Indoor Air Sampling / Corrective Action Work Plan

297 West 5th Avenue
North Pole, Alaska

July 26, 2022

Prepared for:

Mr. David Cornwall

Prepared by:

Alaska Resources and Environmental Services, LLC.

3520 International Street
Fairbanks, AK 99712

Prepared by:

Lyle Gresehover

Lyle Gresehover
Project Manager/Geologist

INTRODUCTION & PURPOSE

This Indoor Air Sampling/ Corrective Action Work Plan was prepared on behalf of Mr. David Cornwall who has contracted with Alaska Resources & Environmental Services (ARES) to perform a limited indoor air investigation at the subject property. Mr. Cornwall is the Owner of the Subject Property located at 297 West 5th Avenue. The ADEC Hazard ID for the site is 4439. The ADEC file # for the site is 100.38.216.

The purpose of this Work Plan is to obtain ADEC approval to conduct a limited indoor air quality assessment of the property and to determine if contaminants of concern (COCs) remain in place at the Subject Property above ADEC indoor air target levels for residential buildings. The data and findings collected from the indoor air assessment will be used to formulate recommendations specific to the site.

Additional work as requested by ADEC per letter dated May 12, 2022 (attached), will be forthcoming in a separate Work Plan pending authorization from the property owner, Mr. Cornwall.

SITE BACKGROUND

Site Description

The subject property is situated on an approximate 0.30-acre site located west of the Old Richardson Highway and north of Fifth Avenue at 297 Fifth Avenue, North Pole, Alaska (Figure 1). The site is located in the U.S. Geological Survey (USGS) Fairbanks D-1 SW quadrangle. The legal description for the property is as follows: Tax Lot 3A Block 14 B.V. Davis Homestead out of Lot 3 Block 14 B.V. Davis Homestead, Township 2 South, Range 2 East, Fairbanks Meridian.

History

Records indicate that in November 2006, a UST heating oil tank suspected of leaking was inadvertently filled. It was estimated that approximately 215 gallons of # 2 diesel fuel may have leaked from the tank before being pumped dry one week after filling. During excavation of the tank, approximately 5 gallons of fuel was recovered from the surface of the groundwater. One soil sample collected from the excavation pit indicated 9 mg/kg benzene, 65,000 mg/kg DRO, and 1,210 mg/kg GRO was present in the soil.

It was also noted that the contaminants most likely extend underneath the building which is located approximately 6’ from the source area. Diesel fuel odors were detected in portions of the interior of the building and crawl space during an inspection by ADEC staff and the owner.

Subsequent corrective actions/site characterization included installation of groundwater monitoring wells, installation of an air handling system in the crawl space and most recently collection of indoor air samples from the crawl space to assess indoor air quality.

Indoor air samples collected by Nortech Environmental in March 2018 detected Isopentane and Freon 11 in the southern and northern crawlspace. Both compounds do not have an ADEC target level and are not a chemical of concern related to the fuel oil release. No other compounds were detected in the south crawlspace. The north crawlspace had additional impacts which included benzene, toluene, ethylbenzene, and xylenes below ADEC residential target levels.

The site is currently in use as a day care facility.

Topography

The United States Geological Survey (USGS) Fairbanks Quadrangle (D-1 SW) provides topographic map coverage of the site. North Pole is located in the northern part of the Tanana Basin, which is a relatively flat floodplain of the Tanana River. The subject property is situated approximately 1.5 miles west of the Tanana River. Based upon the topographic map of the Fairbanks Quadrangle, the site elevation is approximately 435 feet above the mean sea level.

Regional Hydrology

The Chena and Tanana rivers are the dominant influence on ground-water flow in the subject area. Two discharge peaks characterize the Chena River: spring snowmelt runoff and late summer precipitation. The stage of Chena River typically rises and falls in response to stage changes of the Tanana River. The depth to groundwater varies in response to these controlling factors. Based on interpretation of USGS data and historical data, regional groundwater flow direction is generally to the north-northwest. However, the direction of flow can vary slightly depending on the stage of the Chena River and Tanana River. Depth to groundwater in the area is generally 8-10 feet bgs, though seasonal fluctuation can range between 6-12 feet bgs.

Field Work Protocol

Fieldwork described in this report will be conducted in accordance with *ADEC Vapor Intrusion Guidance for Contaminated Sites, November 2017.*

Mr. Dustin Stahl, Project Manager / Geologist for ARES, will oversee sampling activities. Mr. Stahl meets the ADEC qualifications of Qualified Environmental Professional by the Alaska Department under 18 AAC 75.

Field work Activities

Prior to sampling activities, ARES will conduct a site walk-through at least 24 hours before collecting indoor air samples to conduct a building survey. During the walk through and inspection ARES will complete the ADEC Building Survey and Indoor Air Sampling Questionnaire. Additionally, indoor vapor sources that could interfere with detecting COCs intruding into the building from subsurface sources will be removed if possible.

To avoid potential interferences and dilution effects, occupants will be asked to make a reasonable effort to avoid the following for 24 hours prior to sampling:

- Opening any windows, fireplace dampers, openings, or vents;
- Operating ventilation fans unless special arrangements are made;
- Smoking in the building;
- Using a wood stove, fireplace, or other auxiliary heating equipment (e.g., kero-sene heater);
- Operating or storing automobiles in an attached garage;
- Allowing containers of gasoline or oil to remain within the building
- Cleaning, waxing, or polishing furniture, floors, or other woodwork with petroleum- or oil-based products;
- Using air fresheners, scented candles, or odor eliminators;
- Engaging in any hobbies/crafts that use materials containing volatile chemicals;
- Using cosmetics, including hairspray, nail polish, nail polish removers, perfume/cologne, etc.;
- Lawn mowing or paving with asphalt; and
- Using building repair or maintenance products, such as caulk or roofing tar

Indoor Air Analytical Sampling

Indoor air samples will be collected using Radiello-130 Passive adsorption samplers and laboratory analyzed for hexane, cyclohexane, benzene, toluene, ethylbenzene, m,p-xylene, o-xylene, propylbenzene, 1,2,4-Trimethylbenzene, 1,3,5-Trimethylbenzene and naphthalene by modified EPA Method TO-17 (RAD130 Passive SE by Mod EPA TO-17).

In order for detection limits to be below ADEC Indoor air target levels the Radiello-130 Passive adsorption samplers will be deployed for three days. The samples will be deployed on a Friday after the daycare closes and retrieved Monday when the daycare reopens. The building's air handler will be turned off and all vents and window will be closed for the duration of the sampling event.

A total of two (2) analytical samples, one (1) per each previously sampled crawl space area (north crawlspace and south crawlspace) will be collected during the indoor air investigation.

Indoor Air Target Levels are displayed in Table 1 below. Since the building is currently being used for commercial purposes, but it could be used for residential purposes in the future, the results will be evaluated against both ADEC Target Levels for Residential and Commercial Indoor Air.

Table 1
Indoor Air Target Levels

Indoor Air -Chemicals of Concern			
Chemical Name	ADEC Target Levels for Commercial Indoor Air[1] (µg/m3)	ADEC Target Levels for Residential Indoor Air[1] (µg/m3)	ATSDR Inhalation Minimal Risk Levels[2] (µg/m3)
Hexane	3100	730	2100
Cyclohexane	26000	6300	NA
Benzene	16	3.6	10
Toluene	7500	3800	3800
Ethylbenzene	49	11	260
Total Xylenes	440	100	220
Propylbenzene	4400	1000	NA
Naphthalene	3.6	0.83	3.7
1,2,4-Trimethylbenzene	31	7.3	NA
1,3,5-Trimethylbenzene	NA	NA	NA

[1] ***DE**C generally calculates indoor air target levels based on the methods, toxicity information, and exposure parameters provided in DEC's Procedures for Calculating Cleanup Levels and the methods in EPA's Vapor Intrusion Screening Level Calculator.

[2] ATSDR Inhalation Minimal Risk Level based on exposure period of 365 days or more (Chronic levels).

µg/m3 - micrograms per cubic meter

Indoor Air Sampling Protocol

Indoor air samples will be collected using Radiello-130 Passive adsorption samplers RAD-130). RAD-130 samplers will be deployed for a three day period to sample the ambient air of each crawlspace below the building. Code 130 stainless steel net cylinders with activated charcoal will placed in diffusive body (code 120) protectors and connected to supporting plates (code 121). Volatile organic compounds will be trapped by adsorption and will be recovered by carbon disulfide displacement. Analysis will performed by modified EPA-TO-17 method using gas chromatography/mass spectrometry. Radiello sampling and analysis protocol is included in Appendix B. HOBO UX100 Temp data logging thermometers will be deployed on each floor and will record min, max, and average temperature data that will be reported to the lab for sample analysis. Local weather station data will be used to document and report barometric pressure and average outdoor temperature during the sampling event.

ARES proposes to collect two (2) analytical samples, one (1) per each previously sampled crawl space area (north crawlspace and south crawlspace) during the indoor air investigation. New disposable nitrile gloves will be worn during sample deployment and collection. Pens/marker with volatile ink (Sharpies) will not be used to fill out sample labels.

Following collection, samples will be stored and shipped in laboratory supplied sealed glass containers. A signed Chain-of-Custody form will accompany the samples to Eurofins/Air Toxics. Eurofins/Air Toxics is certified by the National Environmental

Laboratory Accreditation Program (NELAP), and Department of Defense (DOD-ELAP) for air and soil-gas analysis.

Schedule of Activities

Proposed activities are scheduled to begin as soon as scheduling permits pending ADEC approval of this Corrective Action Work Plan.

Final Report

Following field activities and receipt of analytical results, a Final Report will be submitted to ADEC upon completion of the project.

APPENDIX A
ADEC Correspondence

THE STATE
of ALASKA
GOVERNOR MIKE DUNLEAVY

Department of Law
CIVIL DIVISION
Environmental Section

1031 West Fourth Avenue, Ste. 200
Anchorage, AK 99501
Main: (907) 269-5100
Fax: (907) 276-3697

May 12, 2022

VIA EMAIL AND MAIL

David Cornwall
607 Old Steese Highway, Suite B
Fairbanks, Alaska 99701

Re: *Cornwall Property HOT (Heating Oil Release)*
AGO No. 2018100738

Dear Mr. Cornwall:

I write on behalf of the Alaska Department of Environmental Conservation (DEC), which formally referred the heating oil release at 297 West 5th Avenue, North Pole to the Alaska Department of Law (LAW) to assist with cleanup.

In November 2006, an underground heating oil tank (no longer in use due to suspicion of leaking) was filled in error. Upon realizing the error, approximately one week after filling, the tank was pumped empty, but at least 215 gallons had already leaked. The full amount of historic releases are unknown. A site chronology can be found at: https://dec.alaska.gov/Applications/SPAR/PublicMVC/CSP/SiteReport/4439.

DEC staff worked with the responsible party in 2007 to begin remediation of released fuel oil, followed by site investigations. Groundwater samples from three well point samples resulted in concentrations exceeding the groundwater cleanup level in the source area of 9.190 mg/L diesel range organics (DRO) and 869 ug/L benzene. Approximately 75 gallons of product were recovered in August 2007. During this time, the building was unoccupied.

Air samples were collected in September 2007 from the crawlspace and confirmed that vapor intrusion was occurring at levels above the EPA residential screening level. Modifications were then made to the crawlspace where the contaminants remained near and underneath the building.

The business was then sold and reopened as a daycare. DEC made recommendations for further work but no additional site characterization occurred, so DEC acquired state funding to conduct an indoor air sample event in 2018. In March

2018, staff with DEC - Contaminated Sites Program accompanied Nortech staff on site to conduct an indoor air quality assessment within the building crawlspace. Nortech concluded the air sample results indicated the air quality within the facility's crawlspace met DEC indoor air target levels. Despite DEC requesting a second air sample event for the autumn of 2018, no additional samples have been collected.

Contamination at the site has not been fully characterized, and the most recent sampling event was now several years ago. DEC requires further characterization, as well as sampling to assess the risk of exposure pathways for contamination into the building. DEC is particularly concerned about monitoring exposure pathways because a daycare operates on this property.

Accordingly, DEC requires a work plan from a qualified environmental professional by **June 17, 2022** to complete the follow characterization and sampling activities:

- An additional indoor air sampling event with the number of samples and distribution to be based upon the March 2018 sample results. The next sample event should be conducted in August or September 2022;
- Collection of soil samples during installation of additional groundwater (GW) monitoring wells and sampling of new and existing GW monitoring wells to establish the extent of the contamination;
- Completion of a well receptor survey; and
- Removal of free product from the water table.

At this time, the State's priority is to have sampling completed to assess indoor air quality. Please note that you are liable for State costs—$23,482.74 as of April 1, 2022—which are secured by a lien on the daycare property. All costs for the State's continued efforts to contact you and move cleanup forward are automatically added to the lien. It is in your best interest to resolve this matter expeditiously.

We appreciate your prompt response and attention to this matter. Please submit the work plan to Laura Jacobs at laura.jacobs@alaska.gov. If you would like to discuss legal matters, you may contact me at jennifer.seely@alaska.gov or (907) 269-5215.

Sincerely,

TREG R. TAYLOR
ATTORNEY GENERAL

By: Jennifer Seely
Jennifer J. Seely
Assistant Attorney General

cc: Laura Jacobs, DEC laura.jacobs@alaska.gov
Janice Wiegers, DEC janice.weigers@alaska.gov
Abigail Krohnfeldt
Lewis Watson, DHSS lewis.watson@alaska.gov

APPENDIX B

Radiello Sampling and Analysis Protocol

FONDAZIONE SALVATORE MAUGERI
AUGEAT SEMPER
CLINICA DEL LAVORO
E DELLA RIABILITAZIONE
I.R.C.C.S.

radiello®

Manual

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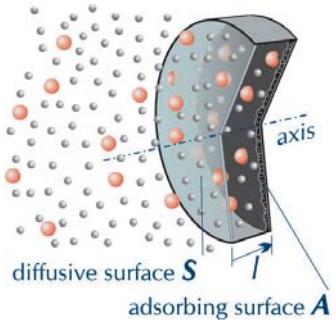
Index

radiello applications

how does the diffusive sampler work?



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.

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

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

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.

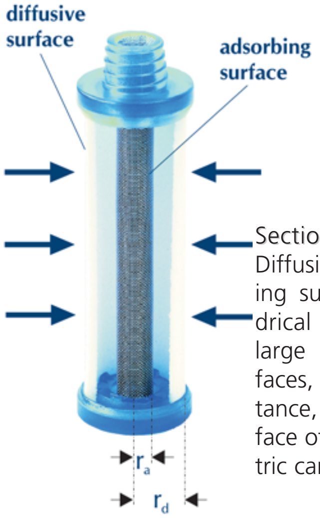
The value of distance ***l*** could also be reduced, but under the critical value of about 8 mm the diffusion law is no longer valid in the case of low air velocity values, since adsorption rate becomes higher than supplying rate of analyte molecules at the diffusive surface.

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.

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 electrton 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.

why is *radiello* so *special?*

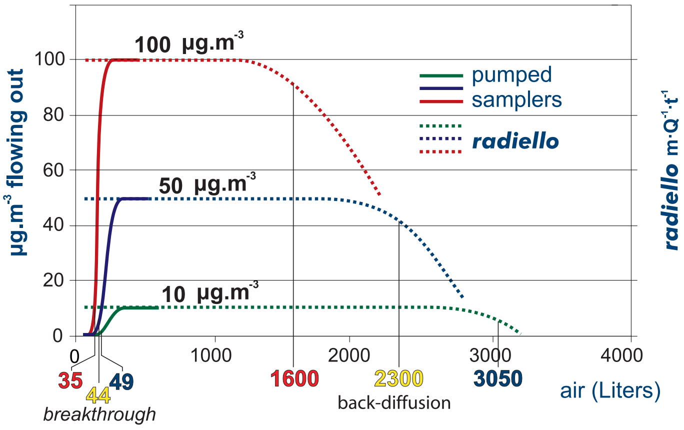
The diffusive sampling does not involve the use of heavy and encumbering pumping systems, does not have energy power supply problems, does not require supervision, is noiseless, is not flammable and does not represent an explosion hazard, can be performed by everybody everywhere and with very low costs.

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}.*



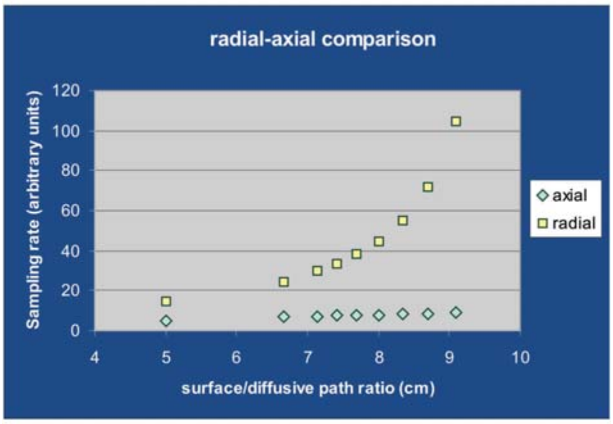
Why diffusive sampling has not been so extensively adopted up to now?

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 symmetry, 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 symmetry 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.

- ✓ **constant**, due to the great adsorbing capacity of the adsorbing cartridge;
- ✓ **reproducible**, by virtue of the stiffness of the diffusive membrane and the cartridge and of the close tolerances characterizing all the components of ***radiello***;
- ✓ **invariable with air speed**, due to the tortuosity of the diffusive path inside the microporous diffusive cylindrical surface;
- ✓ **precisely measured**, because it is not calculated but experimentally measured in a controlled atmosphere chamber in a wide range of concentration, temperature, relative humidity, air speed conditions and with or without interferents....

Moreover, ***radiello***

- ▶ 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 Padova of the Fondazione Salvatore Maugeri-IRCCS

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. See the application section at the back for codes relevant to the different analytes.

Available in 20 pieces per package.

The cartridge has to be introduced into the diffusive body.

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.

code 121

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 120**, 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 120-1**, 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 120-2**, 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 120-3**, 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.

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

code 120 **120-1** **120-2** **120-3**

The label

code 190

Self-adhesive, with printed barcode number. Since each barcode 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.

how to use radiello

before sampling

assembling the supporting plate

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

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

4

and place 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)

user tip

Assemble the supporting plate in your laboratory before the sampling campaign to save time in the field

on-field
to start the sampling

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 does, the cartridge is not correctly positioned and out of axis.**
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.
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.***

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

1

2

Keeping the diffusive body in a vertical position, to screw it onto the support plate

3

user tip

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

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 writing might have become illegible!

DO NOT USE MARKER 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.

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.

radiello
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 to be replaced: repeatedly adsorbed dust may have penetrated the so deeply that they cannot be removed by washing anymore.

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

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 ***ready-to-use 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*** ***radiello*** (polycarbonate cap, glass or plastic tube, special snapping vertical adapter, barcode label and polypropylene container) is available for the sampling of the following compounds:

code	**sampling of**	**contains**
123-1	BTEX and VOCs	white diffusive body and cartridge code 130
123-2	BTEX and VOCs	yellow diffusive body and cartridge code 145
123-3	NO_2, SO_2 and HF	blue diffusive body and cartridge code 166
123-4	aldehydes	blue diffusive body and cartridge code 165
123-5	ozone	blue diffusive body and cartridge code 172
123-6	hydrogen sulfide	white diffusive body and cartridge code 170
123-7	ammonia	blue diffusive body and cartridge code 168
123-8	HCl	white diffusive body and cartridge code 169

IMPORTANT: for the ***ready-to-use*** version ***the supporting plate needs to be ordered separately. The ready-to-use samplers are stable for 3 months.***

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 124-1**
- ✓ special snapping adapters, **code 122-1**
- ✓ polypropylene containers, **code 124-2**
- ✓ supporting plates, **code 121**

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

see left: the supporting plate with the vertical snapping adapter

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

Installation

Fit the diffusive body to the adapter by pushing it till you hear a clicking sound

Detaching

Draw the diffusive body by tilting it with decision

accessories for *radiello*

vertical adapter

code 122

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 122**, fitted to the supporting plate.

Available in 20 pieces per package

code 122

Assembeling the vertical Adapter

place the vertical adapter over the mounting point on the plate

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

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

IMPORTANT

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

shelter

code 196

For outdoor exposures a mountable polypropylene shelter is available which can be hung from lamp posts.

It has been designed to be mounted easily and without any tools 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.

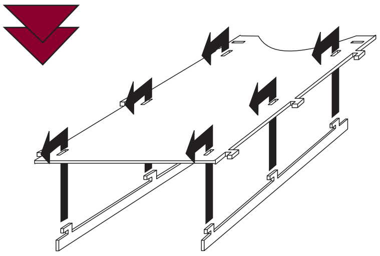
Available in 10 pieces per package

how to assemble the shelter

All of the components are snap-on assembled.

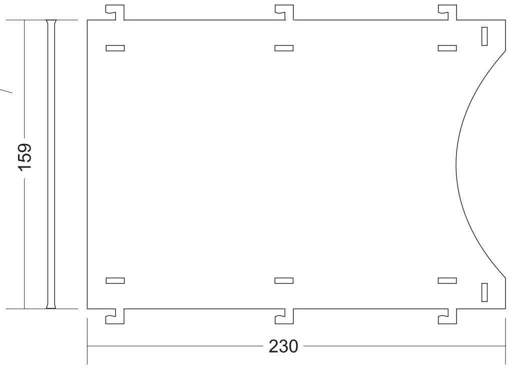
1

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

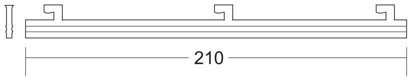


The shelter is composed of:

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

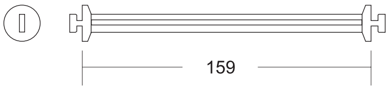


the two supports where to suspend ***radiello***

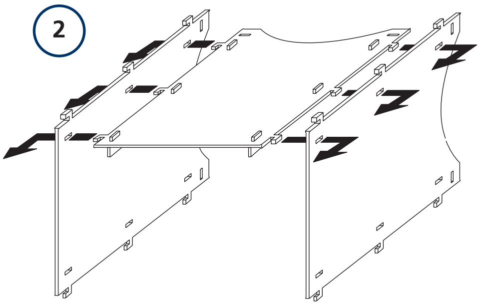


two spacers

two strips shown below left



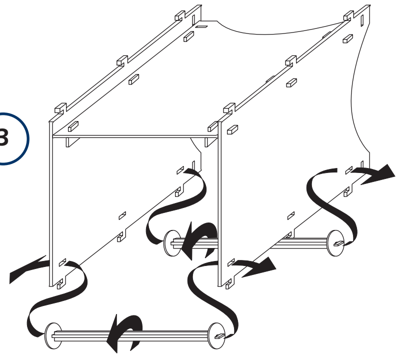
2



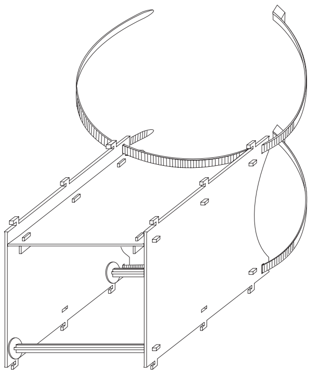
Then fix the two walls on the sides of the roof panel.

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).

3



4



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 198**.

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

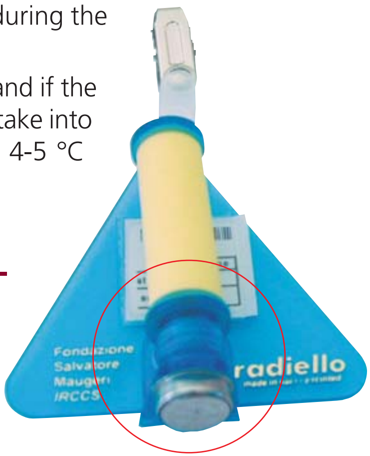
If the pole diameter is larger than the strip length, you can put two or more strips together to extend the fastening system. If the sampling site is very windy, do not introduce more than two ***radiello*** samplers in each shelter, otherwise rain could dampen the outermost samplers.

On-field temperature measurements

codes 126 e 127

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 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?



thermometer - code126
Available as pk. of 3

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

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 126; 126-1 for ready-to-use sampler**). 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!

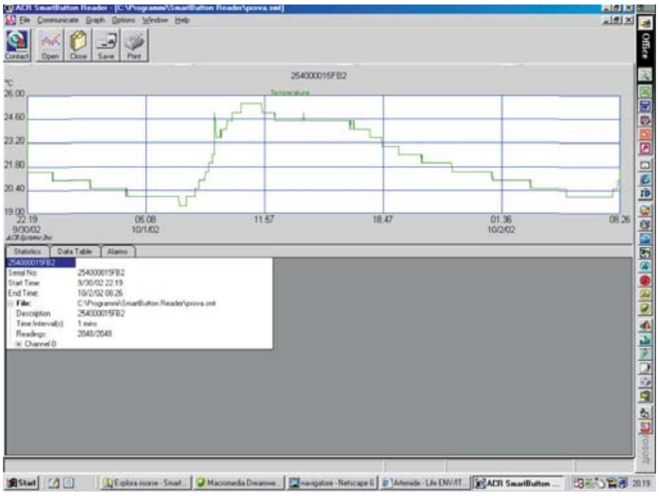
The thermometer is fitted to the supporting plate of ***radiello***: use the sampler normally and measure temperature and pollution at the same time.

A very simple **reader** (**code 127**), 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.

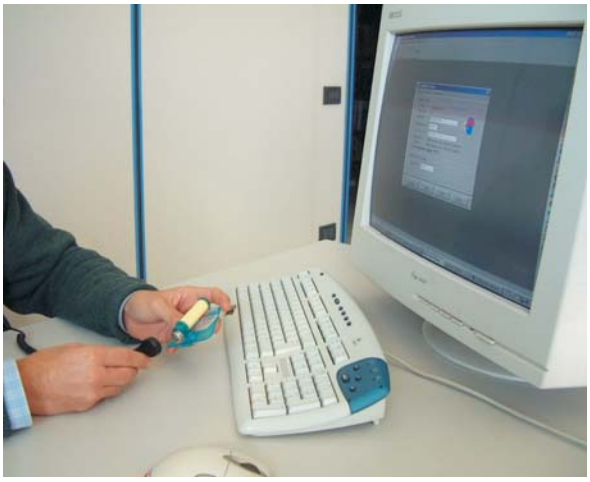
reader with serial port adapter - code 127

user tip

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



2540000015FB2
Serial No: 2540000015FB2
Start Time: 9/30/02 22.19
End Time: 10/2/02 08.26
File: C:\Programmi\SmartButton Reader\prova.smt
Description 2540000015FB2
Time Interval(s) 1 mins
Readings 2048/2048
Channel 0



filtration kit

code 174

Code 174 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 solution for H_2S

code 171

Code 171 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 171 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 $\mu g \cdot ml^{-1}$ 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 $\mu g \cdot ml^{-1}$ of S^{2-}
A	2 of code 171	98	1.145
B	25 of A	25	0.572
C	10 of A	40	0.229
D	5 of A	45	0.115

Code 171 contains 100mL solution that allows you to prepare as many as 50 calibration curves.

Kept closed at room temperature, code 171 solution is stable for at least one year.

calibration solution for aldehydes

code 302

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 302 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 302 is delivered as 10 ml of acetonitrile solution 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	$\mu g \cdot ml^{-1}$ as aldehyde
formaldehyde	50
acetaldehyde	50
acrolein	10
propanal	50
butanal	50
isopentanal	50
pentanal	50
hexanal	50
benzaldehyde	50

calibration kit for BTEX (CS_2 desorption)

code 405

Code 405 calibration kit has been conceived for the analysis of BTEX sampled in urban environments by the cartridge code 130 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 130 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 405	**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 kit for VOCs in workplace environments

code 406

The code 406 kit has been conceived for scheduled quality control of the calibration procedure for the analysis of volatile organic compounds (VOCs) sampled by code 130 cartridges in workplace environments (see page D4).

It is composed of 12 code 130 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.

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.

code 406	**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

calibration kits for BTEX (thermal desorption)

code 407	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 407

Code 407 calibration kit has been conceived for the analysis of BTEX sampled in urban environments by the cartridge code 145 and thermally desorbed (see page E1).

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 145 cartridges, three of which are blanks and nin, 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 of *radiello*

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.

code 175
stainless steel net,
100 mesh,
5.9 mm diameter

code 176
stainless steel net,
100 mesh,
4.8 mm diameter

code 177
stainless steel net,
3x8 µm,
4.8 mm diameter

Barcode adhesive label

Code 190

Available in 198 pieces per package.

Clip

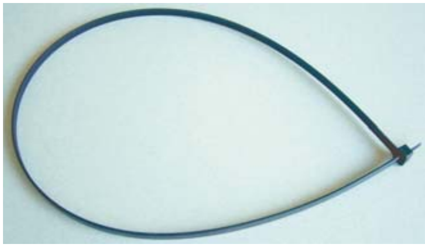
Code 195

Available in 20 pieces per package.

Strip

Code 198

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



Tubes

Available in 20 pieces per package.

code 199-1
glass tube,
working volume
2.8 ml

code 199-2
polypropylene
tube, working
volume 12 ml

Aldehydes

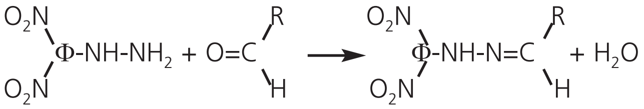
Radiello components to be used:

blue diffusive body code 120-1
supporting plate code 121
vertical adapter code 122 (optional)
chemiadsorbing cartridge code 165
filtration kit code 174 (only for analysis)

Or: *radiello-ready-to-use sampler* code 123-4 (also see page A8)

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-dinitrophenylhydrazone

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

Sampling rates

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

	Q_{298} 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}.

Calculations

The average concentration **C** over the whole sampling time (in μg·m^{-3}) is calculated according to the expression:

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

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 μg·m^{-3} are usually found in outdoor urban measurements while 20-200 μg·m^{-3} are expected in workplace environments. In workplace environments concentrations may be as high as 2,000-3,000 μg·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:

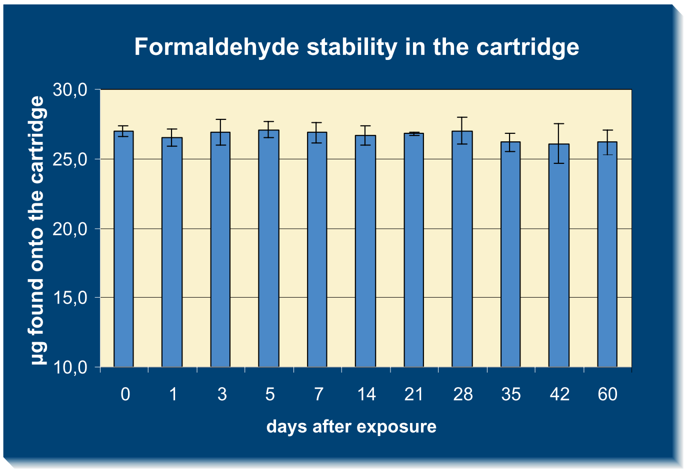
Advised exposure times

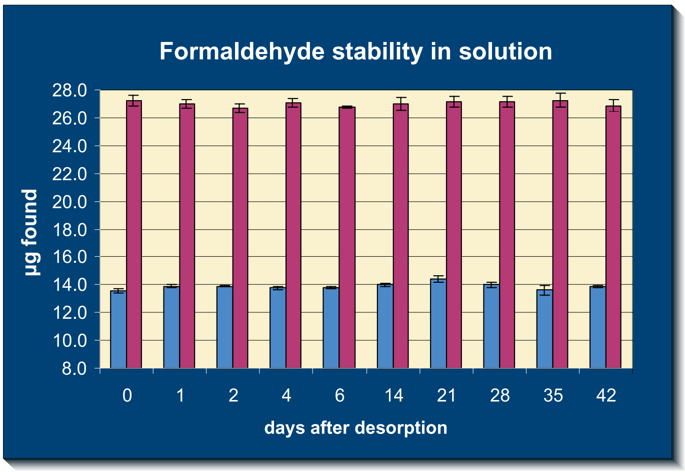
	outdoor environment	indoor environment	workplace environment	
			average conc.	peak conc.
minimum	8 h	8 h	2 h	15 minutes
maximum	7 days	7 days	8 h	1 h

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 in a dark place at 4 °C. Closed in their bags, they are stable at least six months from the production date. Each cartridge has a blank value of formaldehyde less than 0.1 μg, corresponding to a concentration in air less than 0.1 μg·m^{-3} over one week of exposure or 2 μg·m^{-3} over 8 hours. The blank value may increase with time. The expiry date (printed onto the plastic bag) indicates when the expected content of formaldehyde (for a correctly stored cartridge) will probably exceed 0.2 μg.





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.

After exposure keep the cartridges well capped at 4 °C, they are stable for 60 days. After solvent desorption (see Analysis) and extraction of the cartridge from the tube, the resulting solution, well capped and stored at 4 °C, is stable for at least 42 days (see on page C2).

Analysis

USER TIP

For extracting the cartridges use SPECTRANAL Acetonitril Fluka Cat. No. **34921** with low aldehyde content.

For a reliable and rapid filtration employ the filtration kit **code 174**.

To obtain an accurate calibration curve we offer you the calibration solution **code 302**.

Desorption

Materials

- HPLC or spectroscopy 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.

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

Instrumental analysis

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

Materials

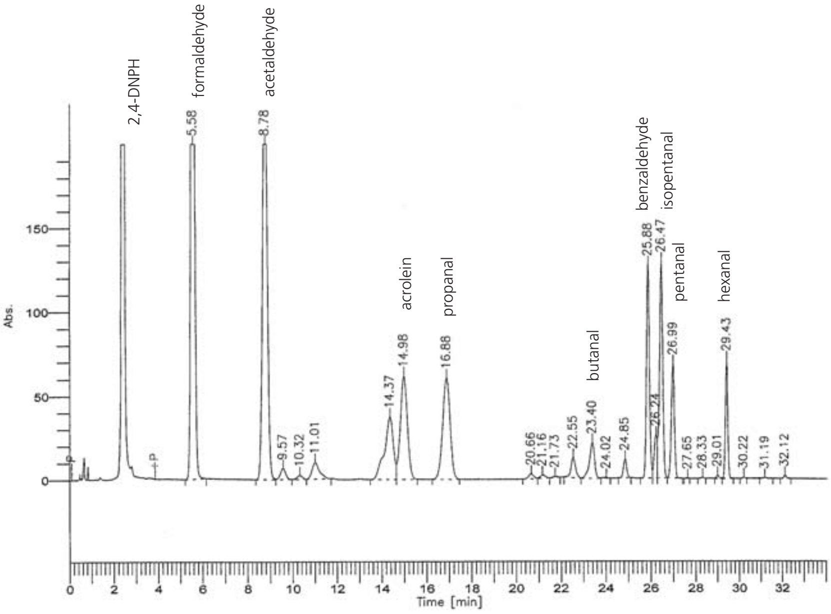
- reverse phase C_{18} HPLC column, length 150 mm, 4.6 mm diameter, 5 μm packing particle size (e.g. Ascentis C18, Supelco cat.no. 581324-U)
- HPLC apparatus capable of elution gradient and UV detection

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.

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.

We have also developed software solutions for the analytical data processing and automated production of analysis reports.

Interferences

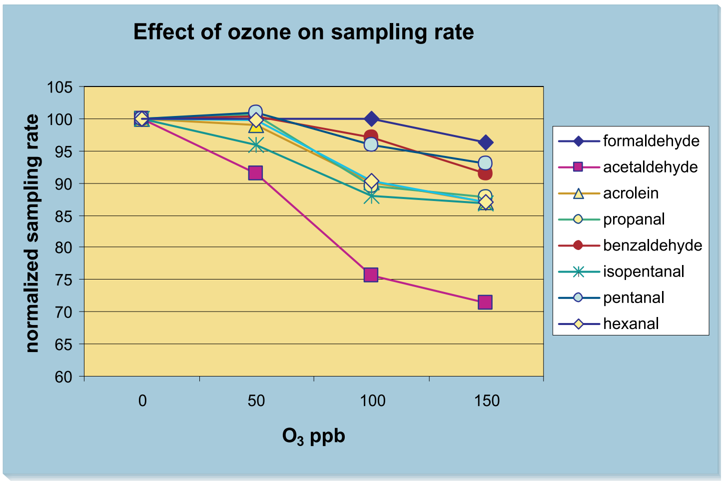
Other carbonyl compounds

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 µg·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.



Sampling rate as a function of ozone concentration normalized to 100 for $[O_3]$ equal to zero. Apart from acetaldehyde, ozone effect becomes relevant only at concentration levels higher than 100 ppb as an average over the whole exposure time interval.

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·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.

Sampling rate for ozone concentration $[O_3]$ in ppb (apply only if $[O_3]$ >100 ; for acetaldehyde $[O_3]$ >50ppb)

analyte	corrected sampling rate Q_{298} ml·min^{-1}
acetaldehyde	$84-0.018[O_3]$*
acrolein	$33-0.027[O_3]$
benzaldehyde	$92-0.05[O_3]$
formaldehyde	$99-0.02[O_3]$
hexanal	$18-0.02[O_3]$
isopentanal	$61-0.06[O_3]$
pentanal	$27-0.01[O_3]$
propanal	$39-0.03[O_3]$

*apply for ozone concentration higher than 50 ppb

Volatile organic compounds (VOCs)

chemically desorbed with CS_2

Radiello components to be used:

White diffusive body code 120
Supporting plate code 121
Vertical adapter code 122 (optional)
Adsorbing cartridge code 130

Or: ***radiello**-ready-to-use* code 123-1 (also see page A8)

Principle

Code 130 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 with particle size 35-50 mesh. Volatile organic compounds are trapped by adsorption and recovered by carbon disulfide displacement, analysis is performed by FID gas chromatography.

Sampling rates

The table on page D2 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 A2, 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 temperaure, 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 $m \cdot s^{-1}$.

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[1] Lugg G.A.: Diffusion Coefficients of Some Organic and Other Vapours 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 over the whole exposure time is calculated according to the following expression

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

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

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

	Q_{298} ml·min^{-1}	linearity range µg·m^{-3}·min	uncertainty at 2σ %	notes
acetone	77	10,000-600·10^6	7.0	**a**
acetonitrile	73	10,000-6·10^6	8.2	**b**
acrylonitrile	75	1,000-50·10^6	2.2	
benzyl alcohol	37	1,000-800·10^6	6.5	
amyl acetate	52	1,000-800·10^6	3.4	
benzene	80	500-500·10^6	1.8	
bromochloromethane	70	50,000-1,000·10^6	1.4	
butanol	74	1,000-500·10^6	5.0	
***sec*-butanol**	64	1,000-300·10^6	5.2	
***tert*-butanol**	62	1,000-300·10^6	5.5	
butyl acetate	60	1,000-1,000·10^6	3.0	
2-butoxyethanol	56	1,000-100·10^6	5.7	
2-butoxyethyl acetate	41	1,000-100·10^6	5.5	
carbon tetrachloride	67	100,000-60·10^6	9.0	
cyclohexane	54	500-500·10^6	4.5	
cyclohexanone	68	5,000-120·10^6	4.2	
cyclohexanol	54	5,000-120·10^6	4.5	
chlorobenzene	68	1,000-1,000·10^6	3.6	
chloroform	75	100,000-60·10^6	9.7	**a**
n-decane	43	500-1,000·10^6	1.1	
diaceton alcohol	43	500-1,000·10^6	4.5	
1,4-dichlorobenzene	51	1,000-1,000·10^6	7.7	
1,2-dichloroethane	77	1,000-500·10^6	8.2	
1,2-dichloropropane	66	500-250·10^6	4.5	
dichloromethane	90	500-60·10^6	8.7	
N,N-dimetylformamide	82	1,000-200·10^6	14.5	**c**
1,4-dioxane	68	1,000-600·10^6	5.5	
n-dodecane	8	1,000-1,000·10^6	4.7	
n-heptane	58	5,000-1,500·10^6	3.0	
n-hexane	66	1,000-1,000·10^6	2.5	
1-hexanol	52	5,000-120·10^6	5.5	
ethanol	102	10,000-500·10^6	7.5	**a-b**
diethyl ether	78	5,000-500·10^6	12.0	**a**
ethyl acetate	78	1,000-1,000·10^6	1.5	
ethylbenzene	68	1,000-1,000·10^6	2.4	
2-ethyl-1-hexanol	43	5,000-500·10^6	10.1	
2-ethoxyethanol	55	500-50·10^6	6.7	**b**
2-ethoxyethyl acetate	54	10,000-100·10^6	2.5	
ethyl-***tert***-butyl ether (ETBE)	61	500-200·10^6	3.0	
isobutanol	77	1,000-300·10^6	2.5	
isobutyl acetate	63	1,000-1,000·10^6	5.2	
isooctane	55	500-1,000·10^6	3.2	
isopropanol	52	10,000-400·10^6	12.0	**b**
isopropyl acetate	66	1,000-1,000·10^6	9.9	
isopropylbenzene	58	1,000-1,000·10^6	2.7	
limonene	43	1,000-1,000·10^6	10.0	
methanol	125	10,000-250·10^6	9.2	**a-b**
methyl acetate	80	1,000-1,000·10^6	12.0	
methyl-***ter***-butyl ether (MTBE)	65	500-200·10^6	2.5	

	Q_{298} 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	
naphthalene	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 page D1, where ***m*** is the minimum revealable mass, experimentally measured for each compound. Under the analytical conditions described on page D4, the limit of quantitation for 7 days exposure usually ranges from 0.05 to 1 µg·m^{-3}, depending on the compound.

Exposure

Code 130 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 of 2,000-3,000 mg·m^{-3}. The outstanding adsorbing capacity of code 130 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 date 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, mantain their content unaltered for at least six months.

Analysis

Extraction

Introduce 2 ml of CS_2 and 100 µl of internal standard solution (see next page) 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.

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	ethylbenzene	0.04-17.7
toluene	0.09-34.8	m-xylene	0.04-17.2
o-xylene	0.04-17.6	p-xylene	0.04-17.2

It is advisable to proceed via consecutive dilutions, starting for example from a stock solution containing 1 ml of each compound in 100 ml. Always use class A volumetric glassware. Introduce 2 ml of each standard solution, along with 100 µl of internal standard, onto a blank code 130 cartridge in its glass tube.

IMPORTANT

always use high purity grade CS_2, for example Fluka Cat. No. 84713 or Aldrich Cat. No. 34,227-0

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...

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.

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 130 cartridge in its glass tube, along with the chosen internal standard solution.

The chosen **internal standard** should have a retention time that does not interfere 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 or Fluka 47520) 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.

USER TIP

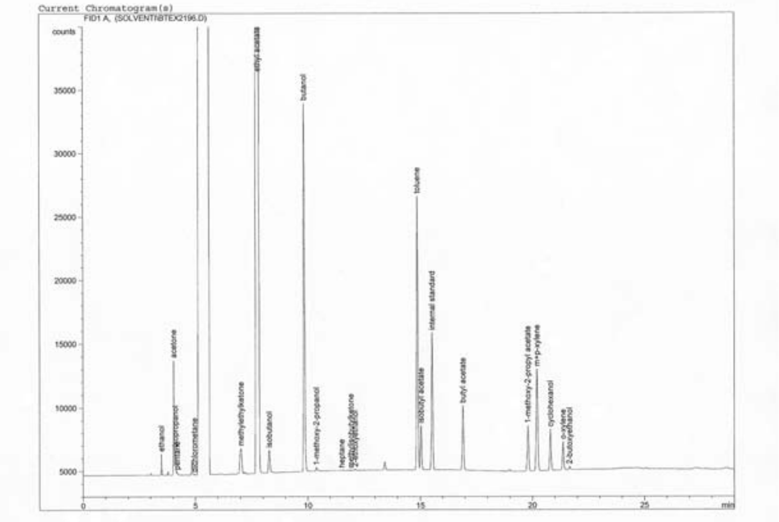
For a very accurate calibration we offer the **preloaded cartridges code 405** (outdoor environment) and **code 406** (workplace environment).

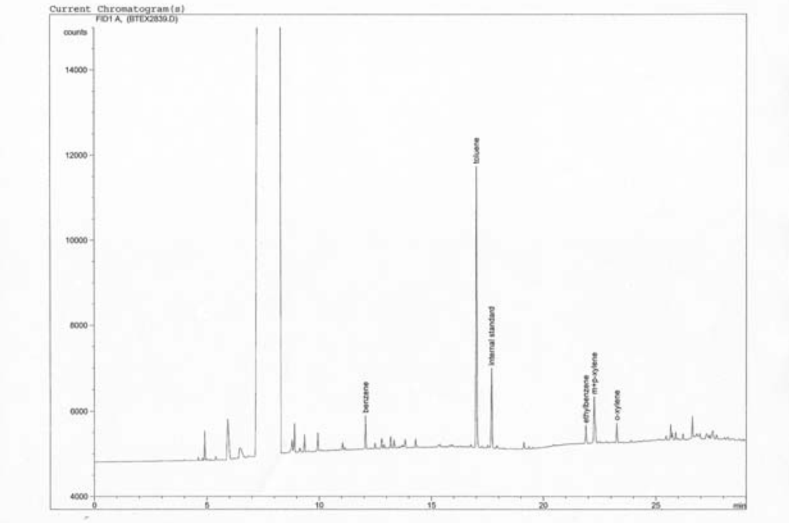
Instrumental analysis (advised)

Capillary gas chromatography with FID detection

outdoor environment samples: 100% dimethylpolysiloxane column 50m x 0.2mm, film thickness 0.5 µm; (e.g. Petrocol DH 50.2, Supelco Cat.No. 24133-U) 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/min up to 90 °C, maintain for 3 minutes, 10 °C/min 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/min up to 80 °C, 15 °C/min up to 135 °C, 20 °C/min 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.

We have also developed software solutions for the analytical data processing and automated production of analysis reports.

	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

What makes the code 130 cartridge incomparable?

the container

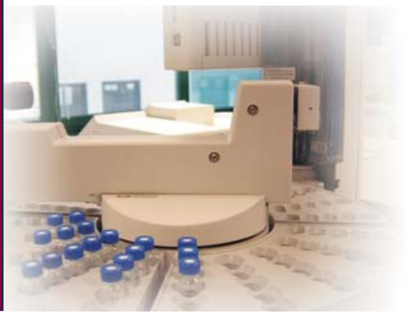
The container is made of stainless steel cloth AISI 316 with 100 mesh grid opening. It is electric welded with no supply of foreign materials. It has tolerance of ± 0.05 mm diameter and of ± 0.1 mm length.

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.



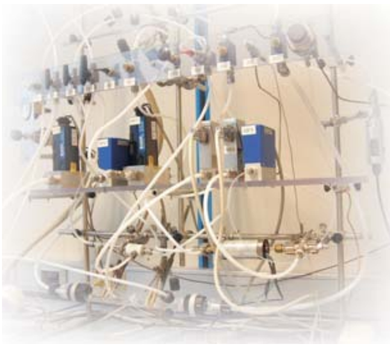
the quality control

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.

the 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) that 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 10^6) 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.



Volatile organic compounds (VOCs)

thermally desorbed

Radiello components to be used:

Yellow diffusive body code 120-2
Supporting plate code 121
Vertical adapter code 122 (optional)
Adsorbing cartridge code 145

Or: *radiello-ready-to-use* code 123-2 (also see page A8)

Principle

Code 145 is a stainless steel net cylinder, with 3x8 µm mesh grid 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.

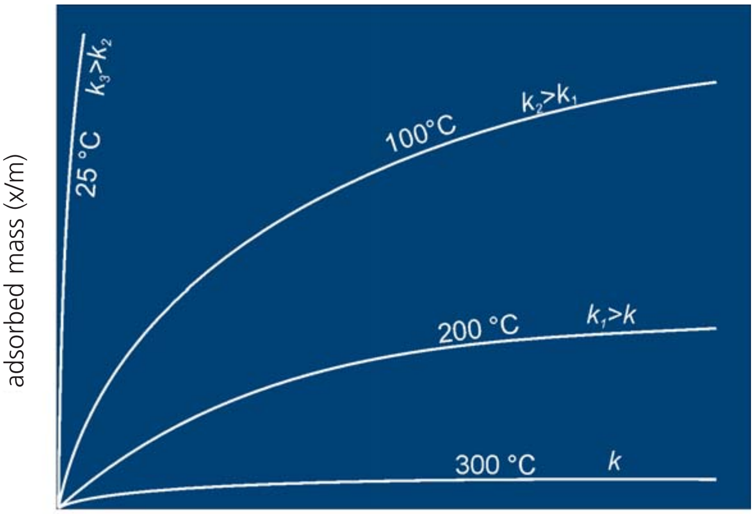
General considerations

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 120) to the yellow one (code 120-2).



Concentration in gas 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.

Smaller average pore size and thicker diffusive membrane make the diffusive path longer and, as a consequence, 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 only small amounts of water are adsorbed by Carbograph 4, they can neverthless interfere with the 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 weaker adsorbent Cabograph is not recommended for workplace measurements, as high concentrations, that can be expected, would overload the sorbent. A stronger adsorbent, like activated charcoal, is needed (see page D1)

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 Q at 25°C (298 K)

	Q_{298} $ml\cdot min^{-1}$	exposure time upper limit (days)	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
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
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 have undergone a complex conditioning procedure that ensures an outstanding chromatographic blank level. If kept in a cool place without VOCs contamination, blank level and adsorbing capacity stay unaltered for at least eighteen months.

After exposure the cartridges, well capped and kept in a cool and solvent-free place, are stable for at least three months.

Analysis

The analytical methods hereafter described have been set up with the Perkin-Elmer Turbomatrix thermal desorber and Agilent 5973 MSD mass spectrometer detector. They may be implemented on other instruments by introducing minor adjustements as suggested by the analyst's experience and characteristics of employed instrumentation.

In the following we propose two methods, one for **BTEX** analysis and another for **VOCs**. The former is suited to outdoor sampling in urban monitoring, where investigation is usually focussed onto benzene, toluene, ethylbenzene and xylene isomers. The latter is conceived for indoor monitoring, allowing quantification of all the compounds listed on page E3 and also extended qualitative analysis. The two methods differ by a few details, such as the higher desorption temperature for VOCs and the higher cryofocusing temperature for BTEX. The latter caution is introduced to avoid freezing of excess humidity gathered during the sampling in the cryofocusing trap.

Desorption

The thermal desorber is equipped with 1/4″ OD SS 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 145 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.

Inner diameter of Perkin-Elmer tubes is not always exactly the same; it may be the case therefore that a cartridge code 145 does not slide easily into the tube. Some pushing tool may be helpful then, such as a 500 μl syringe piston, a glass bar or an iron wire 2-3 mm thick.

In some cases the tube inner diameter is sligthly larger than the cartridge outer diameter: the cartridge can therefore be pushed out from the tube during desorption due to the desorption gas pressure. If this is the case, make use of the springs provided along with the tubes.

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, with the purpose of ensuring good analytical sensitivity or linearity of response.

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

Temperatures and timing

✓ Desorption: 320 °C for 10 minutes
✓ Cryofocusing trap (Tenax TA): during primary desorption manitain 2 °C, secondary desorption at 99 °C/sec up to 290 °C, 1 minute at 290 °C
✓ 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}

VOCs

Temperatures and timing

✓ Desorption: at 370 °C for 15 minutes
✓ Cryofocusing trap (Tenax TA): during primary desorption maintain at -20 °C, secondary desorption at 99 °C/sec up to 290 °C, 1 minute at 290 °C
✓ 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

Analytical parameters for BTEX and VOCs are the same, apart from the duration of chromatographic run and final temperature.

We recommended the following conditions:

Column

100% dimethylpolysiloxane, length 50m x 0.2.mm, film thickness 0.5 µm; (e.g. Petrocol DH 50.2, Supelco Cat.No. 24133-U) the column is directly fitted to the six-port valve of Turbomatrix apparatus.

Temperatures

- ✓ GC oven: 40 °C for 3 minutes, 8 °C/min up to 80 °C, mantain for 1 minute, 20 °C/min up to 250 °C for BTEX and up to 280 °C for VOCs, final isotherm 1.5 minutes for BTEX and 3 minutes for VOC
- ✓ GC-MS interface: 270 °C

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.

We have also developed software solutions for the analytical data processing and automated production of analysis reports.

Flows

- ✓ Carrier gas: helium, 0.8 ml·min^{-1}

On page E6 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}. 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.

USER TIP

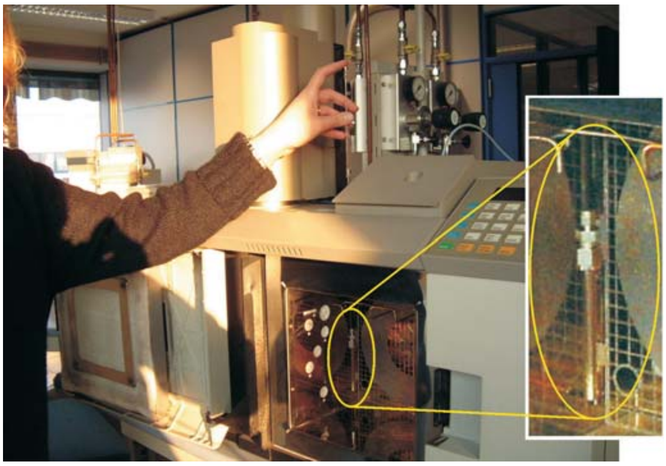
For a very accurate BTEX calibration we offer the **preloaded cartridges code 407.**

Calibration

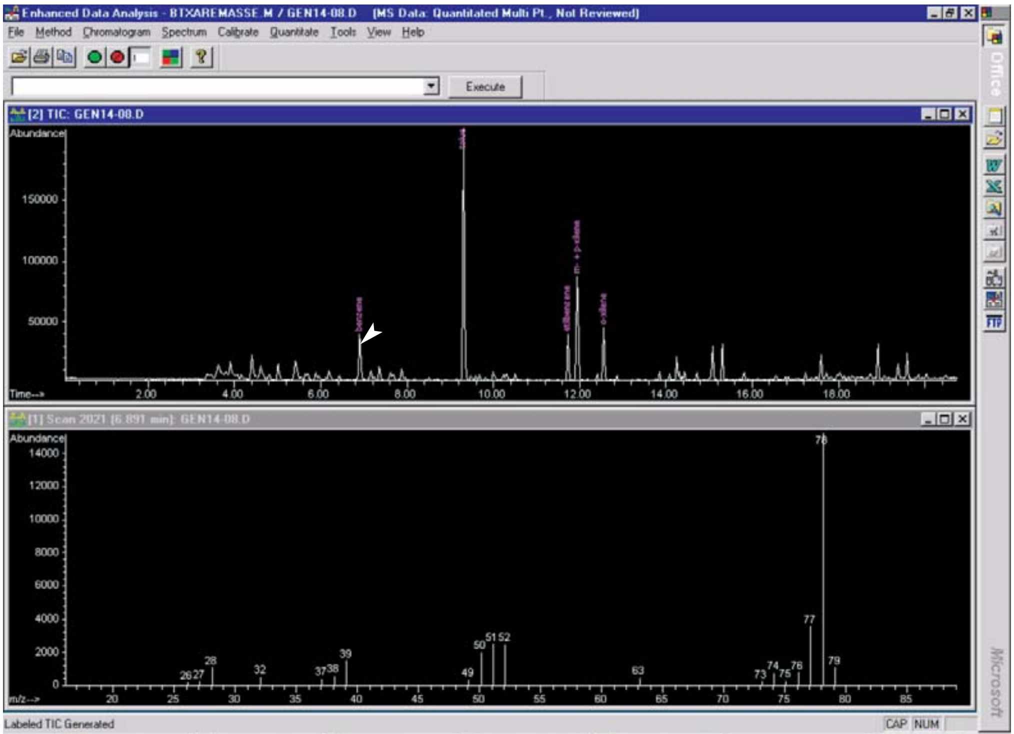
Calibration curves are obtained by gas-phase injection of methanol solutions of the target compounds onto blank cartridges. Injections are performed through a GC injector, where a short piece (10 cm) of wide-bore (0.53 i.d.) deactivated uncoated column is installed. The other end bears a Swagelock reducing 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 200 °C but do not heat the oven. Inject slowly 1 µl of each calibration solution under nitrogen flow (50 ml/min) 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.

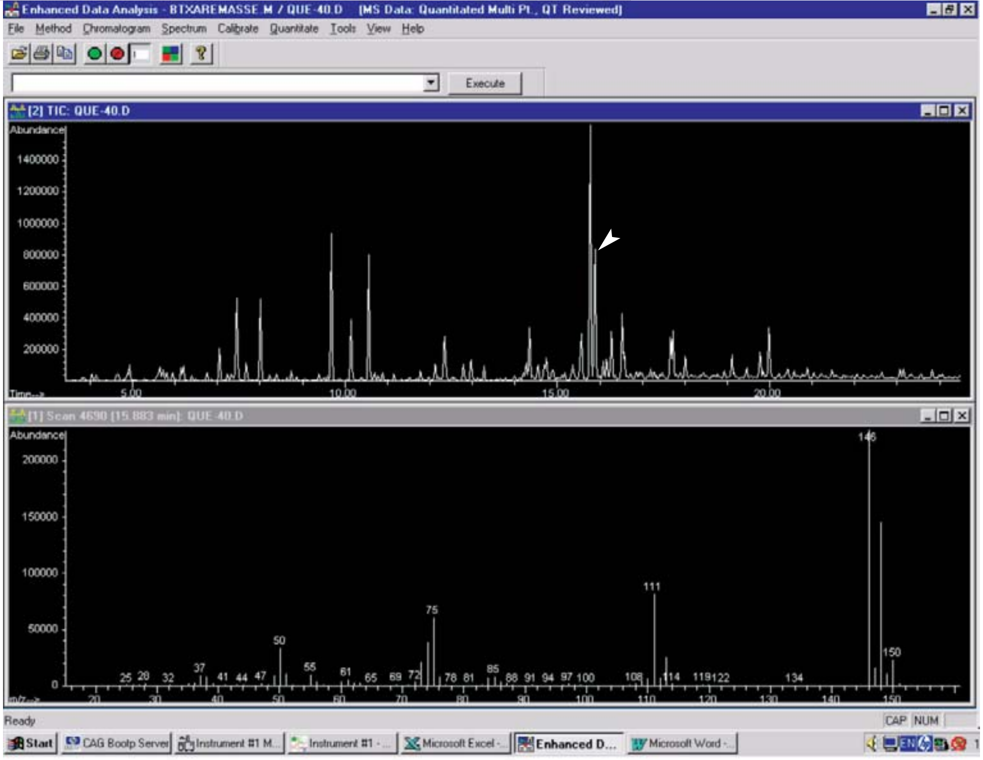


To prepare the calibration standards fit a 1/16”-1/4” Swagelock reducing connection to the GC injector by a short piece (10 cm) of wide-bore deactivated uncoated column.



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 the 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

In principle, the thermal desorption analysis leaves a conditioned cartridge that can be used as it is for another sampling. Actually this is not the case since the desorption yield, even if very high, is never quantitative, particularly for compounds with more than six carbon atoms. We recommende therefore to re-condition the cartridges after analysis, keeping them at 350 °C for eight hours under nitrogen flow.

Graphitized charcoal is a fragile material that exhibits a tendency to turn to dust under mechanical stress during the use on field and in the laboratory. Even if the stainless steel net mesh grid opening is a few micrometers, dust is lost anyway and the cartridge will eventually become empty. As soon as the mass of graphitized charcoal is reduced by 20% the cartridge has to be discarded. Basing onto our experience, this will occur after at least twenty sampling-and-analysis cycles.

Nitrogen and sulfur dioxides (NO_2 and SO_2)

Radiello components to be used:

Blue diffusive body code 120-1
Supporting plate code 121
Vertical adapter code 122 (optional)
Chemiadsorbing cartridge code 166

Or: *radiello-ready-to-use* code 123-3 (also see page A8)

Principle

The cartridge code 166 is made of microporous 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 **Q** at 298 K (25°C) and 1013 hPa is **0.141 ± 0.007 ng·ppb^{-1}·min^{-1}**.

SO_2

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

Effect of temperature, humidity and wind speed

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 **Q_K** is the sampling rate at the temperature **K** ranging from 263 to 313 K (from -10 to 40 °C) and **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

USER TIP

It is advisable to measure the sampling temperature by the thermometer **code 126**.

NO_2

The concentration **C_{NO_2}** is calculated according to the equation:

$$C_{NO2} = \frac{m_{NO_2}}{Q_K \cdot t}$$

where **m_{NO_2}** is nitrite mass in **ng** found on the cartridge, **t** is exposure time in **minutes** and **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:

$$C_{SO2} = \frac{m_{SO_4}}{0.466 \cdot t}$$

where **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.

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.

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 expo sure is 1 ppb for both gases. The uncertainty at 2σ 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·l^{-1} expressed as NO_2^-.

When nitrite ion concentration is higher than 20 µg·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·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.

Ozone (O_3)

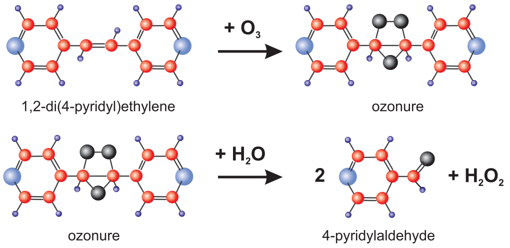
Radiello components to be used:

Blue diffusive body code 120-1
Supporting plate code 121
Vertical adapter code 122 (optional)
Chemiadsorbing cartridge code 172

Or: *radiello-ready-to-use* code 123-5 (also see page A8)

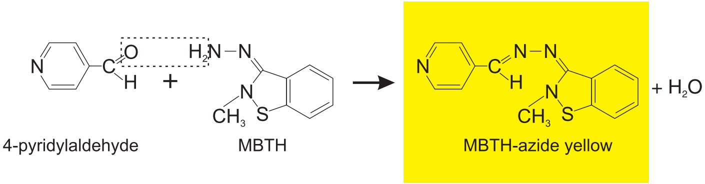
Principle

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 **Q** 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:

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

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.

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 µg·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 µg·m^{-3} for 7 days exposures. The cartridge is saturated after 14 days exposure at 400 µg·m^{-3}. The uncertainty at 2σ 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 liter 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 174**.

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 liter 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.

Hydrogen sulfide (H_2S)

Radiello components to be used

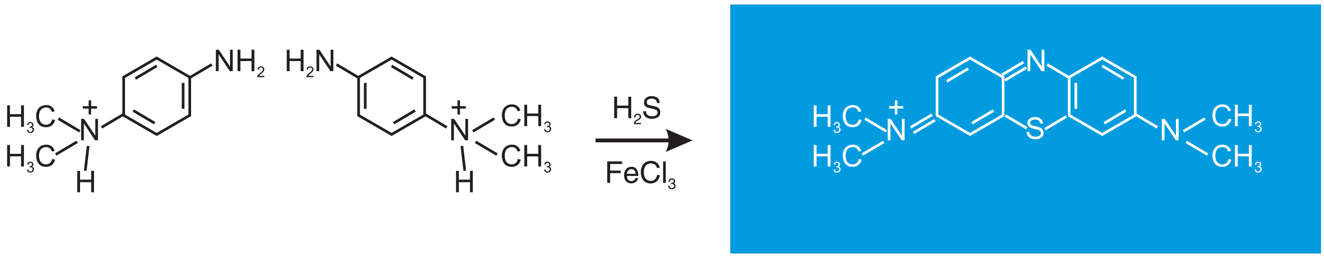
White diffusive body code 120
Supporting plate code 121
Vertical adapter code 122 (optional)
Chemiadsorbing cartridge code 170

Or: *radiello-ready-to-use* code 123-6 (also see page A8)

Principle

The cartridge code 170 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 **Q** 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:

$$Q_K = 0.096 \left(\frac{K}{298}\right)^{3.8}$$

where 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:

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

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.

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

- ✓ *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 liter 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 171, following the instructions included.

USER TIP

Code 171 calibration solution relieves you from the task of preparation and titration of the sodium sulfide solutions.

Ammonia (NH_3)

Radiello components to be used

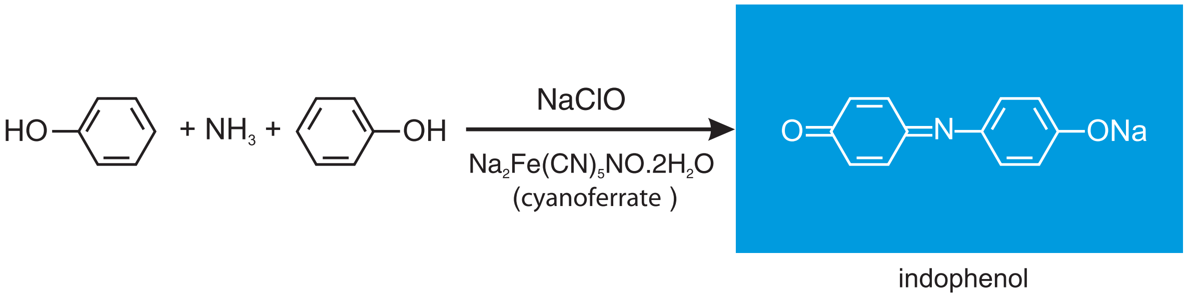
Blue diffusive body code 120-1
Supporting plate code 121
Vertical adapter code 122 (optional)
Chemiadsorbing cartridge code 168

Or: *radiello-ready-to-use* code 123-7 (also see page A8)

Principle

The cartridge code 168 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.



Sampling rate

Sampling rate **Q** 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.

Limit of detection and uncertainty

The limit of detection is 1 µg·m^{-3} for 24 hour exposure. The uncertainty at 2σ 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 liter 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 µg·m^{-3}·min the absorbance value is no longer linear: **dilute 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·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.

Hydrochloric acid (HCl)

Radiello components to be used

White diffusive body code 120
Supporting plate code 121
Vertical adapter code 122 (optional)
Chemiadsorbing cartridge code 169

Or: *radiello-ready-to-use* code 123-8 (also see page A8)

Principle

Code 169 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 **Q** at 298 K (25 °C) and 1013 hPa is **103 ml·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:

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

where Q_K is the sampling rate at temperature **K** and Q_{298} is the sampling rate value at 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:

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

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.

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 196.

Limit of detection and uncertainty

The limit of detection is 10 μg·m^{-3} for 24 hour exposure. The uncertainty at 2σ is 3.5% over the whole allowed exposure range.

Interferents

Gaseous chlorine is adsorbed by silica gel and is revealed as 0.02 ng of chloride ion for 1 μg·m^{-3}·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/liter as Cl^-.

Hydrofluoric acid (HF)

Radiello components to be used:

Blue diffusive body code 120-1
Supporting plate code 121
Vertical adapter code 122 (optional)
Chemiadsorbing cartridge code 166

Or: *radiello-ready-to-use* code 123-3 (also see page A8)

Principle

The cartridge code 166 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 Q at 298 K (25 °C) and 1013 hPa is **187 ml·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·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 µg·m^{-3} is obtained according to the equation:

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

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 µg·m^{-3}·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 196.

Limit of detection and uncertainty

The limit of detection is 7 µg·m^{-3} for 24 hour exposure. The uncertainty at 2σ is 4.5% over the whole exposure range.

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 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 liter 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·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·l^{-1}.

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

Anaesthetic gases and vapours

N_2O, isoflurane, ethrane, halothane and sevorane

Radiello components to be used

Sampling kit code 125, containing 20 single packages each composed of:

1 permeative body (see code 120-3)

1 supporting plate (see code 121)

1 vertical adapter (see code 122)

1 adsorbing cartridge (see code 132)

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 132 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 rates

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

	Q_{298} ($ml \cdot min^{-1}$)
N_2O	1.01
forane (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 $m \cdot s^{-1}$.

Calculations

Concentration in air is obtained by the following equation:

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

where:
C = concentration in mg·m^{-3}
m = mass of analyte found on the cartridge in μg
Q_K = sampling rate in ml·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 forane, 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, forane, ethrane and halothane. For sevorane, 1 hour exposure allows to detect 0.1 ppm.

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

Storage

The sampling kit code 125 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 132 cartridges to perform other sampling campaigns. Adsorbing cartridges need not to be sterile.

IMPORTANT

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

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

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 liter 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

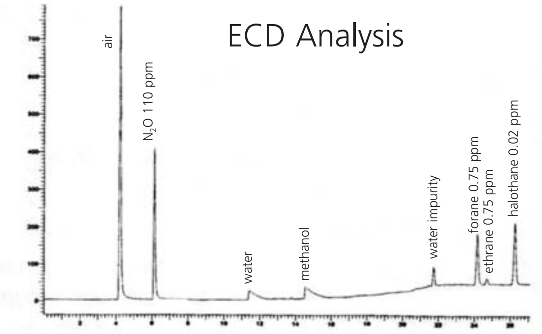
Introduce 10 ml of water/methanol mixture in a headspace vial by a volumetric pipette. Add the ***radiello*** cartridge and cap immediately. Stir and let equilibrate, place the vial in the headspace bath and let equilibrate for one hour at 45 °C.

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, 30m x 0.32mm, film 20µm (e.g. Supel-Q-PLOT, Supelco cat.no. 24242) (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: $Ar\text{-}CH_4$ (CH_4 10% v/v) at 30 $ml \cdot min^{-1}$
- ✓ GC oven: 40° C for 2 min, 10° $C \cdot min^{-1}$ up to 150° C, 6° $C \cdot min^{-1}$ 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):

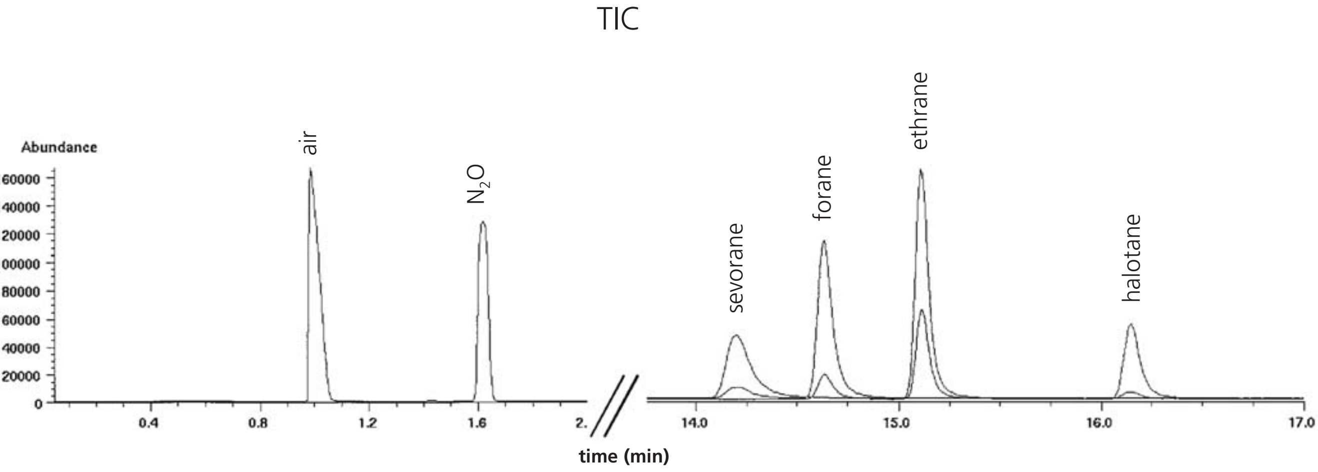
N_2O: <u>44</u>; **forane** and **ethrane**: <u>51</u>, 67, 117; **halothane**: <u>117</u>, 198, 179; **sevorane**: <u>33</u>, 131, 181

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 liter 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 contain 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 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

phenol, methylphenol and dimethylphenol

(thermally desorbed)

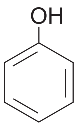
Radiello components to be used

White diffusive body code 120
Supporting plate code 121
Vertical adapter code 122 (optional)
Adsorbing cartridge code 147

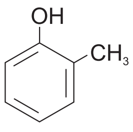
Principle

Code 147 cartridge is a stainless steel net cylinder with 100 mesh grid 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.

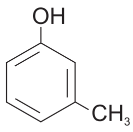
The method has been optimized for the following compounds:



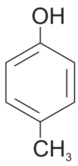
phenol



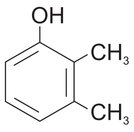
o-cresol



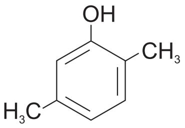
m-cresol



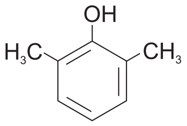
p-cresol



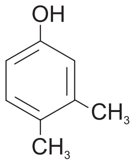
2,3-dimethylphenol



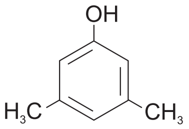
2,5-dimethylphenol



2,6-dimethylphenol



3,4-dimethylphenol



3,5-dimethylphenol

Sampling rates

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

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

where Q_K is the sampling rate at the temperature **K** and Q_{298} is the reference value at 298 K. Sampling rate is invariant with humidity in the range 15 - 90% and with wind speed between 0.1 and 10 m·s^{-1}.

	Q_{298} ml·min^{-1}	limit of detection[1] µg·m^{-3}	uncertainty at 2σ %
phenol	**38**	**0.3**	**24.1**
o-cresol	**45**	**0.4**	**17.5**
m-cresol	**48**	**0.4**	**8.0**
p-cresol	**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] after 24 hours exposure and with MS detection; analytical conditions as described in the Analysis paragraph.

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 µg·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
Q_K = sampling rate at temperature K

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

If cartridges are kept in a cool place without phenol and related compounds contamination, blank level and adsorbing capacity stay unaltered for at least 24 months.

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 as suggested by the analyst's experience and characteristics of employed instrumentation.

Desorption

The thermal desorber is equipped with 1/4" OD SS 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.

Inner diameter of Perkin-Elmer tubes is not always exactly the same; it may be the case therefore that a cartridge code 147 does not slide easily into the tube. Some pushing tool may be helpful then, such as a 500 µl syringe piston, a glass bar or an iron wire 2-3 mm thick. In some cases the tube inner diameter is sligthly larger than the cartridge outer diameter: the cartridge can therefore be pushed out from the tube during desorption due to the desorption gas pressure. If this is the case, just press sligthly one end of the cartridge to make it oval.

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

Temperatures and timing

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

Flows

- ✓ Carrier gas: helium, 24 psi
- ✓ Desorption flow: 100 ml·min^{-1}
- ✓ Inlet split: 80 ml·min^{-1} (flow from tube to cryofocusing trap: 20 ml·min^{-1})
- ✓ Outlet split: 25 ml·min^{-1}

Instrumental analysis

Column

100% dimethylpolysiloxane, length 50m x 0.2mm, film thickness 0.5 µm; (e.g. Petrocol DH 50.2, Supelco Code 24133-U) the column is directly fitted to the six-port valve of Turbomatrix apparatus

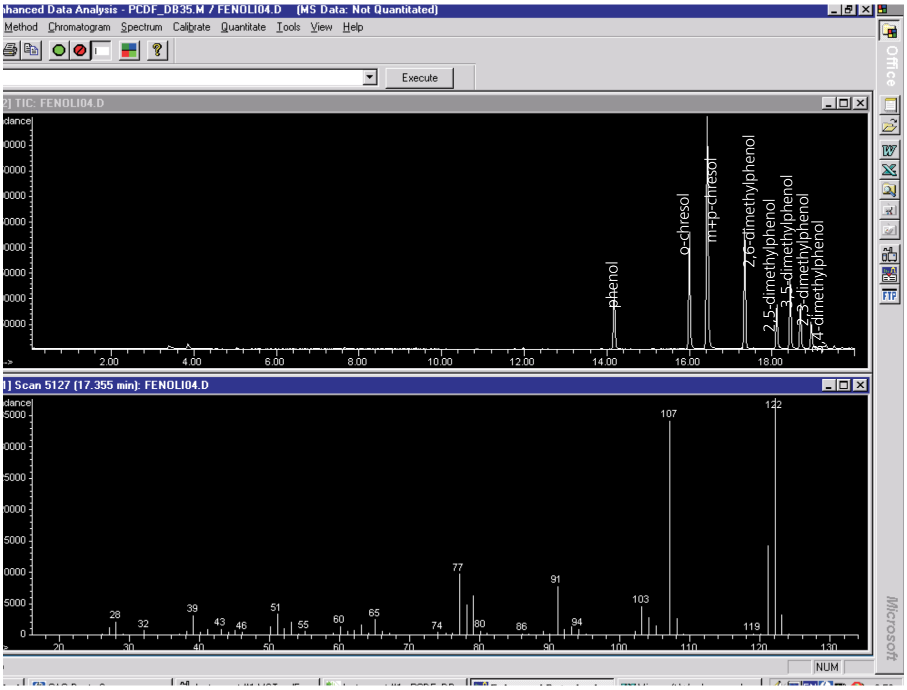
Temperatures

- ✓ GC oven: 50 °C for 2 minutes, 8 °C/min up to 160 °C, 12 °C/min up to 260 °C, final isotherm 2 minutes
- ✓ GC-MS interface: 260 °C

Flows

- ✓ helium carrier gas: 0.8 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 injections of methanol solutions of the analyzed 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" to 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 147 cartridge in a Turbomatrix tube and fit the tube to the Swagelock nut. Keep the injector at 200 °C but do not heat the oven. Slowly inject 1 µl of each calibration solution under nitrogen flow (50 ml·min^{-1}) and let the system purge for 2 minutes. Analyze the cartridge as you would do with a sample.

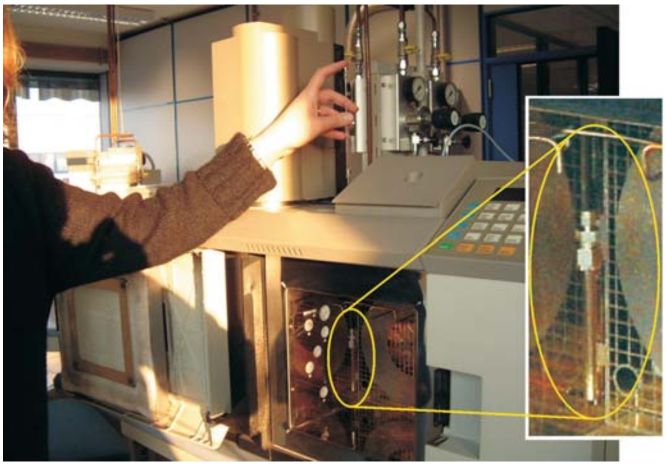
We suggest you to prepare a complete set of calibration solutions by subsequent dilutions such as they contain, for example, 4, 2, 1, 0.05 and 0.010 µg·µl^{-1} of each compound.

Cartridge recovery

Recovery yield of phenol and related compounds is higher than 98%. Nevertheless, traces of analyzed compounds remain on the cartridge, but a thorough regeneration can be performed as follows.

Wash the cartridge with methanol (5 ml in a glass tube are enough) stirring from time to time. Let it dry in the air and finally condition it at 300 °C for two hours under nitrogen or helium flow.

Thermal stability of Tenax-TA is good enough to allow a great number of sampling, analysis and conditioning cycles, provided that conditioning temperature does not exceed 300 °C and nitrogen or helium employed do not contain more than 10 ppm of oxygen.



Calibration standards are easy to prepare by applying to the gas chromatograph injector a Swagelock reducing connection (1/16 to 1/4"); injections are performed through a GC injector, where a short piece of wide-bore (0.53 mm i.d.) deactivated uncoated column is installed.

Analytical service for radiello diffusive sampler

Analytical services are also available to European users directly through the Fondazione Salvatore Maugeri. Users can send the sampled cartridges in for analysis and results. For more information on prices and conditions of this service, please contact directly

FONDAZIONE SALVATORE MAUGERI - IRCCS
Centro di Ricerche Ambientali
Via Svizzera, 16
35127 PADOVA

Italy

tel. +39 0498 064 511
fax +39 0498 064 555
e.mail fsmpd@fsm.it
web www.radiello.com

Index by code

Radiello Code	Supelco Cat. No.	Description	Page
120	**RAD120**	diffusive body, white	A5, A8
120-1	**RAD1201**	diffusive body, blue	A5, A8
120-2	**RAD1202**	diffusive Body, yellow	A5, A8
120-3	**RAD1203**	permeative diffusive body, silicone membrane	A5
121	**RAD121**	triangular support plates	A5, A8
122	**RAD122**	vertical adapters for personal sampling	B1
122-1	**RAD1221**	vertical snapping adapters for ready-to-use sampler	A8
123-1	**RAD1231**	ready-to-use sampler BTEX/VOCs (chemical desorption)	A8
123-2	**RAD1232**	ready-to-use sampler BTEX/VOCs (thermo desorption)	A8
123-3	**RAD1233**	ready-to-use sampler NO_2/SO_2/HF	A8
123-4	**RAD1234**	ready-to-use sampler aldehydes	A8
123-5	**RAD1235**	ready-to-use sampler Ozone	A8
123-6	**RAD1236**	ready-to-use sampler H_2S	A8
123-7	**RAD1237**	ready-to-use sampler NH_3	A8
123-8	**RAD1238**	ready-to-use sampler HCl	A8
124-1	**RAD1241**	screw caps for ready-to-use sampler	A8
124-2	**RAD1242**	containers, polypropylene for ready-to-use sampler	A8
125	**RAD125**	sterile sampler for anaesthetic gases and vapours	L1
126	**RAD126**	thermometer kit	B3
126-1	**RAD1261**	thermometer kit for ready-to-use sampler	B3
127	**RAD127**	thermometer reader with serial port	B3
130	**RAD130**	adsorbing cartridges for BTEX/VOCs (chemical desorption)	D1
132	**RAD132**	adsorbing cartridges for anaesthetic gases/vapours	L1
145	**RAD145**	adsorbing cartridges, for BTEX/VOCs (thermo desorption)	E1
147	**RAD147**	adsorbing cartridges for phenols	M1
165	**RAD165**	adsorbing cartridges for aldehydes	C1
166	**RAD166**	adsorbing cartridges for HF/NO_2/SO_2,	F1
168	**RAD168**	adsorbing cartridges for NH_3	I1
169	**RAD169**	adsorbing cartridges for HCl	J1
170	**RAD170**	adsorbing cartridges, for H_2S	H1
171	**RAD171**	calibration solution for H_2S	B4, H2
172	**RAD172**	adsorbing cartridges for ozone	G1
174	**RAD174**	filtration kit - syringes & filters, 0.45um porosity	B4, C3
175	**RAD175**	empty cartridges, 5.9mm OD, SS net, 100 mesh	B6
176	**RAD176**	empty cartridges, 4.8mm OD, SS net, 100 mesh	B6
177	**RAD177**	empty cartridges, 4.8mm OD, SS net, 3x8µm porosity	B6
190	**RAD190**	barcode label, self-adhesive	A5, B6
195	**RAD195**	clips for triangular support plates	B6
196	**RAD196**	protective shelter for outdoor sampling	B1
198	**RAD198**	plastic strips for protective shelter	B2, B6
199-1	**RAD1991**	empty glass tubes, 2.8mL, with stopper	B6
199-2	**RAD1992**	empty polypropylene tubes, 12mL, with stopper	B6
302	**RAD302**	calibration solution aldehydes	B4, C3
405	**RAD405**	calibration kit for BTEX - (chemical desorption)	B5
406	**RAD406**	calibration kit VOCs - (chemical desorption)	B5
407	**RAD407**	calibration kit BTEX - (thermal desorption)	B6

Index by subject

Sigma-Aldrich Worldwide Locations

Argentina
SIGMA-ALDRICH DE ARGENTINA, S.A.
Tel: 54 11 4556 1472
Fax: 54 11 4552 1698
Email: cservice-argentina@sial.com

Australia
SIGMA-ALDRICH PTY., LIMITED
Free Tel: 1800 800 097
Free Fax: 1800 800 096
Tel: 612 9841 0555
Fax: 612 9841 0500
Email: ausmail@sial.com

Austria
SIGMA-ALDRICH HANDELS GMBH
Tel: 43 1 605 81 10|
Fax: 43 1 605 81 20
Email: ATOrders@europe.sial.com

Belgium
SIGMA-ALDRICH NV/SA.
Free Tel: 0800-14747Free
Fax: 0800-14745
Tel: 03 899 13 01
Fax: 03 899 13 11
Email: becustsv@europe.sial.com

Brazil
SIGMA-ALDRICH BRASIL LTDA.
Tel: 55 11 3732-3100
Fax: 55 11 3733-5151
Email: sigmabr@sial.com

Canada
SIGMA-ALDRICH CANADA LTD.
Free Tel: 800-565-1400
Free Fax: 800-265-3858
Tel: 905-829-9500
Fax: 905-829-9292
Email: canada@sial.com

China
SIGMA-ALDRICH (SHANGHAI)
Trading Co. Ltd.
Tel: +86-21-61415566
Fax: +86-21-61415567
Email: China@sial.com

Czech Republic
SIGMA-ALDRICH S.R.O.
Tel: +420 246 003 200
Fax: +420 246 003 291
Email: czeorders@europe.sial.com

Denmark
SIGMA-ALDRICH DENMARK A/S
Tel: 43 56 59 10
Fax: 43 56 59 05
Email: denorder@europe.sial.com

Finland
SIGMA-ALDRICH FINLAND
Tel: (09) 350 9250
Fax: (09) 350 92555
Email: finorder@europe.sial.com

France
SIGMA-ALDRICH CHIMIE S.À.R.L.
Tel appel gratuit: 0800 211 408
Fax appel gratuit: 0800 031 052
Email: fradvsv@europe.sial.com

Germany
SIGMA-ALDRICH CHEMIE GMBH
Free Tel: 0800-51 55 000
Free Fax: 0800-649 00 00
Email: DEOrders@europe.sial.com

Greece
SIGMA-ALDRICH (O.M.) LTD
Tel: 30 210 9948010
Fax: 30 210 994383
Email: GRCustSV@europe.sial.com

Hungary
SIGMA-ALDRICH Kft
Tel: 06-1-235-9054
Fax: 06-1-269-6470
Ingyenes zöld telefon: 06-80-355-355
Ingyenes zöld fax: 06-80-344-344
Email: info@sigma.sial.hu

India
SIGMA-ALDRICH CHEMICALS
PRIVATE LIMITED
Telephone
Bangalore: 91 80 6621 9600
New Delhi: 91-11-4165-4255
Mumbai: 91-22-2570-2364
Hyderabad: +91 40 6684 5488
Fax
Bangalore: 91 80 6621 9650
New Delhi: 91-11-4165-4266
Mumbai: 91-22-2579-7589
Hyderabad: +91 40 6684 5466
Email: india@sial.com

Ireland
SIGMA-ALDRICH IRELAND LTD.
Free Tel: 1800 200 888
Free Fax: 1800 600 222
Tel: 353 1 4041900
Fax: 353 1 4041910
Email: EIOrders@europe.sial.com

Israel
SIGMA-ALDRICH ISRAEL LTD.
Free Tel: 1-800-70-2222
Tel: 08-948-4100
Fax: 08-948-4200
Email: isrtechserv@europe.sial.com

Italy
SIGMA-ALDRICH S.r.l.
Telefono: 02 33417310
Fax: 02 38010737
Numero Verde: 800-827018
Email: itclient@europe.sial.com

Japan
SIGMA-ALDRICH JAPAN K.K.
Tokyo Tel: 03 5796 7300
Tokyo Fax: 03 5796 7315
Email: sialjpts@sial.com

Korea
SIGMA-ALDRICH KOREA
Tel: 031-329-9000
Fax: 031-329-9090
Email: sakr@sial.com

Malaysia
SIGMA-ALDRICH (M) Sdn. Bhd
Tel: 603-56353321
Fax: 603-56354116
Email: sam@sial.com

Mexico
SIGMA-ALDRICH QUÍMICA, S.A. de C.V.
Free Tel: 01-800-007-5300
Free Fax: 01-800-712-9920
Email: mexico@sial.com

The Netherlands
SIGMA-ALDRICH CHEMIE BV
Tel Gratis: 0800-0229088
Fax Gratis: 0800-0229089
Tel: 078-6205411
Fax: 078-6205421
Email: nlcustsv@europe.sial.com

New Zealand
SIGMA-ALDRICH PTY., LIMITED
Free Tel: 0800 936 666
Free Fax: 0800 937 777
Tel: 61 2 9841 0500
Fax: 61 2 9841 0500
Email: ausmail@sial.com

Norway
SIGMA-ALDRICH NORWAY AS
Tel: 23 17 60 60
Fax: 23 17 60 50
Email: nororder@europe.sial.com

Poland
SIGMA-ALDRICH Sp. z o.o.
Tel: 061 829 01 00
Fax: 061 829 01 20
Email: plorders@europe.sial.com

Portugal
SIGMA-ALDRICH QUÍMICA, S.A.
Free Tel: 800 202180
Free Fax: 800 202178
Tel: 21 9242555
Fax: 21 9242610
Email: poorders@eurnotes.sial.com

Russia
SIGMA-ALDRICH RUS, LLC
Tel: +7 (495) 621-5828/5923/6037
Fax: +7 (495) 621-5828/5923/6037
Email: ruorder@sial.com

Singapore
Sigma-ALDRICH PTE. LTD.
Tel: 65-67791200
Fax: 65-67791822
Email: sapl@sial.com

South Africa
SIGMA-ALDRICH
SOUTH AFRICA (PTY) LTD.
Free Tel: 0800 1100 75
Free Fax: 0800 1100 79
Tel: 27 11 979 1188Fax: 27 11 979 1119
Email: rsa@sial.com

Spain
SIGMA-ALDRICH QUÍMICA, S.A.
Free Tel: 900 101376
Free Fax: 900 102028
Tel: 91 661 99 77
Fax: 91 661 96 42
Email: esorders@europe.sial.com

Sweden
SIGMA-ALDRICH SWEDEN AB
Tel: 020-350510
Fax: 020-352522
Outside Sweden Tel: +46 8 7424200
Outside Sweden Fax: +46 8 7424243
Email: sweorder@europe.sial.com

Switzerland
SIGMA-ALDRICH CHEMIE GmbHSwiss
Free Call: 0800 80 00 80
Tel: +41 81 755 2828
Fax: +41 81 755 2815
Email: CHEOrders@europe.sial.com

United Kingdom
Sigma-Aldrich Company Ltd.
Free Tel: 0800 717181
Free Fax: 0800 378785
Tel: 01747 833000
Fax: 01747 833313
SAFC (UK): 01202 712305
Email: ukorders@europe.sial.com

United States
SIGMA-ALDRICH
P.O. Box 14508
St. Louis, Missouri 63178
Toll-Free: (800) 325-3010
Call Collect: (314) 771-5750
Toll-Free
Fax: (800) 325-5052
Tel: (314) 771-5765
Fax: (314) 771-5757
Email: techservice@sial.com

Internet
sigma-aldrich.com

World Headquarters
3050 Spruce St., St. Louis, MO 63103
(314) 771-5765
sigma-aldrich.com

Technical Service US: techservice@sial.com
Technical Service EUR: EurTechServ@europe.sial.com
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