

Formaldehyde and formaldehyde-releasing agents are widely used in manufacturing of building materials, cars, plywood, polymers, glues and adhesives. It is also commonly used in household items, personal care products and cosmetics as a preservative and disinfectant. Due to high toxicity and suspected carcinogenicity the products are tested to determine free formaldehyde content and ensure the safety of the consumers. Testing is also important to monitor production of resins and other polymers and to ensure the quality of final materials.

HPLC method with post-column derivatization allows for quantifying free formaldehyde in a wide range of products and materials and is the basis of the analytical method listed in Cosmetic Safety Technical Specification 2015. The method is simple, selective, and very sensitive. This method is suitable for the determination of free formaldehyde content in water-based cosmetic products, cream emulsions, and gel cosmetics. Potential interferences are either separated from formaldehyde on HPLC column or do not react with post-column reagent and are not detected.

Different analytical columns could be used to separate Formaldehyde and all of them can be successfully used with post-column derivatization technique.

Method

Leather samples (According to ISO 177226-1)

Weigh approximately 2 g of leather pieces to the nearest 0.01 g into a 100 ml glass Erlenmeyer flask. Add 50 ml of 0.1% sodium dodecylsulfonate or sodium dodecylsulfate solution (previously preheated at 40 °C) and fit the Erlenmeyer flask with a glass stopper. Shake the contents of the flask in the water bath for 60 min at 40 °C. Immediately filter the warm extract solution by vacuum through a glass fiber filter into a flask. Cool the filtrate and analyze.

Fabric Samples (According to ISO 14184-1)

Cut specimens into small pieces, and weigh approximately 1 g of the pieces to an accuracy of 10 mg. If the formaldehyde content is low, increase the test specimen weight to 2.5 g in order to achieve a sufficient accuracy. Put the weighed pieces into a 250 ml flask with a stopper and add 100 ml of water. Cap tightly and place in a water bath at 40 °C for 60 min. Shake the flask at least every 5 min. Filter the solution into another flask through a glass filter and analyze.

Cosmetics Samples (According to Cosmetic Safety Technical Specification 2015, China)

Accurately weigh out 0.2 g of sample into a centrifuge tube. Add 10 mL of phosphoric acid solution (2 mL/L in DI water). If needed, 10 mL of Methylene Chloride could be added to remove non-polar compounds. Shake the mixture for 1 min and centrifuge at 5000 rpm for 5 min. Filter the water portion through 0.45 µm filter before injecting.

Resins and Other Samples

Extract samples with water by shaking for 60 min at 40 °C. For samples containing oils and fats partition with Methylene Chloride to remove oils. Choose sample/extraction solution ratio based on expected Formaldehyde content. Use additional dilutions as necessary.

Analytical Conditions

Column: Waters Atlantis® HILIC Silica, 5 µm, 4.6 x 250 mm

Column Temperature: 40 °C

Flow Rate: 0.5 mL/min

Mobile Phase: 15% 0.05 M Ammonium Acetate in water, 85% Acetonitrile

Injection Volume: 10-50 µL

or

Column: Reversed-phase C₁₈ column, 5 µm, 4.6 x 250 mm

Column Temperature: 30 °C

Flow Rate: 1.0 mL/min

Mobile Phase: 2 mL/L of Phosphoric acid in DI water

Post-Column Conditions

Post-Column System: Onyx PCX, Pinnacle PCX or Vector PCX

Reactor Volume: 0.5 mL

Reactor Temperature: 100 °C

Reagent: P/N 3700-5000 or 3700-5100
0.81 M Ammonium Acetate
0.12 M Glacial Acetic Acid
0.05 M 2,4-Pentanedione

Reagent Flow Rate: 0.4 mL/min

Detection: FLD, λ_{EX}: 412 nm, λ_{EM}: 510 nm or UV/Vis 410 nm

Calibration curve

Range: 0.05 – 5 ppm, R² = 0.999

Table 1. Recoveries of Free Formaldehyde in Cosmetics

Sample Type	Hand Cream	Hair Gel	Hair Color
Formaldehyde in the blank	0.0002 %	0.0001 %	0.0001 %
RSD, N=3	0.3 %	5.7 %	2.3 %
Spike level 1	0.001 %	0.001 %	0.001 %
Recoveries, N=3	97.4 %	96.9 %	92.5 %
RSD, N=3	0.7 %	2.4 %	1.8 %
Spike level 2	0.005 %	0.005 %	0.005 %
Recoveries, N=3	98.3 %	95.9 %	93.9 %
RSD, N=3	0.6 %	0.9 %	0.7 %

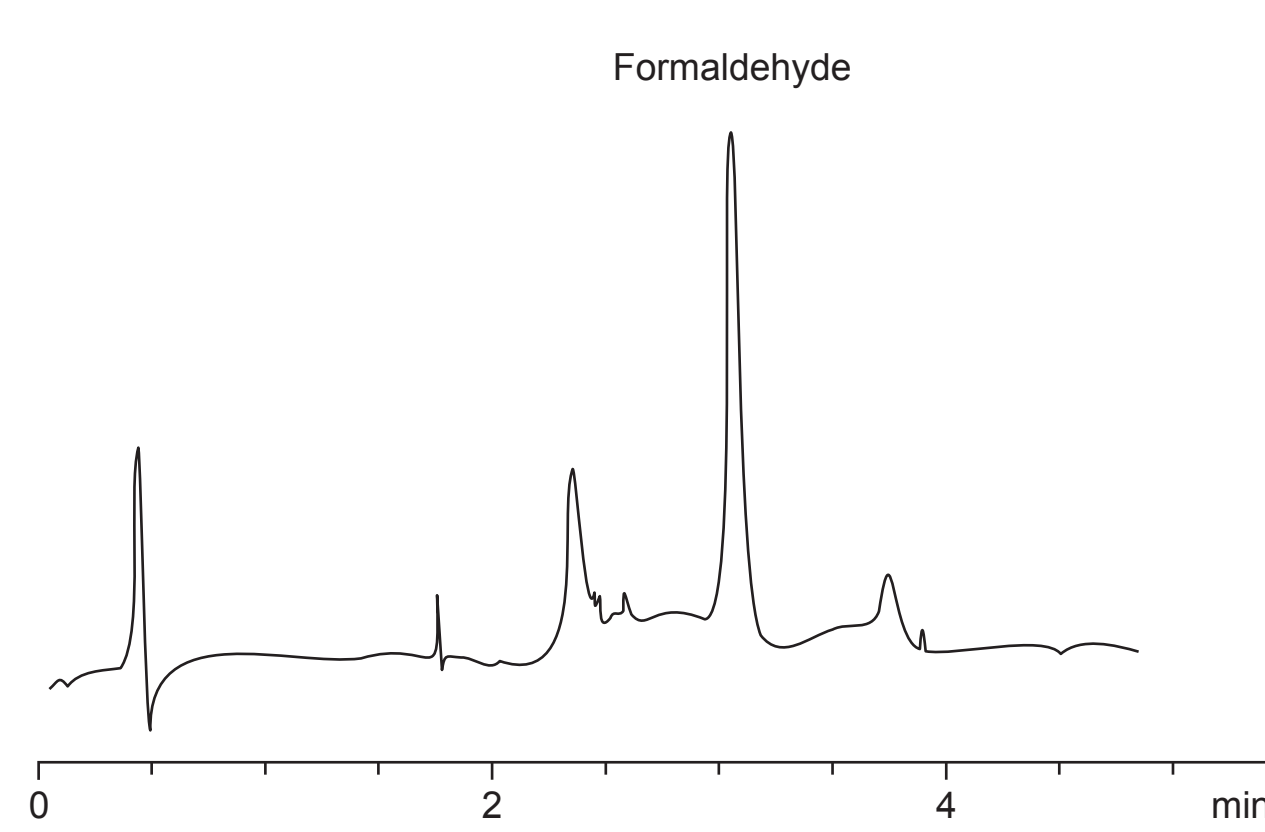


Fig 1. Chromatogram of hand cream blank, containing 0.0002 % of free formaldehyde

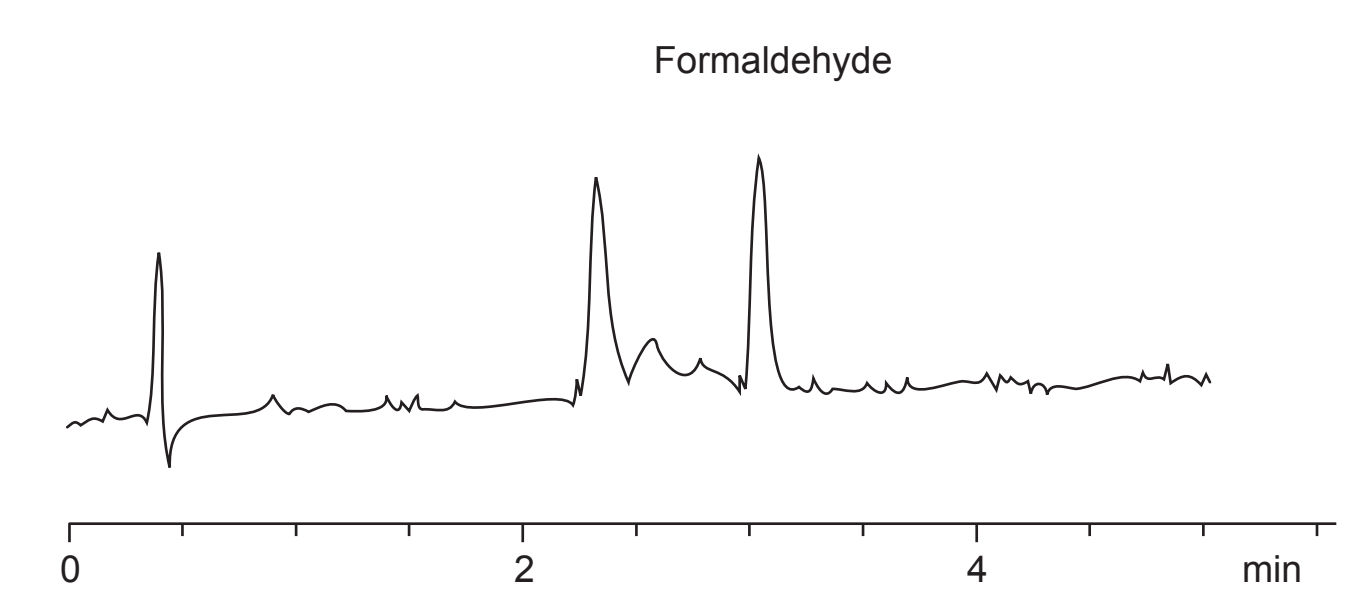


Fig 2. Chromatogram of hair color blank, containing 0.0001 % of free formaldehyde

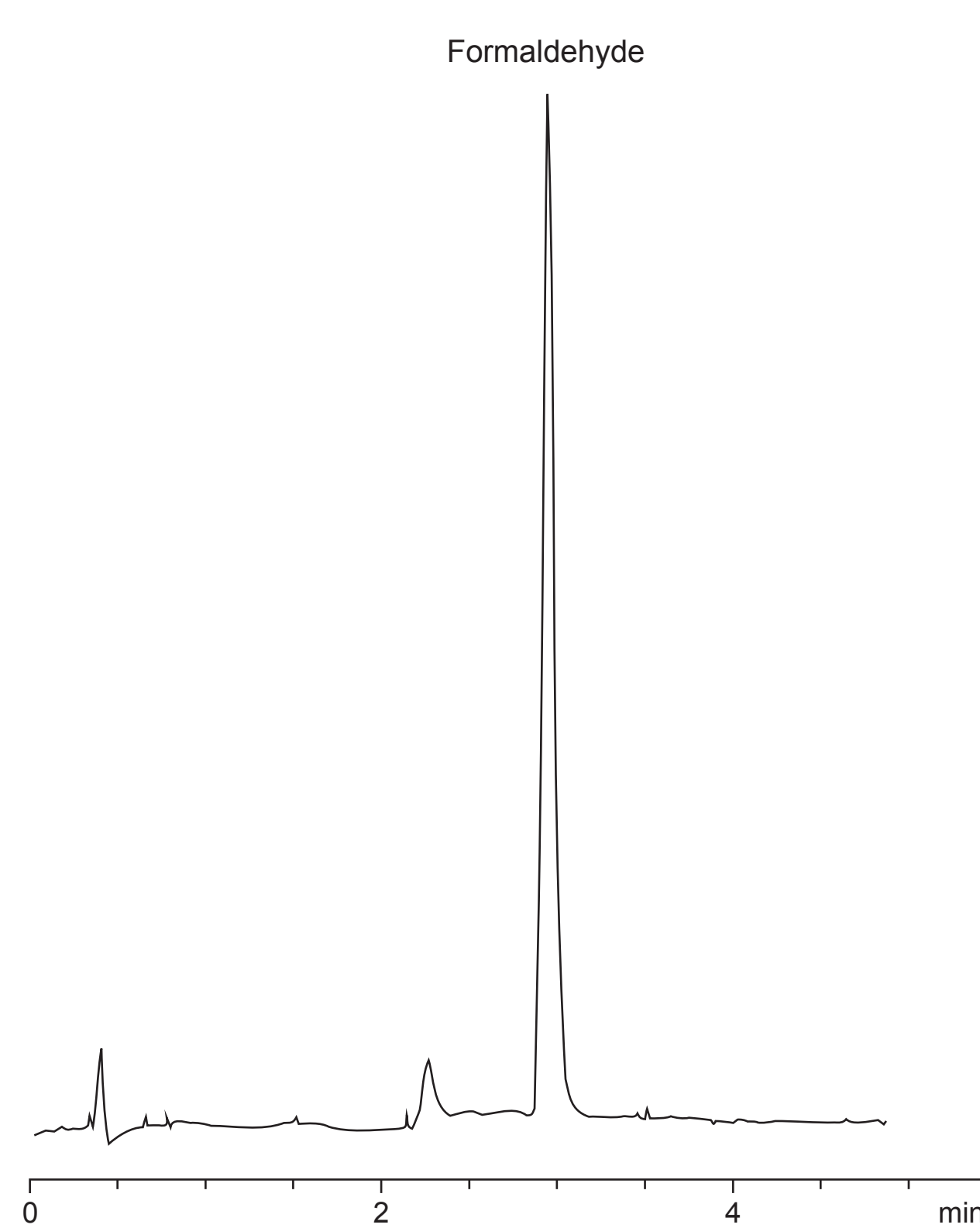


Fig 3. Chromatogram of hair gel sample spiked at 0.001 % of free formaldehyde

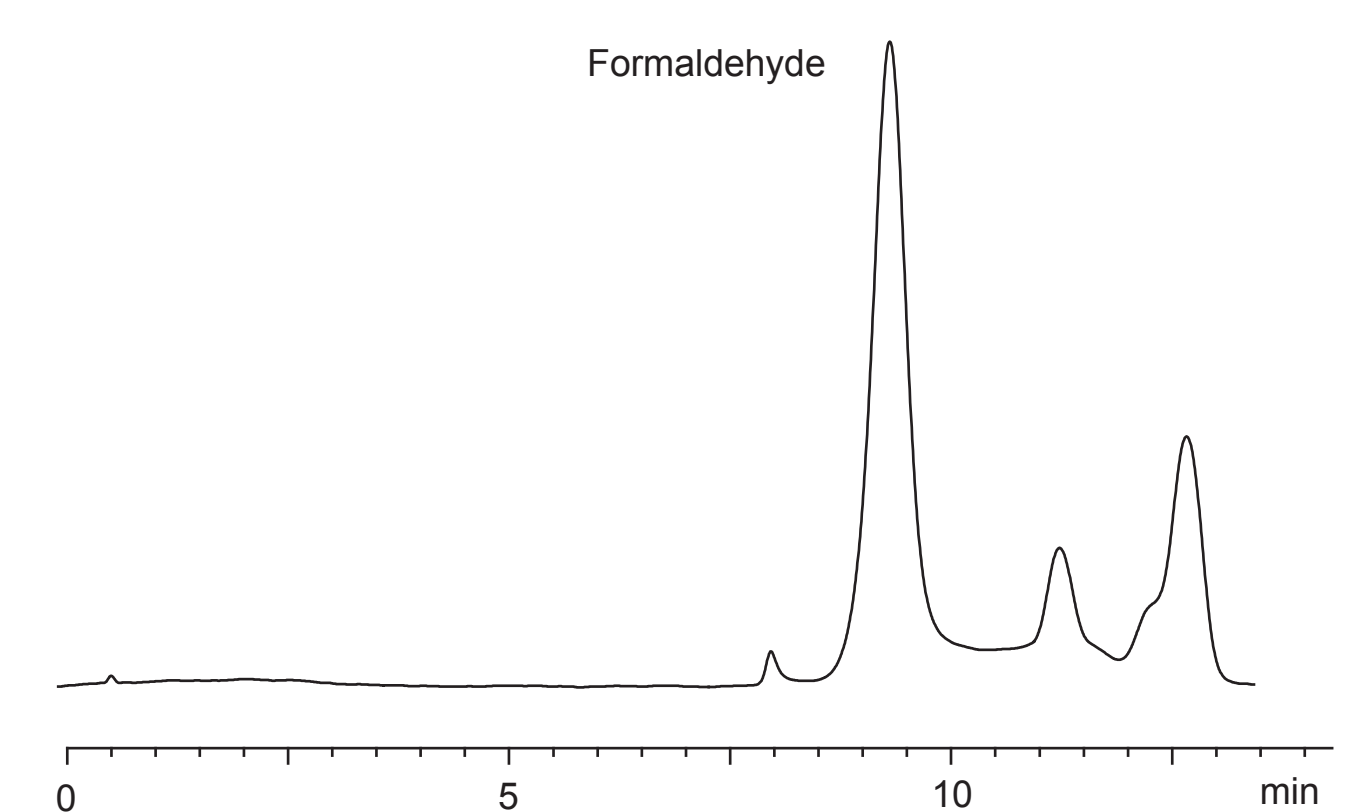


Fig 4. Chromatogram of phenolic resin sample containing 0.02% of Formaldehyde

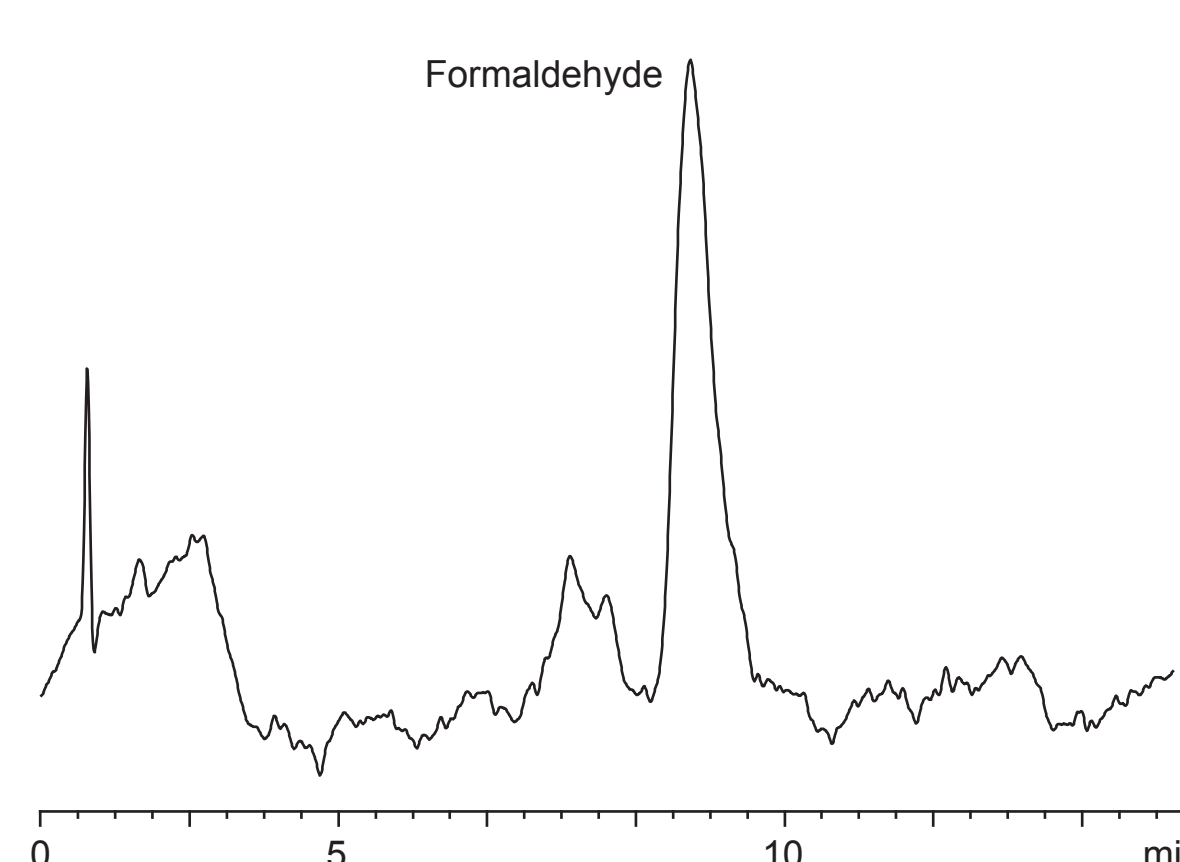


Fig 5. Chromatogram of leather sample containing 5 ppm of Formaldehyde

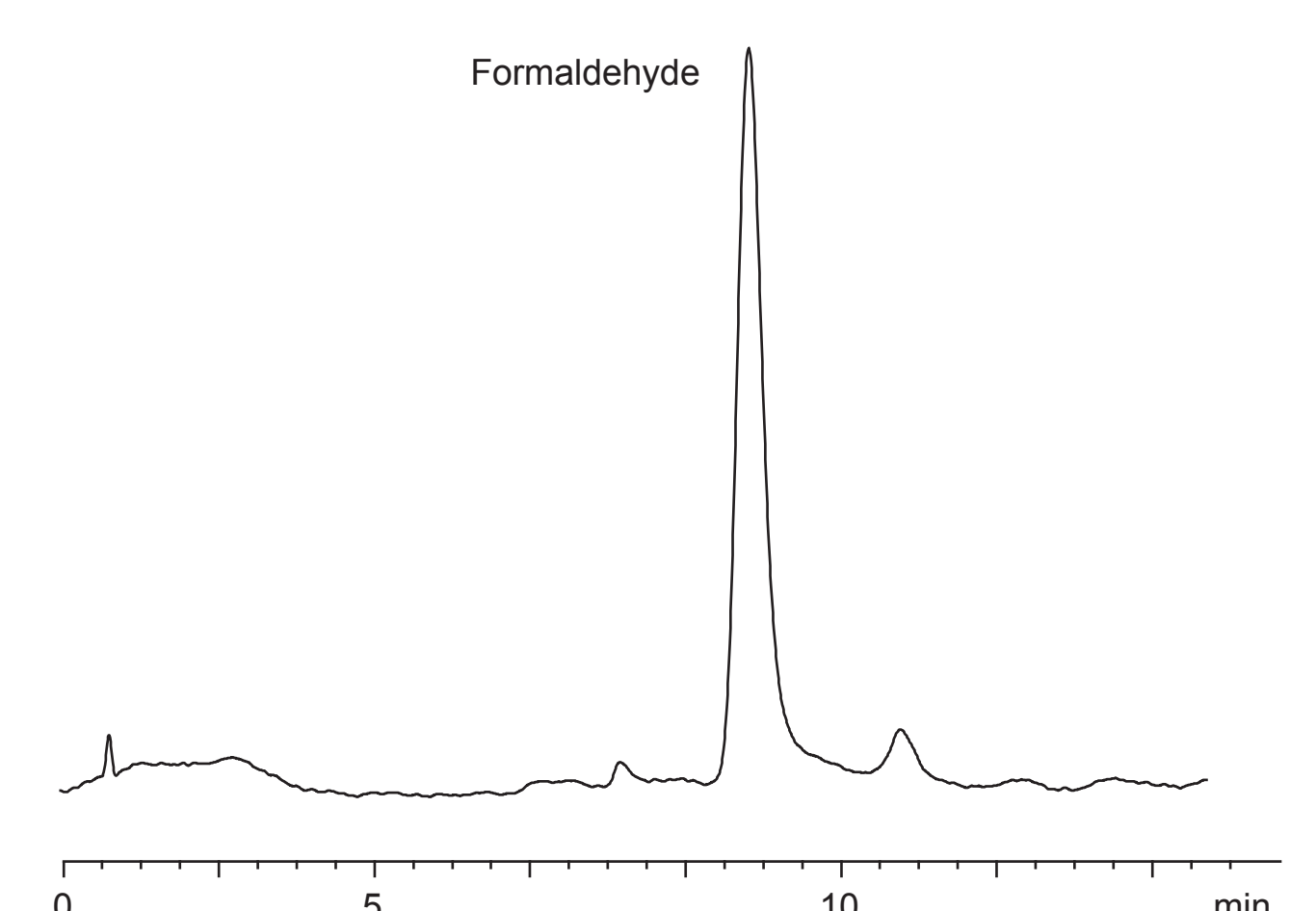


Fig 6. Chromatogram of fabric sample containing 160 ppm of Formaldehyde