

A SENSITIVE METHOD FOR DETERMINATION OF ORGANIC ACIDS IN AIR AND OTHER ENVIRONMENTAL COMPARTMENTS.

H. Frank & D. Renschen

Institut für Toxikologie, Wilhelmstraße 56, D-72074 Tübingen, Germany .

Organic acids are important atmospheric degradation products of volatile organic air pollutants (VOC). For instance, benzoic acid is regularly found at levels of several hundred nanograms per cubicmeter of ambient air, most likely a product of atmospheric oxidation of toluene; ambient air levels of the latter range from 5 to 50 $\mu\text{g}/\text{m}^3$ in suburban air in Germany. Ecotoxicologically more relevant are secondary air pollutants of C_2 -chlorocarbons: haloacetic acids are formed by atmospheric oxidation of the former. Most of the latter are known for their high toxicity, and especially their exquisite algal toxicity suggest them as important environmental pollutants.

Haloacetic acids have so far escaped a systematic study because of the low sensitivity and selectivity of their determination in environmental samples. Airborne organic acids have been monitored sporadically by denuder sampling, derivatization to the respective methylesters, and subsequent gas chromatographic separation followed by flame-ionization or mass spectrometric detection; in some cases, ion chromatography with conductivity detection has been employed. The detection limits of these methods are in the range of several nmol/L for precipitation samples. In plant and other biosphere samples, the interference of matrix components has so far not allowed to determine their concentrations.

We have now developed a new method for quantitative analysis of organic acids in biological and environmental samples by capillary gas chromatography and negative-ion chemical-ionization mass spectrometry of the corresponding pentafluorobenzyl esters, monitoring the respective negative carboxylate ions. The conventional derivatization of base-catalyzed esterification with pentafluorobenzyl bromide and diisopropylethylamine yields many by-products; with complex samples such as plant extracts the trace analysis of the respective acids is virtually impossible in the relevant range. Therefore, extracts of air condensate, of rain and surface waters, and of plant homogenates have been derivatized with 1-(pentafluorophenyl)-diazethane which proceeds with yields of more than 80% under little side-product formation. However, great care must be taken to avoid contaminations by haloacetates (especially monochloroacetate) of laboratory glass ware, of water, reagents, and solvents employed for sample preparation/derivatization.

Representative concentrations in rain and plant material from non-polluted regions are between 1 nmol/kg trichloroacetate (rain, lowest values) and several hundred nmol/kg monochloroacetate (conifer needles).