Formaldehyde Quantitation In Cigarette Smoke By Thermal Desorption

Application Note
Environment
Tobacco

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Formaldehyde has been classified as a carcinogen by the IARC since 2004. Formaldehyde in cigarettes is produced in mainstream smoke (the combination of inhaled & exhaled smoke). A general observation is that the first puff of a cigarette generates the largest amount of formaldehyde in mainstream smoke. More elevated levels are detected in side stream smoke (smoldering cigarette). Most commercial cigarettes produce from about 20 µg to 60 µg of mainstream formaldehyde and about 350µg to 450 µg from the side stream. The added presence of saccharides, from natural products such as maple syrup or honey, affects the amount of formaldehyde produced in mainstream smoke.

Formaldehyde quantitation directly using GC/MS has presented challenges. The common derivatizing agent DNPH using HPLC has problems with separation and detection limits. The use of pentafluorophenyl hydrazine (PFPH) as a derivatizing agent gives the formaldehyde analysis lower detection limits and better separation than the DNPH/HPLC method.

For this application, a 1000 nM solution of PFPH was prepared in methanol. A 6 mm Tenax tube was placed on a Dynatherm Model 60 Spiking Station with the frit facing in. With helium flowing through the tube at 25 ml/min, 0.4 ml of the PFPH/methanol was injected into the Tenax tube. After about 30 seconds, the tube was removed, placed in its glass container and capped.

Sampling of the mainstream smoke was accomplished by using a Xitech 1067 dual channel air sampler. The PFPH treated Tenax thermal desorption tube was connected to the instrument via an interface connector/ferrule (tube frit out). A cigarette was placed at one end of the rubber connector tube with the other end interfaced to the fritted glass Tenax tube end (see Figure 2). The cigarette was initially match lit as the Xitech 1067 was actuated and the mainstream smoke was sampled at a rate of 35ml/minute for 5 seconds. After initial sampling, two other tubes were sampled at the same rate and time. Three different brands of cigarettes (one filtered, two unfiltered) were sampled. After sampling, each tube was placed back into its glass container and allowed to stay undisturbed overnight. The samples were then run on a CDS Autosampler interfaced to a GC/MS.

Small aliphatic aldehydes and ketones react with the PFPH stoichometrically to produce unique hydrazones. The PFPH hydrazone mass ion for formaldehyde is m/z 210 (Fig 1). This strong molecular ion is very useful in identification of the formaldehyde, so the mass spectrometer was run in single ion mode. The bar graph in Figure 3 shows that with brands X and Z, with initial mainstream smoke, the formaldehyde is high. Brand Y shows essentially no initial formaldehyde elevation. Brand Z has the lowest mainstream formaldehyde after the initial sampling.

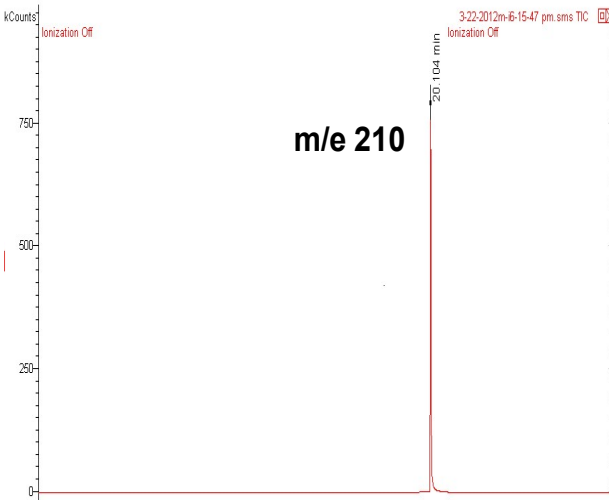

Figure 1. SIM chromatogram of the formaldehyde hydrazone.

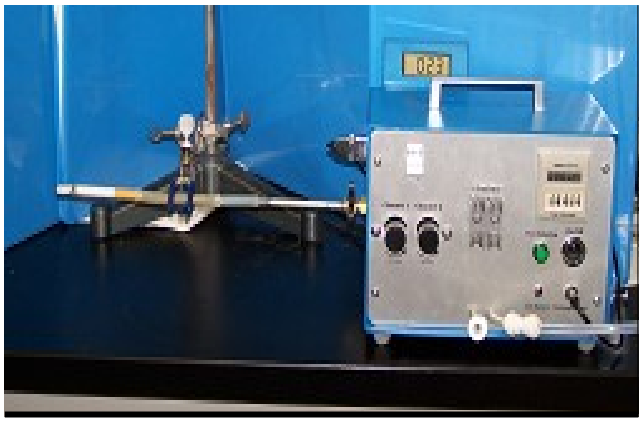

Figure 2. Sampling Device

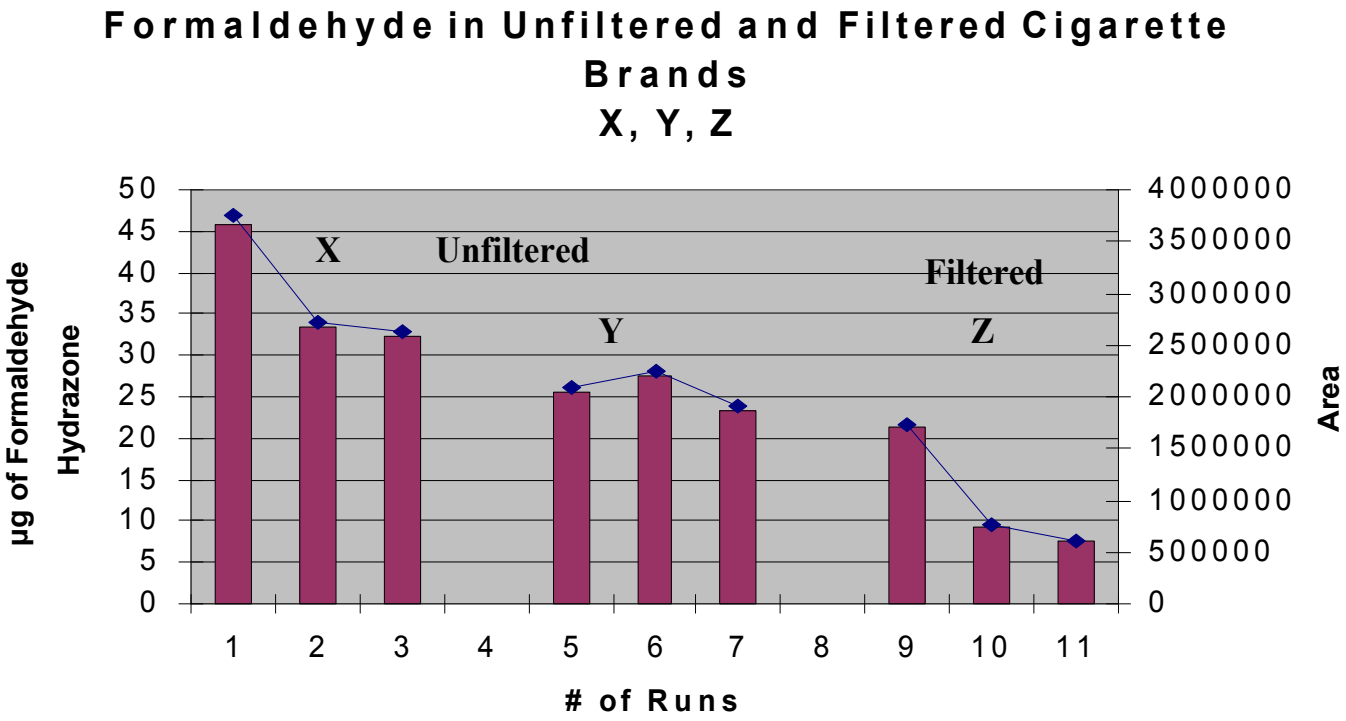

Figure 3. Micrograms of formaldehyde in cigarette smoke