

Sampling of Carbonyls A Sampling Media Perspective

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Formaldehyde, acetaldehyde, glutaraldehyde and acetone are the most commonly sampled carbonyls. These compounds are collected onto sampling media treated with 2,4-dinitrophenylhydrazine (DNPH) that derivatize the carbonyls to the more stable hydrazone derivatives. The derivatives are then measured by reversed-phase HPLC combined with UV detection. There are several analytical methods available to collect and measure carbonyls in indoor and ambient environments which range from the use of glass impingers to filter methods to solid-phase extraction (SPE) cartridges through both active and passive sampling techniques. Furthermore, in the past decade, passive sampling has become an accepted method for sampling and measurement of carbonyls.

Trends in Carbonyl Measurement

In 2005, the Occupational Safety and Hazard Administration (OSHA) released Method 1007 for the measurement of formaldehyde using passive diffusive samplers. Several different samplers were investigated in the method, including the radial DSD-DNPH sampler. At the time, the radiello[®] Aldehyde sampler was not available in the United States for inclusion in the method. Both the DSD-DNPH and radiello[®] devices are suitable for the method and provide faster sampling rates, greater sensitivity, and capacity by design compared to axial or badge type samplers.

DSD-DNPH Aldehyde Sampler (28221-U) is a type of radial sampler that was introduced first in Japan. It was an integral device for monitoring carbonyls in indoor air, specifically related to "Sickhouse Syndrome". It is used similarly to the radiello[®] sampler and can be desorbed in the device with no media transfer. The sampling rate for formaldehyde is 71.9 mL/min.

The radiello[®] Aldehyde Sampler (RAD165) can be used for sampling a wide range of aldehydes such as formaldehyde, acetaldehyde, benzaldehyde, butanal, hexanal, glutaraldehyde and more. Sampling rates are faster than other available passive samplers, i.e. formaldehyde sampling rate is 99 mL/min compared to other popular axial devices with sampling rates 28.6 mL/min

The BPE-DNPH Rezorian[™] cartridge is a dual-bed sampler containing BPE and DNPH coated silica gel. It is an innovative device designed for sampling carbonyls in ambient, indoor and industrial atmospheres. Like traditional DNPH sampling devices, it contains a bed of 2,4-DNPH but offers the advantage of a 1,2-bis(2-pyridyl)ethylene (BPE) silica gel bed in the front, functioning as a built-in ozone scrubber; and unlike potassium iodide (KI) scrubber, it is not affected by high humidity or rainy conditions.



DSD-DNPH Aldehyde Sampler



Radiello[®] Aldehyde Sampler



BPE-DNPH Rezorian[®] cartridge

Traditional Sampling Methods

Solid sorbent-based media such as high purity silica gel coated with 2,4-DNPH is more widely used for sampling carbonyls. The following regulatory methods specify a single bed of 350 mg silica gel coated with 1 mg of 2,4-DNPH in solid-phase extraction (SPE) style cartridge: NIOSH 2016, ASTM D5197, EPA TO-11A, and EPA IP-6A with a carbonyl capacity: <math>< 75 \mu\text{g}</math> (formaldehyde equivalent). There are a wide variety of cartridge configurations suitable for your application containing low background and low-pressure drop (Lp) DNPH packings:

The traditional glass sorbent tube design for NIOSH 2016 Appendix B contains two beds of high purity DNPH with a front bed of 300 mg and a back-up bed of 150 mg capacity. This tube is available in two different sizes – 6 mm O.D tube for sampling at lower flow ranges up to 0.4 L/min and an 8 mm O.D. tube which extends the flowrate range up to 2.0 L/min.



The LpDNPH S10 cartridge is a 3 mL SPE style cartridge with a slip luer design and a built-in reservoir for easy extraction and elution. Reusable adapters are available. The S10 Starter Kit contains all needed adapters (tubing and cartridge adapter).



The LpDNPH S10L cartridge is a 3 mL reversible cartridge design for EPA Method TO-11A which is designed for the analyst who prefers shorter dimensions and does not require an adapter for sampling. The cartridge is eluted by connecting to an empty SPE cartridge that acts as a reservoir for gravity-fed elution solvent. The S10L is equivalent to both the Waters Sep-Pak® cartridges and XpoSure™ cartridges.



LpDNPH S10x cartridge is shorter than the S10 cartridge and is designed to fit into automated systems.



DNPH Rezorian™ cartridge is a 3 mL cartridge which features luer-lock end-fittings that can be used to connect a pump tubing to two cartridges in a series for “piggybacked” sampling to monitor breakthrough or an increased capacity.



Sampling Carbonyls in Higher Concentration Environments



In some instances, a high capacity carbonyl sampling device may be required for a high concentration environment. The need for such a device is commonly determined when the capacity of a traditional device is exceeded. There are sampling devices designed to meet these special conditions, known as the LpDNPH H Series. These cartridges contain silica gel with a higher loading of 2,4-DNPH plus, for the H30 and H300 type cartridges, a larger bed weight.

LpDNPH H10 cartridge is a 3 mL S10 style cartridge with a higher loading capacity. Carbonyl capacity: <math><225 \mu\text{g}</math>

LpDNPH H30 cartridge is a 6 mL SPE style cartridge containing a 1-gram bed of higher loading capacity DNPH. Carbonyl capacity: <math><643 \mu\text{g}</math>

LpDNPH H300 cartridge is a 20 mL SPE style cartridge containing 10 grams of higher loading capacity DNPH. Carbonyl capacity: <math><6.4 \text{ mg}</math>

Sampling Carbonyls in the Presence of High Ozone Levels



Ozone is known to interfere with carbonyl sampling and therefore must be removed or “scrubbed” from the sampling environment. The most commonly used ozone scrubber is 1.5 g of potassium iodide (KI) which prevents negative ozone interference in DNPH coated devices. KI scrubbers are available in both a reversible SPE tube design, like the S10L (top), and the Rezorian™ tube (bottom) design. Typical ozone scrubbers have an ozone capacity of 100,000 ppb/hr when tested at 200 ppb ozone, 50% RH, 25 °C. Potassium iodide scrubbers are not recommended for high humidity environments. For sampling carbonyls in high humidity environments, we recommend the 2-in-1 BPE-DNPH cartridge or a BPE ozone scrubber as an alternative to potassium iodide scrubber.

Other Sampling Methods for Carbonyls



For sampling selected carbonyls where particles are a concern, filter methods are commonly used for compounds such as glutaraldehyde (OSHA 64), crotonaldehyde (OSHA 81), and valeraldehyde (OSHA 85). The glass fiber filters are coated with 2,4-DNPH, actively sampled in a cassette and desorbed in the same manner as a traditional DNPH device.

Summary

There are a wide variety of carbonyl sampling devices available to suit the sampling needs of your application, from your preferred sampling device for sample collection and how the device connects to the sampling pump; special devices suitable for sampling in high concentration environments to ozone scrubbers. Furthermore, if you prefer not to use a sampling pump, there are radial passive samplers available with fast sampling rates.

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