Supporting information

Rapid Hydrocarbon Analysis using a Miniature Rectilinear Ion Trap Mass Spectrometer†

Ewa Sokol,[a, b] Kathleen E. Edwards,[b] Kuangnan Qian,[b] and R. Graham Cooks[a]

[a]Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

[b]Analytical Science Lab, ExxonMobil Research & Engineering Co., Annandale, NJ 08801, USA

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Corresponding authors:
R. Graham Cooks
Department of Chemistry,
560 Oval Drive, Purdue University,
West Lafayette, IN 47907-2084
Tel. 765 494 5263
Fax. 765 494 9421
cooks@purdue.edu

Kuangnan Qian
[b]Analytical Science Lab,
ExxonMobil Research & Engineering Co.,
Annandale, NJ 08801, USA
kuangnan.qian@exxonmobil.com

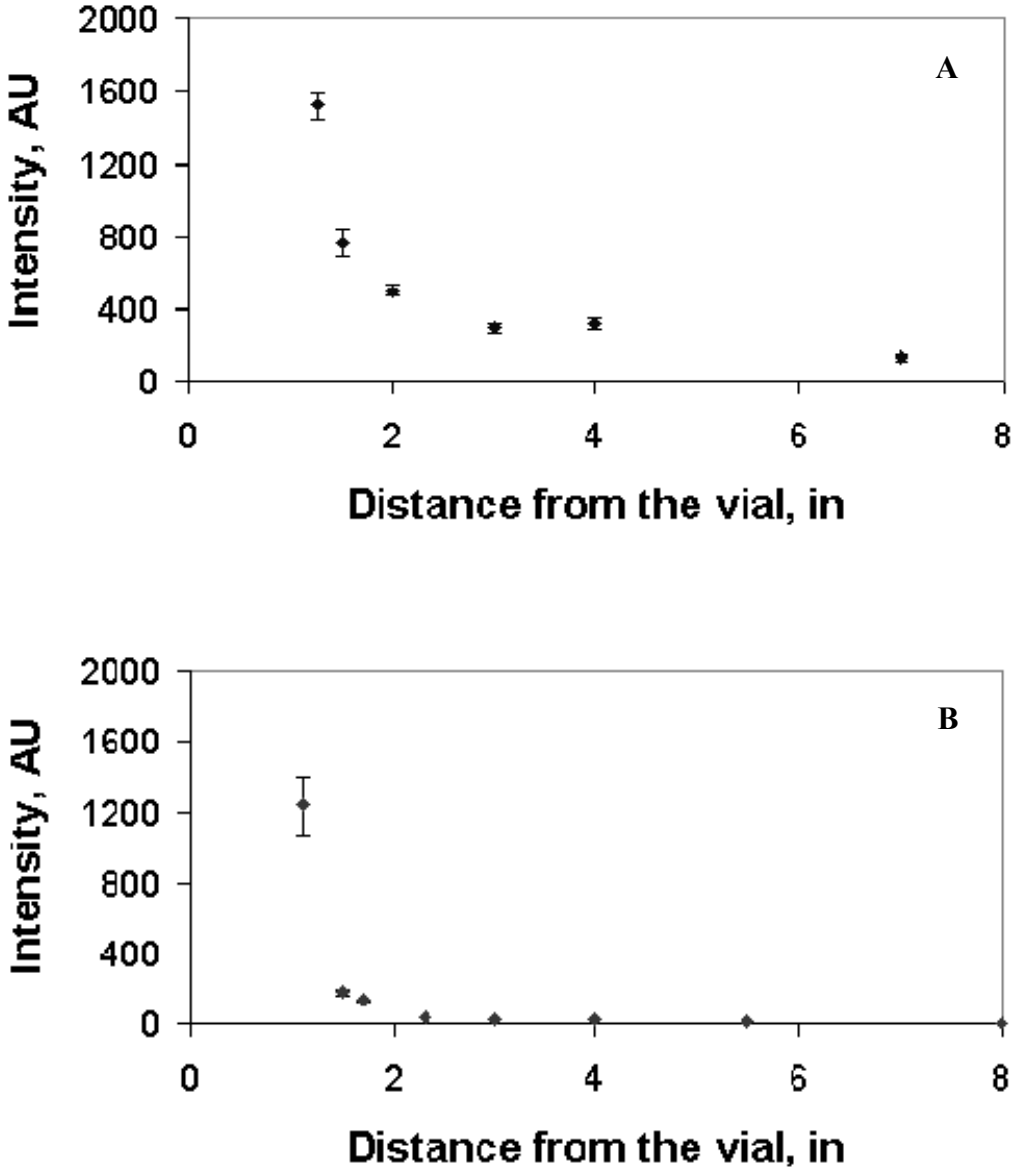

Fig. S1 Detection and identification of malodorous compounds. Response of the instrument to the presence of odorous chemicals in air is plotted versus distance between the home-built sampler and the vial containing analyte. (A) Vapors of acetic acid, based on appearance of acetic acid fragment ion $[CH_3CO]^+$ m/z 43. (B) Vapors of butanethiol, based on appearance of butanethiol molecular ion $[C_4H_9SH]^+$ m/z 90

In this study, the Mini 10.5 miniature mass spectrometer fitted with a membrane inlet was applied to the analysis of trace hydrocarbons in aqueous solution. Mixtures of selected hydrocarbons, typically present in crude oil[12] (Fig. S2†), were examined in order to evaluate the performance of the Mini MIMS system as well as the standard operating conditions for the mixture analysis. Please note that few aliphatic hydrocarbons were detected. Molecular ions corresponding to heptadecane or hexadecane were not observed, a fact that might be explained by the low water solubility of these compounds, 0.000294 mg/L and 0.0009 mg/L respectively.[5] On the other hand, hexane is more soluble in water (9.5 mg/L) but characterized by a relatively low octanol-water partition coefficient (Log P = 3.90)[5] and it penetrates the membrane more slowly than do the other hydrocarbons used in these experiments. Consequently successful detection of aliphatic hydrocarbons may require 10 – 30 minutes sampling of water containing hydrocarbon traces (results not shown).

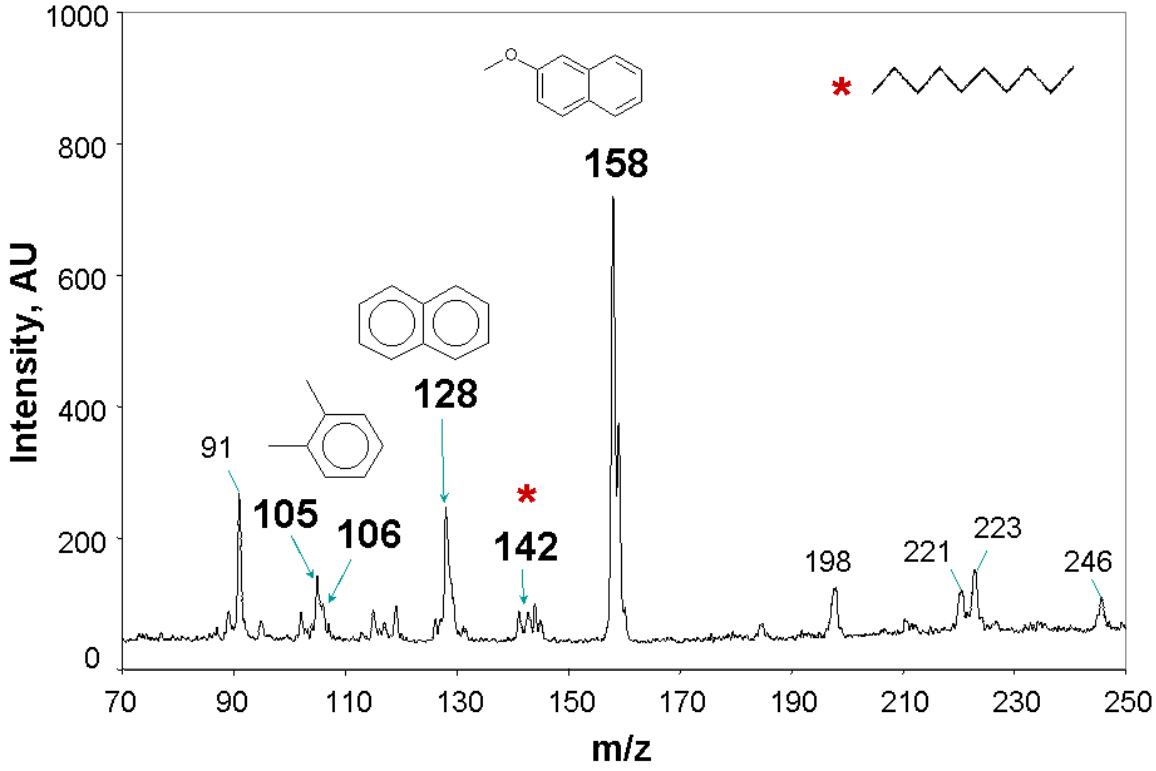

Figure S2. EI mass spectrum of 300 ppm of hydrocarbon mixture (decane, heptadecane, hexadecane, hexane, naphthalene methoxynaphthalene, xylenes) in aqueous solution recorded using the Mini 10.5 equipped with poly(dimethylsiloxane)) membrane inlet

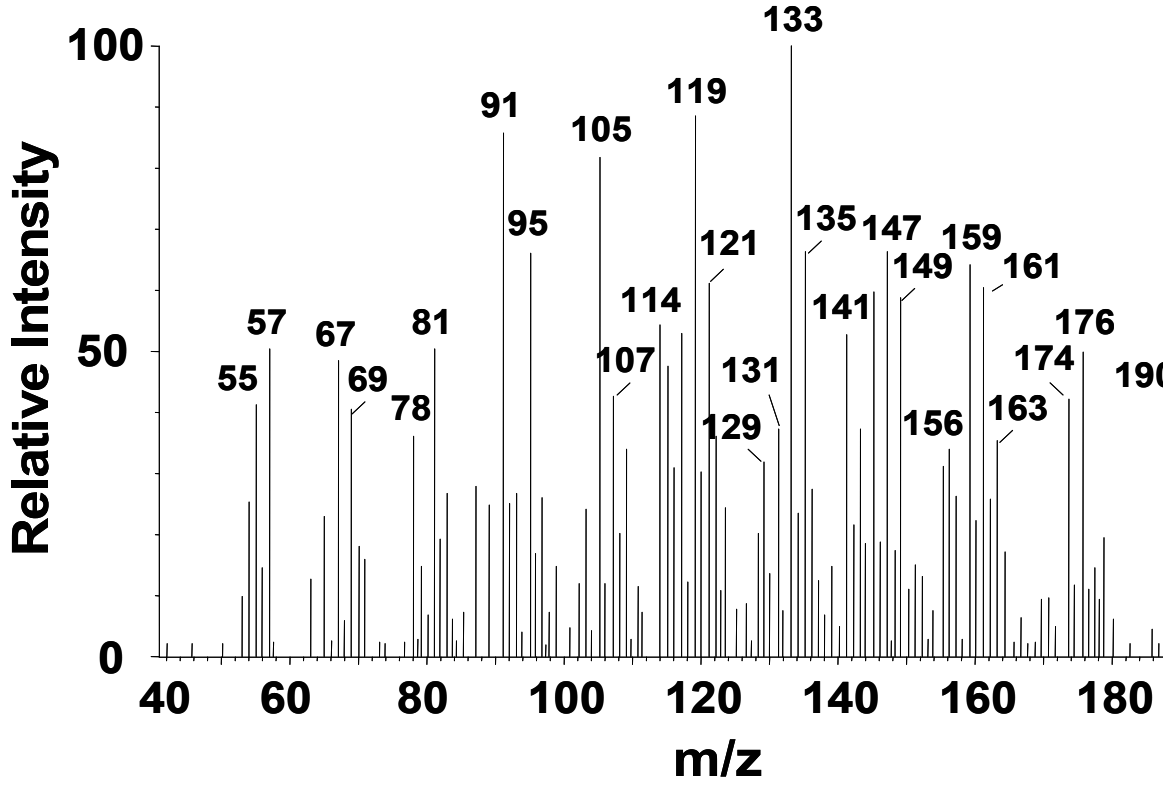

Figure S3. EI mass spectrum of naphtha mixture in aqueous solution recorded using the Mini 10.5 equipped with poly(dimethylsiloxane)) membrane inlet, data was recorded in the centroid mode

The results of naphtha sample analysis using the Mini 10.5 MIMS allowed identification of compound types, according to the number of hydrogens relative to the number of carbons[31] as well as identification of individual members of homologous series of particular compound types. Hydrocarbons have the molecular formula: C_nH_{2n+z}, and cases where z has a negative value are frequently referred to as the hydrogen deficient. The z-value decreases by 2 for every degree of unsaturation (ring or double bond) allowing determination of compound type and the molecular size.

The mass spectral data were centroided and the total ion current (TIC) was analyzed. The extraction of z-series ions from the TIC involves the following steps: (i) extraction of ion chronogram for ions of a selected mass; (ii) selection of appropriate time windows for integration; (iii) correction of the integrated intensities based on relative sensitivity factors for the compound class (iv) repetition of steps (i) through (iii) for all the masses and (v) normalization of the outcome.[32]

Since the whole process is fairly complex and requires experience, a custom-designed Microsoft Excel spreadsheet was used for calculations.[31] A coarse estimate of hydrocarbon distributions in the aqueous sample is shown in Fig. S4†. This initial study shows the feasibility of miniature mass spectrometry for ultra-fast detection and composition analysis of traces of hydrocarbons in aqueous solutions. The adequacy of this method for quantification purposes will be further investigated.

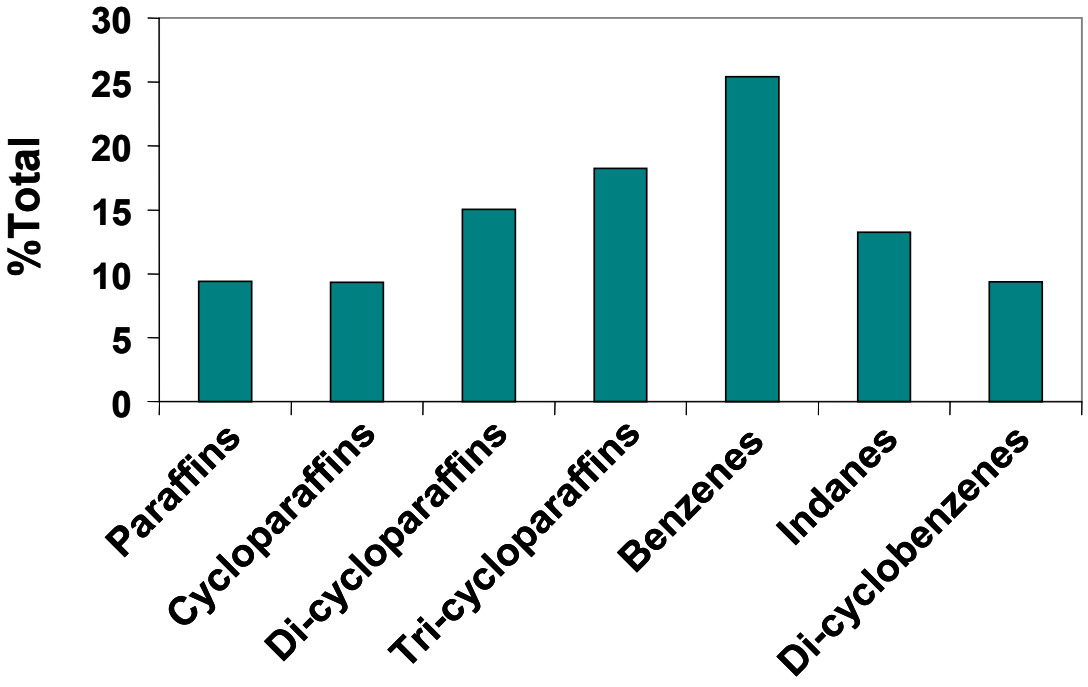

Figure S4. Estimated distribution of hydrocarbons in an aqueous sample containing a naphtha mixture recorded using the Mini 10.5 equipped with poly(dimethylsiloxane)) membrane inlet