Choline chloride–ethylene glycol based deep-eutectic solvents as lixiviants for cobalt recovery from lithium-ion battery cathode materials: are these solvents really green in high-temperature processes?

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Electronic Supplementary Information (ESI)

Experimental

Products

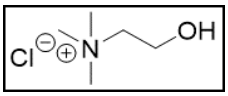
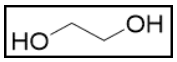
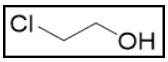
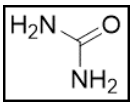
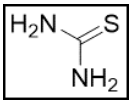
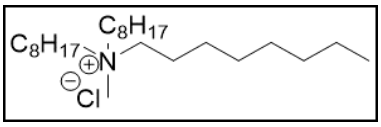
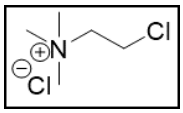
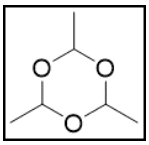
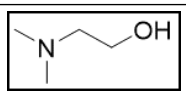
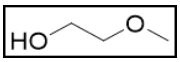
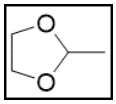
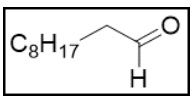
Lithium cobalt oxide ($LiCoO_2$, LCO, 0.005 mm, 97%) was purchased from Alfa Aesar (Kandel, Germany). Choline chloride (ChCl, >99%), Triton X-100 surfactant (95%), methanol (MeOH, >99%), ethylene glycol (EG, >99%), betaine hydrochloride (>99%), acetaldehyde (>99%), tributylamine (>99%) and trimethylamine (50% in H_2O) were purchased form Acros Organics (Geel, Belgium). Methyltrioctylammonium chloride (TOMAC, >98%) was obtained by J&K Scientific (Pelt, Belgium). Sulfolane (>99%) was bought from Sigma–Aldrich (Overijse, Belgium). Tetrapropylammonium chloride (Pr_4NCl, >98%), tetrabutylammonium chloride (Bu_4NCl, >98%) , chlorocholine chloride ($ChCl_2$, >98%), metacholine chloride (M-ChCl, >98%), trimethylbutylammonium chloride (Me_3NBuCl, >98%), tetraethylammonium chloride (Et_4NCl >98%) and tetramethylammonium chloride (Me_4NCl >98%) were purchased from TCI Europe (Eschborn, Germany). Dimethylaminoethanol (DMAE, >99%), 2-methoxyethanol (2-ME, >99%) and 2-bromoacetophenone (>98%) were obtained from Merck (Overijse, Belgium). Acetic acid (>99%) was obtained from VWR (Leuven, Belgium). Decanal (>95%) was obtained from Alkemi (Lokeren, Belgium). Nitric acid (65%) was obtained from Chem-Lab nv (Zedelgem, Belgium). Sulfuric acid (>95%) and potassium iodide (KI, 99%) were purchased from Fisher Chemicals (Loughborough, UK). Aqueous ICP standards cobalt, lithium and scandium were obtained from Merck (Overijse, Belgium). All chemicals were used as received without any further purification. Ultrapure water (18.2 MΩ cm) was provided by a Millipore Milli-Q Reference A+ system.

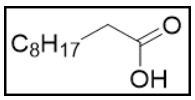
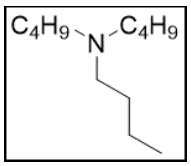
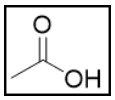
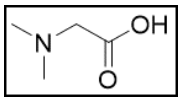
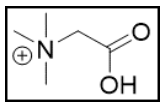
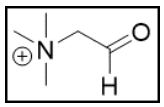
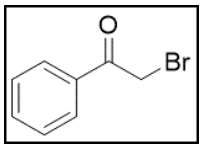
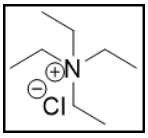
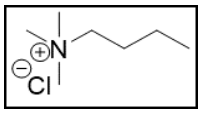
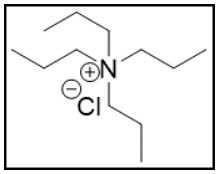
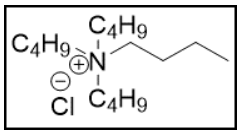
Instrumentation

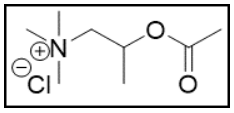
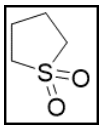
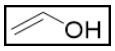
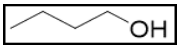
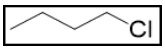
Metal concentrations in the PLS were determined by inductively coupled plasma – optical emission spectroscopy (ICP-OES) using an Optima 8300 spectrometer equipped with an axial (AX)/radial (RAD) dual plasma view, a GemTip Cross-Flow II nebulizer, a Scott double pass with inert Ryton spray chamber and a demountable one-piece Hybrid XLT ceramic torch with a 2.0 mm internal diameter sapphire injector. Dilutions were prepared with 2 vol% nitric acid solutions and all ICP-OES sample analyses were performed in triplicate. Samples were diluted 2000 times and scandium was used as internal standard. Metal concentrations in decanal and TOMAC were determined by using a total X-ray reflection fluorescence spectrometer (TXRF; Bruker S2 Picofox), equipped with a molybdenum X-ray source and operated at a voltage of 50 kV. The quartz glass sample carriers were first heated for 30 min at 60 °C in a hot air oven. Sample preparation was done by mixing 10 µL of loaded light phase together with 50 µL of gallium ICP standard and 940 µL of ethanol. Analysis was done by adding 3 µL of this prepared sample on the preheated carriers followed by drying 30 min at the same temperature. Detection of chlorine gas formed during leaching was done by a GasAlert extreme Cl_2 0-50 ppm GAXT-C-DL chlorine detector. TGA measurements were done on a NETZCH STA 449 F3 Jupiter under a flow of synthetic air with a heating rate of 5 K/min. The chlorine concentration of ChCl:EG (1:2) was determined by an automatic argentometric titration using a Mettler-Toledo DM141-SC combined silver ring electrode in combination with a Mettler-Toledo T5 Excellence and an InMotion Autosampler Flex. Samples were prepared by weighing a calculated amount of sample and diluting it in ca. 40 mL milliQ. Subsequently, ca. 2 mL of 5 vol% of Triton X-100 was added, the pH was increased to approximately 4.5–5.0 with 0.1 mol L^{-1} H_2SO_4 and the solution was titrated with a calibrated 0.05 mol L^{-1} $AgNO_3$ titrant. GC-MS measurements were done on a PerkinElmer

Autosystem XL/Turbomass Kolom equipped with a PerkinElmer column of 60 cm length and 0.25 mm diameter, coating Perkin 5MS and film thickness of 1 μm. The operational parameters were: injection volume = 1 μL; oven temperature = 45−230 °C; injection temperature = 220 °C; source temperature = 200 °C; helium pressure on the carrier = 15 psi; split flow = 15 mL min^{-1}. Liquid GC-MS samples were prepared in 1.5 mL glass vials by diluting the PLS samples in methanol. For injection of the headspace gas, a gas syringe was inserted through the septum of the cap of the 10 mL vial after leaching, and the gas was herein expanded. Subsquently, 10 μL of the expanded gas was manually injected in the GC inlet. The composition of these gas phases during leaching was also analyzed by FTIR spectroscopy. A sample of the headspace inside the vial was taken similarly, but then with a 1 mL plastic syringe with a needle of 0.8 mm diameter. This sample was injected through a septum into a nitrogen flow which was introduced into a Gasmet DX4000 FTIR gas-analyzer. The IR data were processed with Calcmet Standard software version 12.161.[1] The composition of the liquid PLS phases were analyzed by FT-IR as well, using a Bruker Vertex 70 device. Spectra were recorded in the range of 4000–400 cm^{-1} with ATR mode and processed with OPUS 6.5 software. LC-MS analysis was performed using an Agilent 1 100 system, consisting of a G1311A quaternary pump and solvent module, a G1322A vacuum degasser, a G1313A autosampler (ALS), a G1315A diode-array (DAD) detector (operating at 280 nm) and a G1316A thermostat-controlled column compartment (TCC, kept at a constant temperature of 25 °C). The LC system was equipped with a Grace Prevail reversed-phase C18 3 mm column (length: 150 mm, ID: 2.1 mm) and coupled to an Agilent 6 110 single-quadrupole mass spectrometer with an electrospray ionization (ESI) source (capillary voltage: 3500 V), operating in the positive mode. Samples (injection volume: 10 mL) were run in a mixture of methanol, water and 0.1% formic acid using a linear gradient program going from 0% to 100% methanol over a period of 40 min.[2]

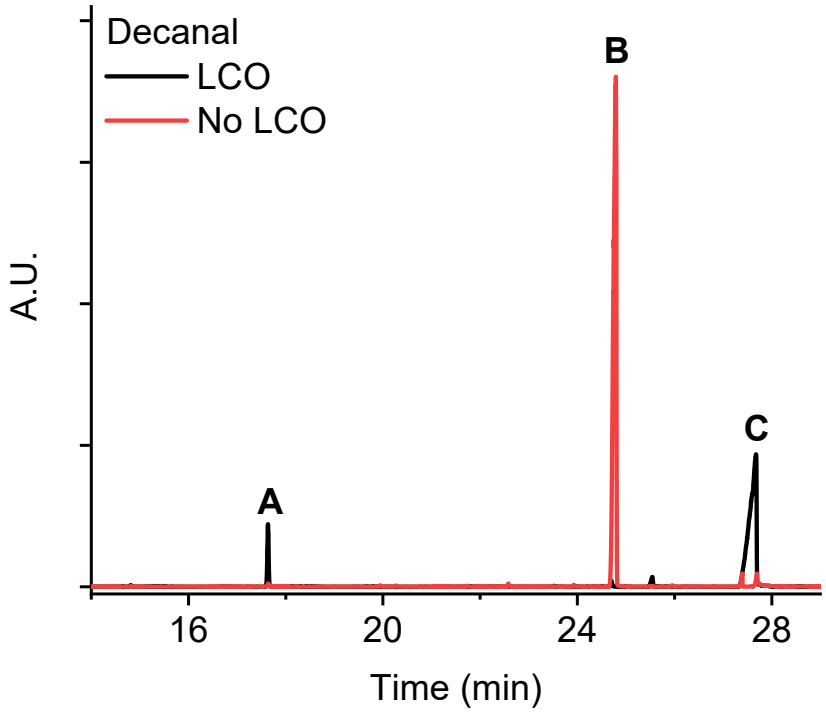
Table T1: list of abbreviations and structures that are mentioned in the manuscript.

Name	**Abbreviation**	**Structure**
Choline chloride	ChCl	
Ethylene glycol	EG	
Trimethylamine	\	
2-chloroethanol	\	
Acetaldehyde	\	
Urea	\	
Thiourea	\	
Methyltrioctyl ammonium chloride	TOMAC	
Chlorocholine chloride	$ChCl_2$	
Paraldehyde	\	
Dimethylaminoethanol	DMAE	
2-methoxyethanol	2-ME	
Methyl chloride	\	
2-methyl-1,3-dioxolane	\	
Decanal	\	

Decanoic acid	\	
Tributylamine	\	
Acetic acid	\	
Dimethylglycine	\	
Betaine	\	
Betaine aldehyde	\	
2-bromoacetophenone	\	
Tetramethyl chloride	Me_4NCl	
Tetraethyl ammonium chloride	Et_4NCl	
Trimethylbutyl ammonium chloride	Me_3NBuCl	
Tetrapropyl ammonium chloride	Pr_4NCl	
Tetrabutyl ammonium chloride	Bu_4NCl	

Meta choline chloride	M-ChCl	
Sulfolane	\	
Ethenol	\	
Butanal	\	
Butanol	\	
1-chlorobutane	\	

Results and discussion



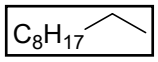
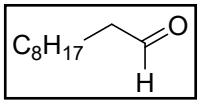
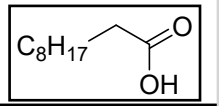
	Decanal		
	$T_{retention}$ (min)	Compound	Structure
A	17.8	Decane	
B	24.7	Decanal	
C	27.8	Decanoic acid	

Figure S1: GC-MS chromatograms of decanal after heating (no LCO) and leaching of LCO, both at 180 °C for 24 hours.

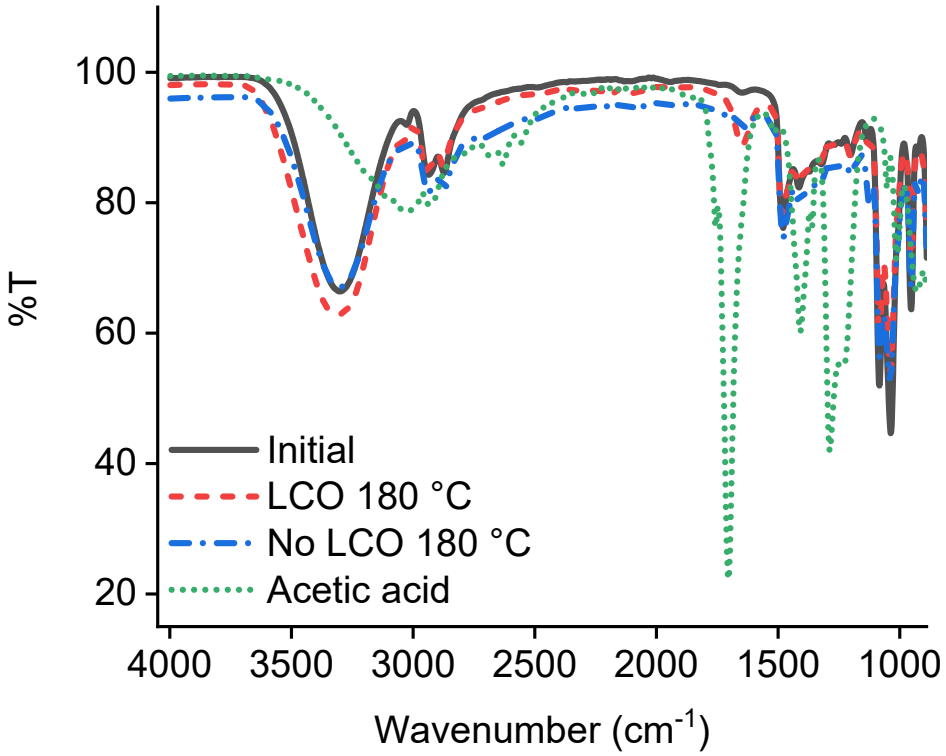


Figure S2: FT-IR spectra of acetic acid, ChCl:EG (1:2) initially, ChCl:EG (1:2) after leaching of LCO and ChCl:EG (1:2) after heating (no LCO). Heating and leaching were done at 180 °C for 24 hours.

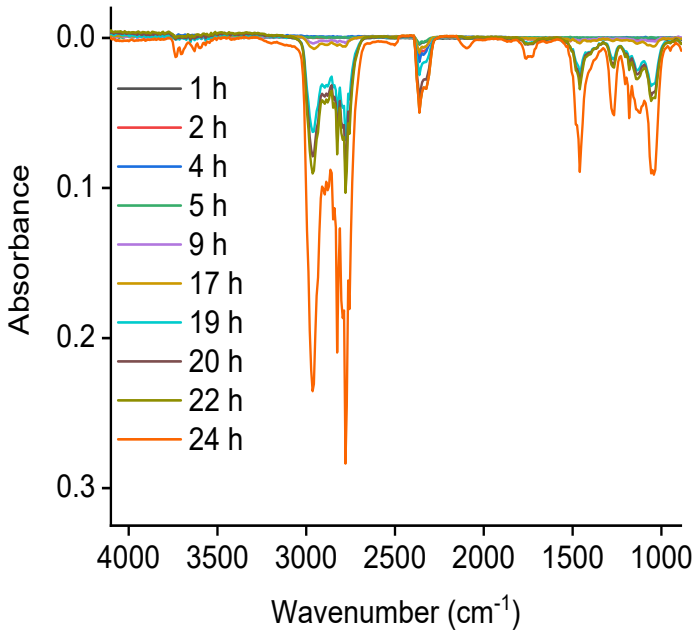


Figure S3: Gas phase FT-IR spectra of ChCl:EG (1:2) during leaching of LCO at 180 °C for 24 hours.

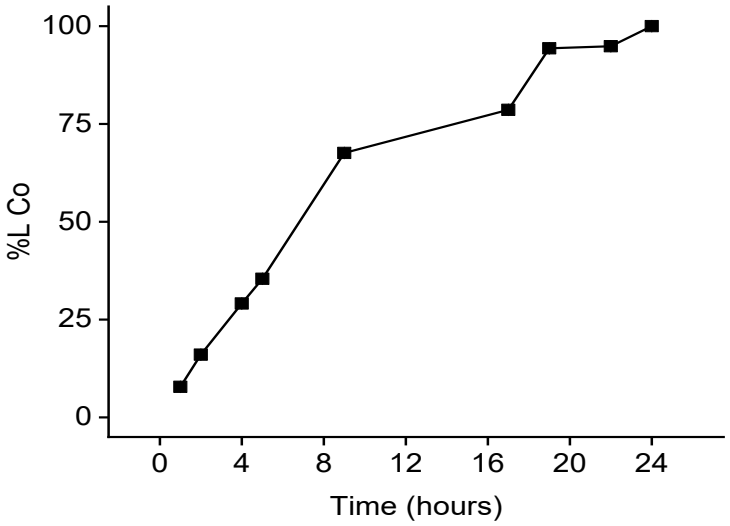


Figure S4: Leaching efficiency of cobalt over time when ChCl:EG (1:2) leached LCO at 180 °C, 900 rpm.

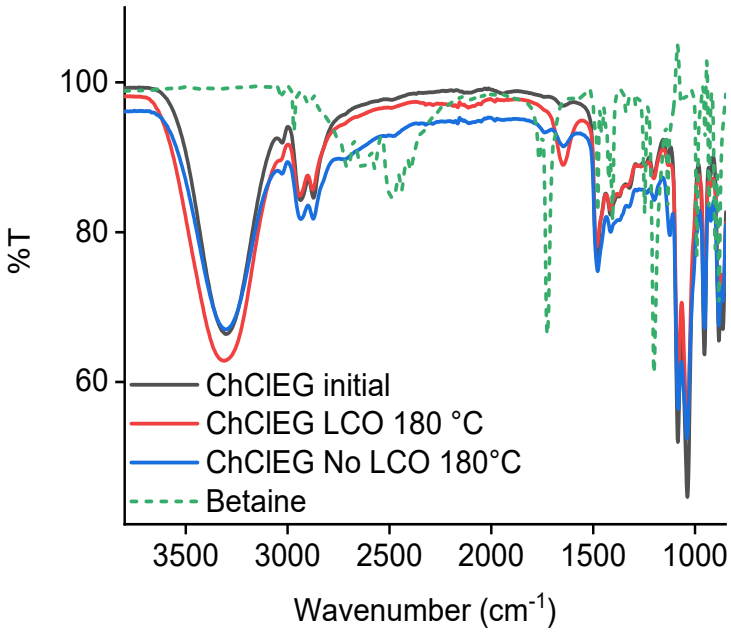


Figure S5: FT-IR spectra of betaine, ChCl:EG (1:2) initially, ChCl:EG (1:2) after leaching LCO and ChCl:EG (1:2) after heating (LCO absent). Heating and leaching were done at 180 °C for 24 hours.

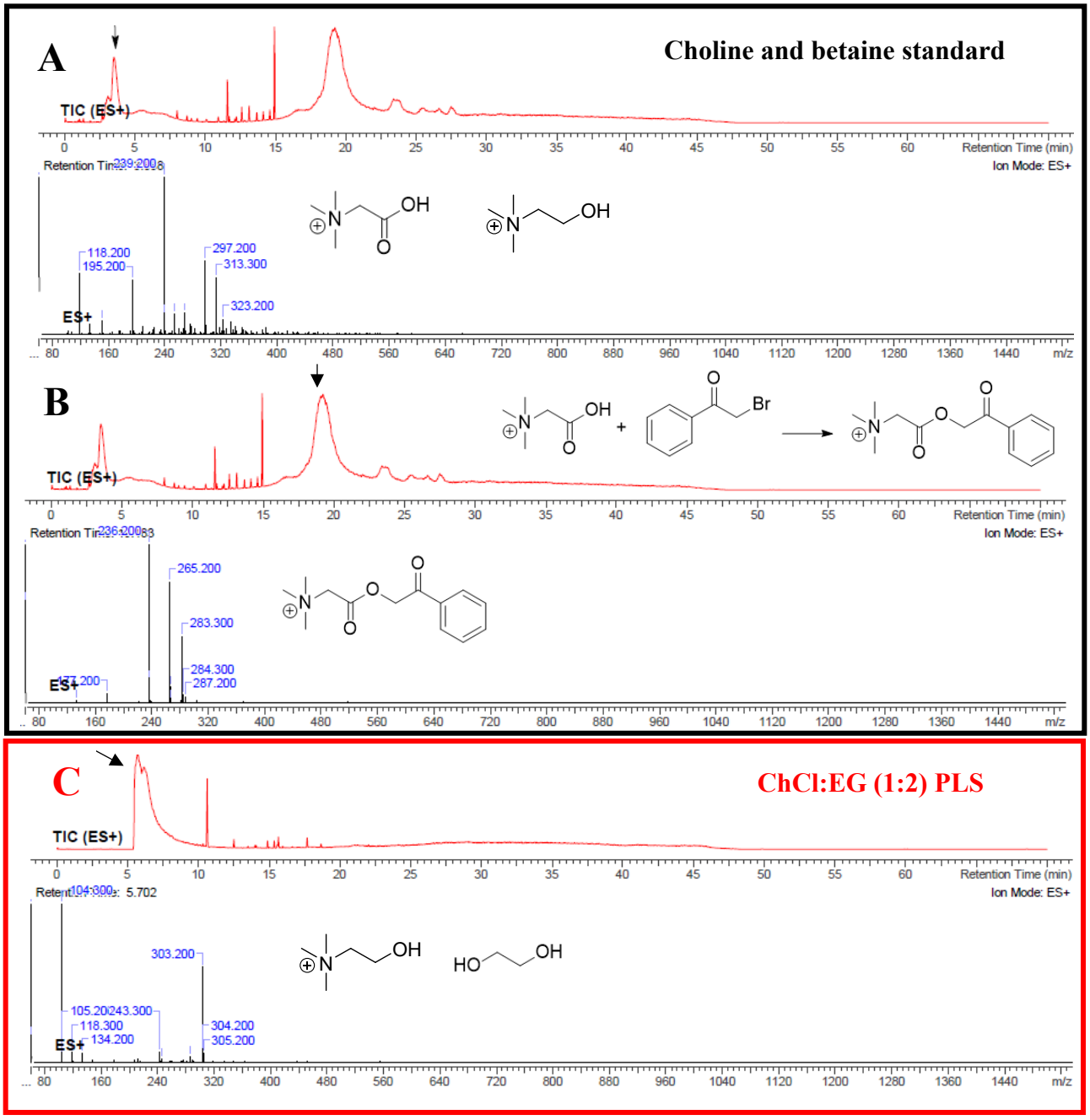
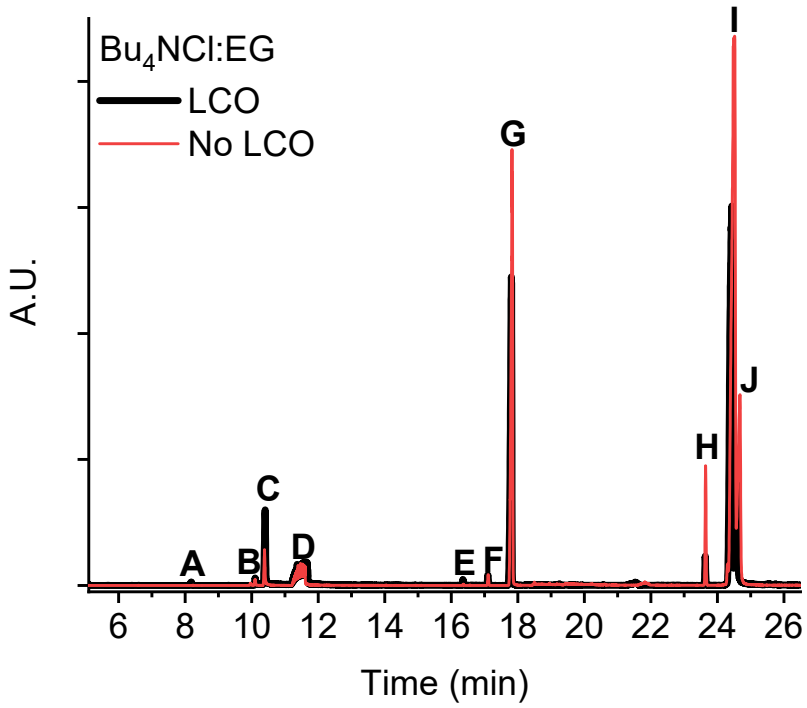


Figure S6: LC-MS chromatograms and mass spectra of the derivatization reaction in the black box: choline chloride and betaine as standards (A) and the derivatized betaine product (B). LC-MS spectrum of the derivatization reaction on the ChCl:EG (1:2) PLS in the red box: no derivatized betaine product detected (C).



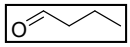
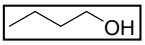
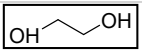
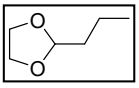
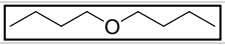
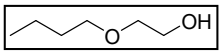
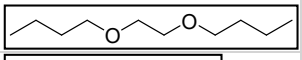
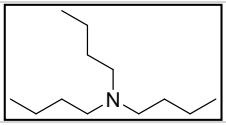
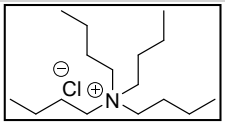
	$T_{retention}$ (min)	Compound	Structure
A	8.2	Butanal	
B	10.1	1-chlorobutane	
C	10.4	1-butanol	
D	11.5	Ethylene glycol	
E	16.3	2-propyl-1,3-dioxolane	
F	17.1	N-butyl ether	
G	17.8	2-butoxyethanol	
H	23.6	1,2-dibutoxyethanol	
I	24.4	Tributylamine	
J	24.6	Tetrabutylammonium chloride	

Figure S7: GC-MS chromatograms of Bu_4NCl:EG (1:2) after heating (no LCO) and leaching of LCO, both at 180 °C for 24 hours.

References

1 M. Stalpaert, N. Peeters and D. De Vos, *Catal. Sci. Technol.*, 2018, **8**, 1468–1474.

2 D. Copmans, A. M. Orellana-Paucar, G. Steurs, Y. Zhang, A. Ny, K. Foubert, V. Exarchou, A. Siekierska, Y. Kim, W. De Borggraeve, W. Dehaen, L. Pieters and P. A. M. de Witte, *Neurochem. Int.*, 2018, **112**, 124–133.