

RCHO: Sampling and analysis (classical DNPH method)

«Carbonyls» were sampled using SiO₂-C18 cartridges (Sep-Pak Classic from Waters) coated with 2,4-dinitrophenylhydrazine (DNPH from Spectrum), purified by recrystallization and checked by high-performance liquid chromatography (HPLC) with UV detection. The «carbonyls» were trapped making them react with DNPH inside the cartridges to form the corresponding stable 2,4-dinitrophenylhydrazone derivatives. A commercial hydrazone standard mixing solution (SUPELCO CARB-«Carbonyl» DNPH Mix 1), containing formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, butyraldehyde, and benzaldehyde, was used. Five-point calibration curves were constructed between 2.0 and 50 mg L⁻¹, using a correlation coefficient better than 0.99 as acceptable criteria. Acetone and acrolein were quantified together due to difficulties in resolving its chromatographic peaks using an isocratic elution.

Two blank cartridges were used for each sampling. In all sampling, it was used two cartridges in series to evaluated possible breakthrough. When >5% was found in the back cartridge, the sampling was discharged. The differences between the three samples showed a deviation under 12%, indicating a good reproducibility of the samples collected.

The samplings were performed using a battery-operated air pump (SKC PCXR4), a digital flow meter (SKC Accuflow), the SiO₂-C18 cartridges impregnated with DNPH, and Teflon tubes. The samplings were performed under a stable engine temperature (20 min after ignition). The sampling time was between 10 and 20 min at a constant flow of 50 mL min⁻¹.

The sampled material was eluted from the cartridges by washing it with acetonitrile to a 5 mL volumetric flask. An aliquot of 100 µL of this solution was injected in a Rheodine injector model 7125i with a sampling loop of 20 µL. A Novapak C18 3.9 mm×150 mm×4 µm column was used, coupled to a Perkin-Elmer Series 200 detector at 365 nm. An isocratic Perkin-Elmer pump (Series 200) was used in a constant flow of 1.5 mL min⁻¹ of a mobile phase of 50% of acetonitrile and 50% of water.