EVALUATION OF NON-INVASIVE APPROACHES FOR THE ANALYSIS OF EXOGENOUS AND ENDOGENOUS VOCS

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ABSTRACT

Non-invasive techniques for monitoring volatile metabolites in body fluids and exhaled breath have become increasingly established in areas such as human biomonitoring, clinical diagnostics, and forensics. Since only trace amounts of VOCs are emitted by the human body, pre-concentration is required prior to analysis. Although sampling of e.g. exhaled air offers promising advantages such as large sample quantities, this step often represents the bottleneck in the analysis workflow.

Therefore, different sampling approaches have been evaluated for the analysis of human-emitted VOCs in exhaled breath as well as skin emissions and subsequent thermal desorption coupled with gas chromatography – mass spectrometry. Taking into account the effects of sampling parameters such as sorbent type, sampling volume and moisture effects, various approaches have been tested in a targeted approach using reference substances and non-invasive sampling of VOCs derived from the human body in a nutritional study.

Time profiles of exogenous and endogenous VOCs could be observed by the analysis of exhaled breath and skin emanations after the ingestion of garlic capsules. Comparing the nutritional target profiles, a holistic view of volatile metabolites was achieved.

NUTRITIONAL STUDY – GARLIC INGESTION

The analysis of exhaled breath (by 5x BioVOC & Tenax GR/Carbopack B TD tubes) and skin emanations (direct & indirect sampling by TF-Membrane) were applied during a nutritional study, after the ingestion of garlic capsules (750mg garlic extract).

Significant profiles of exogenous VOCs could be detected in exhaled breath (allyl methyl sulfide) and by direct sampling of skin emanations (furfural), shown in Fig. 7. Furthermore, the endogenous VOCs dimethyl selenide (exhaled breath) and dimethyl disulfide (skin emanations by indirect sampling) increased after garlic intake.

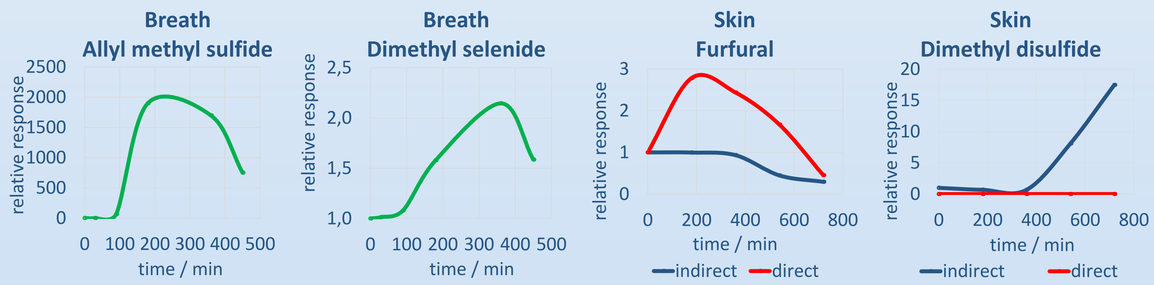

Fig. 7 Exogenous and endogenous VOCs with a significant time profile detected in exhaled breath (green lines) as well as skin emanations by direct (red lines) and indirect (blue lines) sampling.

SAMPLE PREPARATION – EXHALED BREATH

Sampling volume

Sampling via the BioVOC breath sampler was evaluated for up to fifteen repeated collections. For most of the target compounds, a linear trend of the overall area response was observed for up to 5 collections (Fig. 1).

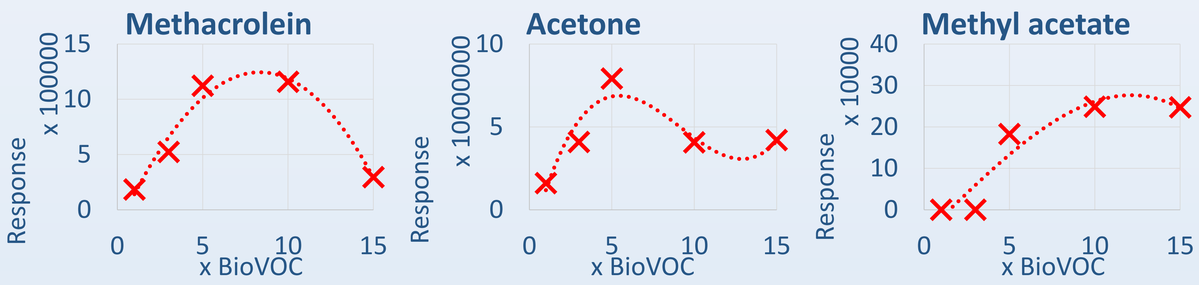

Fig. 1 Evaluation of the number of repetitive collections using the BioVOC sampler.

Adsorbent type

Different adsorbent types were evaluated including Tenax TA and a combination of Tenax GR and Carbopack B applying increasing sample volumes (0% RH). In general, a linear trend was observed for up to 645ml (5xBioVOC) sampling volume (Fig. 2).

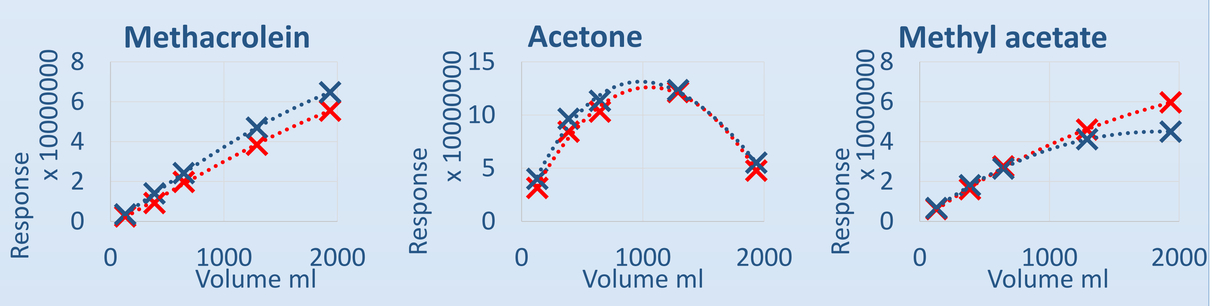

Fig. 2 Evaluation of different adsorbent types including Tenax TA (red marks) and a combination of Tenax GR and Carbopack B (blue marks) applying dry sampling conditions.

Moisture

Tenax GR/CarbopackB was evaluated applying different humidity levels. Humid conditions have a significant impact on acetone. However, most of the target compounds did show similar results for dry and humid conditions (Fig. 3).

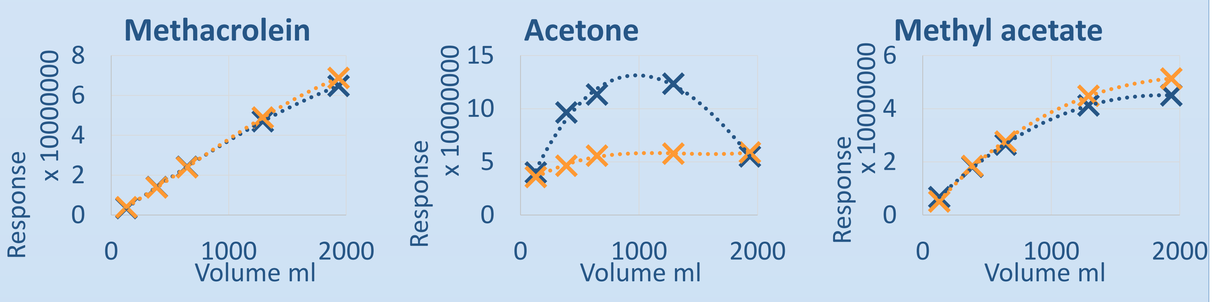

Fig. 3 Evaluation of Tenax GR/CarbopackB applying different humidity levels.
Orange marks: 100% relative humidity, blue marks: 0% relative humidity.

SAMPLE PREPARATION – SKIN EMANATIONS

Sampling set-up

Emanations from skin secretions were sampled in direct as well as indirect skin contact by sorptive sampling (Fig. 4). For direct sampling of skin emanations, the device was in contact with the skin surface, whereas for indirect sampling a metal mesh was attached between the device and skin surface.

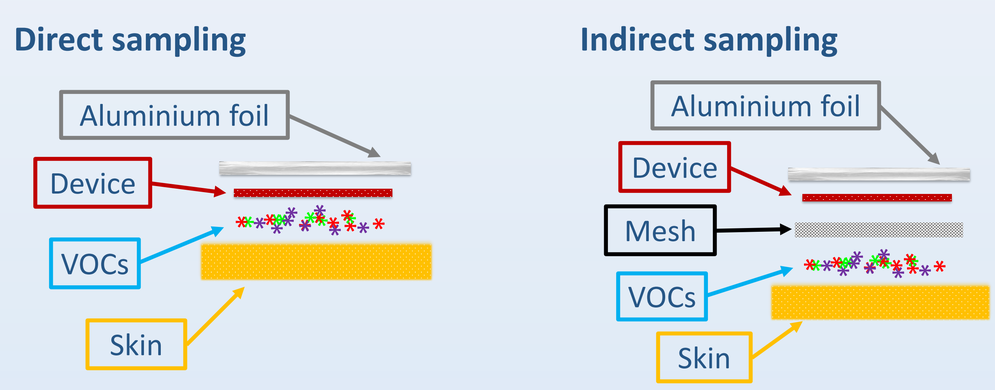

Fig. 4 Schematic of the set-up for in-vivo sampling of VOCs in skin emanations by a) direct and b) indirect sampling.

Both sampling approaches, direct and indirect sampling, were applied to the extraction of skin emanations by Stir Bar Sorptive Extraction using Twister, thin film solid phase microextraction based on DVB/PDMS (TF-SPME) and thin film microextraction applying PDMS Membranes (TF-Membrane). The responses of the “classic” compounds emitted by human skin for direct (‘d’) and indirect (‘ind’) sampling are shown in Fig. 5. No significant differences between direct and indirect sampling could be observed for the target compounds. Therefore, it is assumed that the sampling approach (direct or indirect) does not influence the target VOC results.

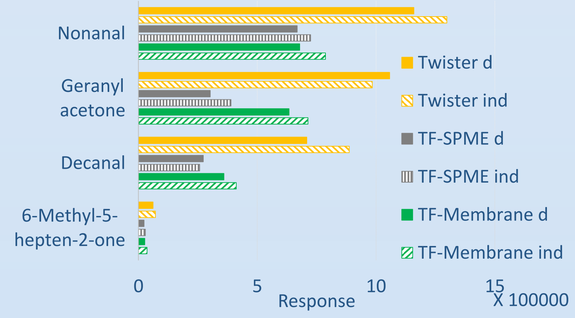

Fig. 5 Direct (‘d’) and indirect (‘ind’) sampling of skin emanations by Twister$_{20mmx1mm}$, TF-SPME$_{DVB/PDMS}$ and TF-Membranes$_{PDMS,\ thickness\ 610\mu m,\ circular\ area\ 79mm^2}$.

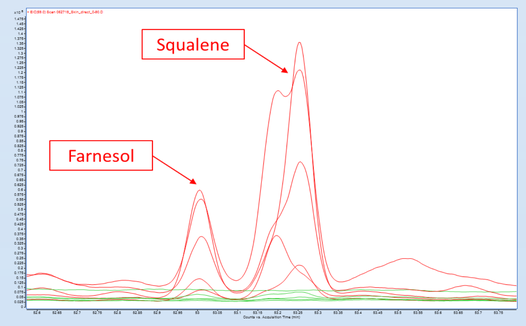

Fig. 6 EIC chromatogram of m/z=69 (53-54min) resulting from direct (red traces) and indirect sampling (green traces) of skin emanations.

By the investigation of semi-volatile organic compounds in several samples from direct and indirect extraction, higher responses of squalene (present in sebum) and farnesol could be detected in samples from direct extraction (Fig. 6). Therefore, it can be furthermore concluded that by direct sampling, (unwanted) higher boiling compounds are introduced in the analytical system that might influence the analysis.

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