Supporting Information

Condensed phase membrane introduction mass spectrometry with *in situ* liquid reagent chemical ionization in a liquid electron ionization source (CP-MIMS-LEI/CI)

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Table S1: Analyte physicochemical properties[S-1]

Phthalate	Molar mass (g/mol)	Water solubility (mg/L)	Vapor pressure (mmHg)
Bis(2-ethylhexyl)	390.57	0.27	0.000000142
Diethyl	222.24	1080	0.0021
Dibutyl	278.35	11.2	0.0000201

Table S2: Proton affinity data for that of the neutral molecule[S-2]

	Proton affinity (kJ/mol)
Acetonitrile	779.2
Acetaldehyde	768.5
Ethyl Ether	828.4
Formaldehyde	712.9
Methyl Benzoate	850.5

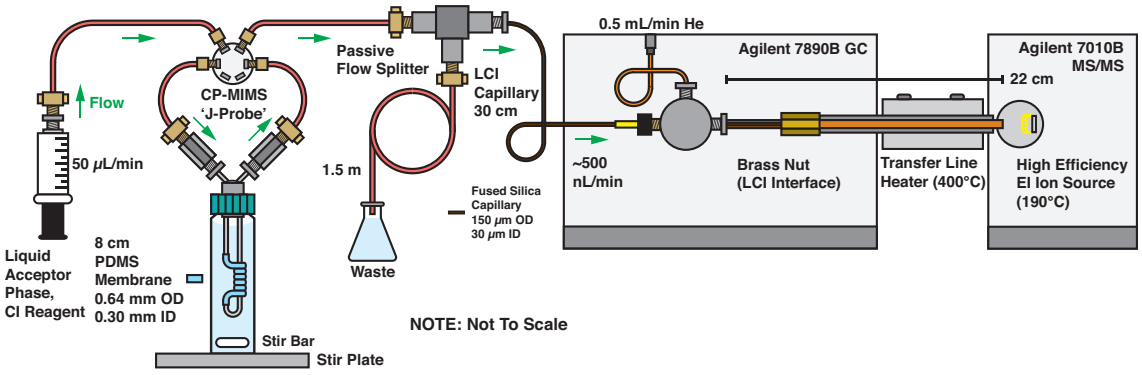

Figure S1: Experimental schematic for condensed phase membrane introduction mass spectrometry coupled to liquid electron ionization with *in situ* liquid reagent chemical ionization (CP-MIMS-LEI/CI).

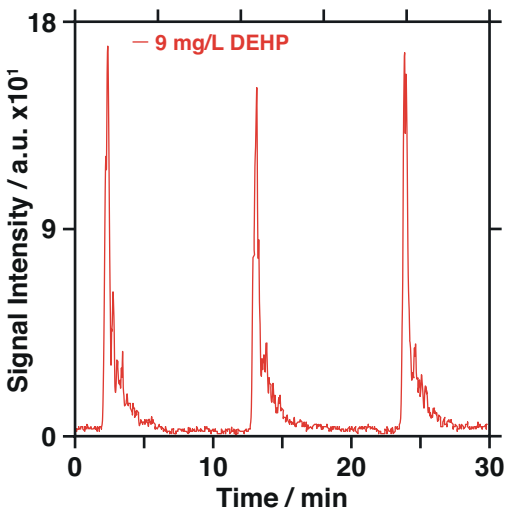

Figure S2: Triplicate measurements of 9 mg/L DEHP from 2-propanol by CP-MIMS-LEI/CI using 'stopped-flow' mode.

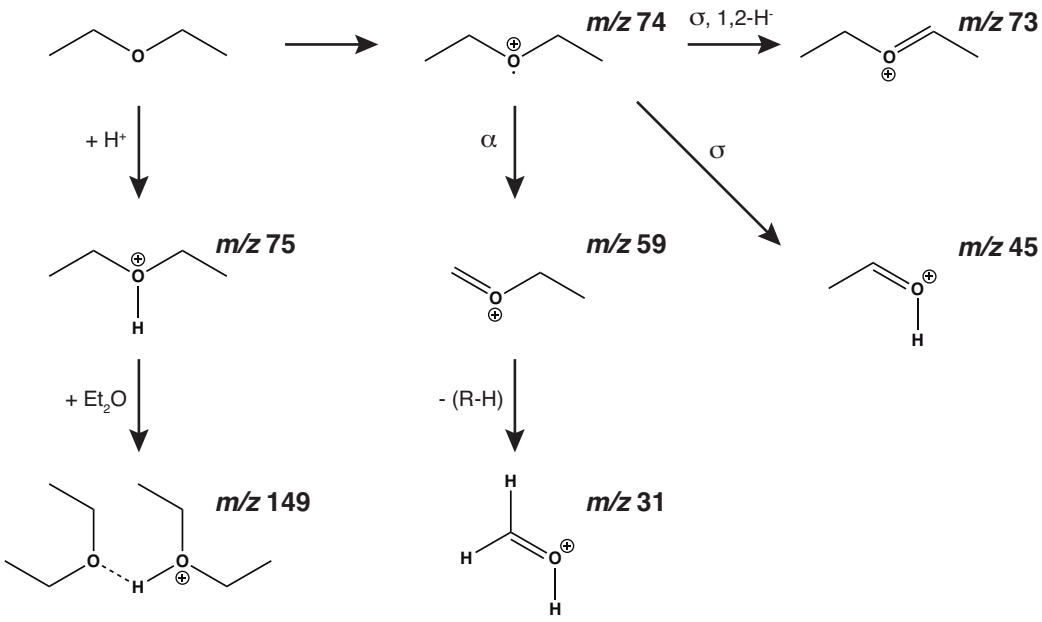

Figure S3: Fragmentation and chemical ionization of ethyl ether

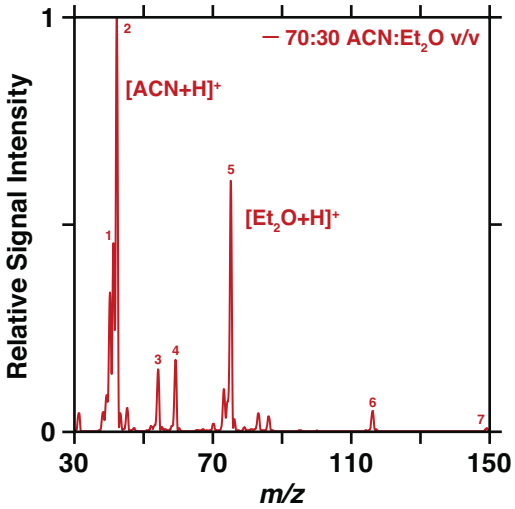

Figure S4: Full scan mass spectra of 70:30 acetonitrile:ethyl ether v/v with LEI/CI – quadrupole mass spectrometry. List of major peaks with proposed molecular formulae: 1) *m/z* 41 $[CH_3CN]^{\bullet+}$; 2) *m/z* 42 $[CH_3CN\text{-}H]^+$; 3) *m/z* 54 $[C_3H_4N]^+$; 4) *m/z* 59 $[(CH_2)O(C_2H_5)]^+$; 5) *m/z* 75 $[(C_2H_5)_2O\text{-}H]^+$; 6) *m/z* 116 $[((C_2H_5)_2O)(CH_3CN)\text{-}H]^+$; 7) *m/z* 149 $[((C_2H_5)_2O)_2\text{-}H]^+$

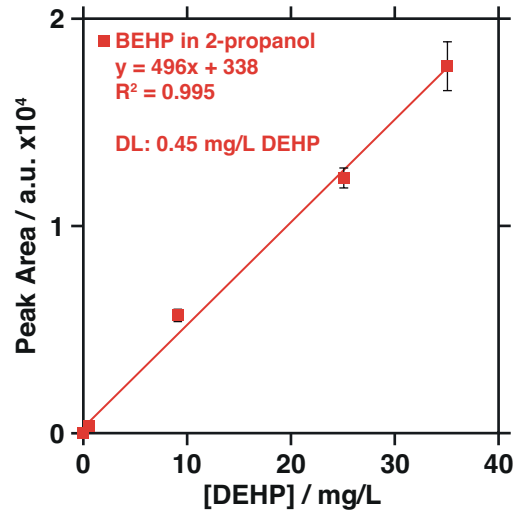

Figure S5: Bis(2-ethylhexyl) phthalate (DEHP) calibration in 2-propanol (0.5, 9, 25, 35 mg/L) using 5 minute 'stopped-flow' analyses. Error bars represent the standard deviations of triplicate measurements.

References

S1. SRC Physical Properties Database. http://esc.syrres.com/fatepointer/search.asp (accessed August 1, 2018).

S2. Hunter, E. P.; Lias, S. G. Evaluated Gas Phase Basicities and Proton Affinites of Molecules: An Update. *J. Phys. Chem. Ref. Data* **27**, 413-656 (1998)