

Summary

This dissertation develops a quantitative method for the measurements of interactions of Volatile Organic Compounds (VOCs) and surfaces of commercially available pipes usually used for VOC's sampling. VOCs are widely measured at ppb and ppt level in many fields of life, from therapy monitoring to climate change monitoring and to indoor air quality. The need for accuracy has always been stressed in all these fields. The interactions between gas mixtures and solid surfaces in the sampling lines and instruments play an essential role in calculating the total uncertainty of VOC concentration. The amount of substances in the gas mixture is affected by its reversible and irreversible interactions with the wall of the sampling line. These interactions between VOCs and different surfaces are of different nature, from sorption to chemical reactions or permeation depending upon the nature and thermodynamic properties of the VOC, the properties of the wall, the VOC concentration, temperature, humidity, and air velocity. There was a need of a specific study to quantify the interactions since not enough data are available in the literature. An equilibrium constant (K_e) is measured as the ratio of the maximum amount of substance per unit area segregated during equilibrium ($C_{A,e}$) on the test pipe's internal surface to the gas concentration. The $C_{A,e}$ and K_e are estimated for different materials at different conditions. The characteristic time (t_c) of the dynamic in which the phenomenon occurs is measured, which is particularly important to define whether the phenomenon should be considered or neglected with respect to the time in which the process of interest takes place. The dynamic of the phenomenon can be analyzed based on the rate of reaction at which equilibrium occurs. In polymeric materials, the irreversible losses due to permeation is significant and can be measured as mass per unit area per unit time (J) is measured to quantify these losses. The pipe's memory effect plays a role in the repeated use of sampling and is estimated as a mass release from unit area per unit time i.e., release rate (M). This research proposes and discusses the methods to quantify maximum surface concentration ($C_{A,e}$), Equilibrium constant (K_e), irreversibly reaction rate (J), and release rate due to memory (M). The sensibility of the methods on residence time, surface area, gas velocity, temperature, and pressure has been evaluated to identify the main influence quantities and biases for correction of the results and the limits of the applicability of the method. An experimental set-up

has been designed in which a mixture containing a single VOC was flushed inside a clean test pipe. A fast response detector (Flame Ionization Detector (*FID*)) was used to retrieve the signal of VOC concentration. The amount of VOC that interacted to the wall from the mixture was calculated from the depletion of the signal. Air-Acetone (C_3H_6O) mixture at the ppm level with certified uncertainty that has a high response on the detector is used for the experimentation as a representative VOC mixture. Four different common materials were tested with two different internal diameters at different lengths having the same surface area.

The proposed methodologies were applied to 4 different materials. As expected, the interactions with Sulfinert® treated stainless steel were the lowest, followed by Copper, and the highest for electropolished Stainless steel followed by Perfluoroalkoxy (PFA). An attempt to quantify the Kinetic constant k_{kin} was made, and regression to the experimental data for all materials was performed, but the model was not fitted to any of the data, which indicates these interactions are not simple and can be the sum of different phenomena. The irreversible losses due to permeation or reaction were negligible for Sulfinert®, and these were pretty measurable for PFA and Stainless steel. The release amount due to memory was following the same order of magnitude as that of irreversible reacted mass flux. The effect of temperature and pressure was evident and considered as bias to the measurements and the results were corrected accordingly to a reference temperature and pressure. The effects of fluid dynamics and residence time were investigated and were found negligible for all the tested pipes. and the methodology for estimation of losses can be extended to lower concentration, different applications and used in comparing the response of different materials that are usually used for sampling at lower concentration.