to install and secure a Vapor Pin™ in a flush mount configuration.

Purpose:

The purpose of this SOP is to detail the methodology for installing a Vapor Pin™ and Secure Cover in a flush mount configuration. The flush mount configuration reduces the risk of damage to the Vapor Pin™ by foot and vehicular traffic, keeps dust and debris from falling into the flush mount hole, and reduces the opportunity for tampering. This SOP is an optional process performed in conjunction with the SOP entitled "Installation and Extraction of the Vapor Pin™". However, portions of this SOP should be performed prior to installing the Vapor Pin™.

Equipment Needed:

- Vapor Pin™ Secure Cover (Figure 1);
- Vapor Pin™ Drilling Guide (Figure 2);
- Hammer drill;
- 1½-inch diameter hammer bit (Hilti™ TE-YX 1½" x 23" #00293032 or equivalent);
- 5/8-inch diameter hammer bit (Hilti™ TE-YX 5/8" x 22" #00226514 or equivalent);
- assembled Vapor Pin™;
- #14 spanner wrench;
- Wet/Dry vacuum with HEPA filter (optional); and
- personal protective equipment (PPE).

**Figure 1.** Vapor Pin™ Secure Cover.

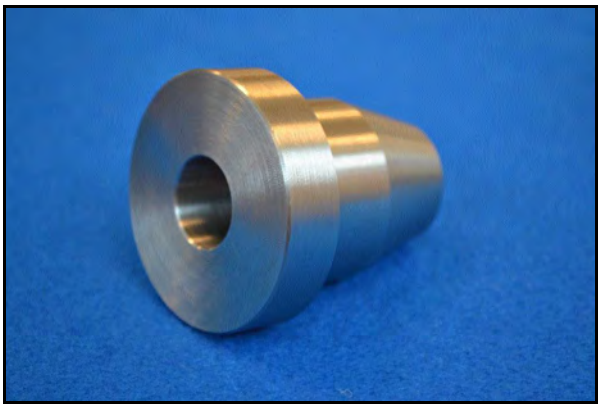


**Figure 2.** Vapor Pin™ Drilling Guide.

Installation Procedure:

1) Check for buried obstacles (pipes, electrical lines, etc.) prior to proceeding.

2) Set up wet/dry vacuum to collect drill cuttings.

3) While wearing PPE, drill a 1½-inch diameter hole into the concrete slab to a

depth of approximately 1 3/4 inches. Pre-marking the desired depth on the drill bit with tape will assist in this process.

4) Remove cuttings from the hole and place the Drilling Guide in the hole with the conical end down (Figure 3). The hole is sufficiently deep if the flange of the Drilling Guide lies flush with the surface of the slab. Deepen the hole as necessary, but avoid drilling more than 2 inches into the slab, as the threads on the Secure Cover may not engage properly with the threads on the Vapor Pin™.

**Figure 3**. Installing the Drilling Guide.

5) When the 1½-inch diameter hole is drilled to the proper depth, replace the drill bit with a $^{5}/_{8}$-inch diameter bit, insert the bit through the Drilling Guide (Figure 4), and drill through the slab. The Drilling Guide will help to center the hole for the Vapor Pin™, and keep the hole perpendicular to the slab.

6) Remove the bit and drilling guide, clean the hole, and install the Vapor Pin™ in accordance with the SOP "Installation and Extraction of the Vapor Pin™.

**Figure 4**. Using the Drilling Guide.

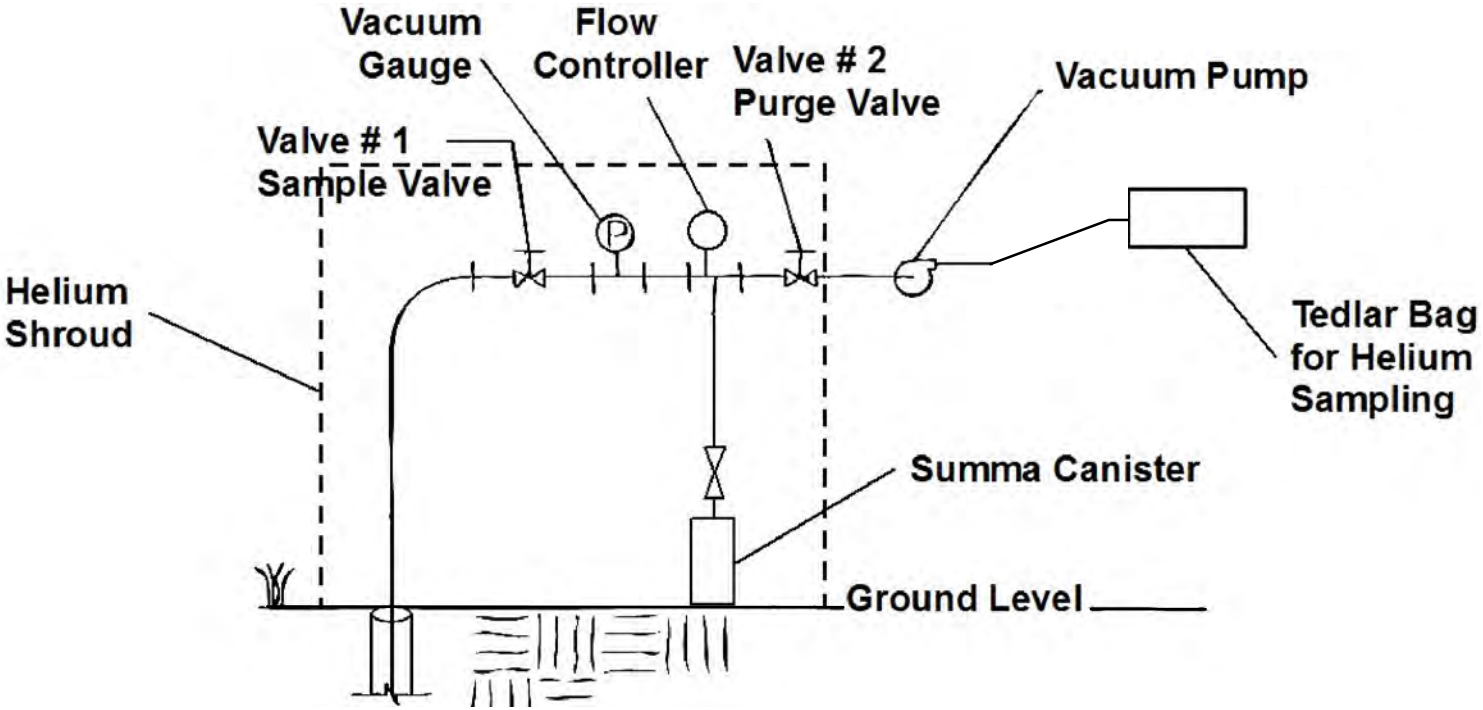
7) Screw the Secure Cover onto the Vapor Pin™ and tighten using a #14 spanner wrench by rotating it clockwise (Figure 5). Rotate the cover counter clockwise to remove it for subsequent access.

**Figure 5**. Tightening the Secured Cover.

Limitations:

On slabs less than 3 inches thick, it may be difficult to obtain a good seal in a flush mount configuration with the Vapor Pin™.

# Figure
# Sub-Slab Soil Gas Sampler System




Source: CH2MHill, Corvallis Applied Sciences Laboratory

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