

Electronic Supplementary Information

The electrochemical oxidation of toluene catalyzed by Co(II) in N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide

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Experimental

Instrumental Analysis

(i) Gas Chromatography – Mass Spectrometry (GC-MS) analyses

The ionic liquid sample after electrolysis (3.0 ml) was extracted with an equal volume of diethyl ether by vortex mixer for 1 min in a 10 mL tube. The mixture was then centrifuged for 10 min, and the top layer (diethyl ether) was removed using a separating funnel. A gas chromatography coupled mass spectrometer (GC-MS, Shimadzu-QP 2000, HT3) with head space auto sampler equipped with a DB5-MS capillary column (30 m length, 250 μm diameter, 0.25 μm thickness) was used for all analyses. The column temperature was maintained at 45 $^{\circ}\text{C}$ for 1 min, then the temperature was raised to 250 $^{\circ}\text{C}$ at a heating rate of 60 $^{\circ}\text{C}$ per min. and the total run time was 45 min. The injector kept at 100 $^{\circ}\text{C}$ was operated with 30:1 split ratio with the injection volume of 1.0 μL . Ultrahigh pure Helium was used as carrier gas with 40 psi and column head pressure at 8 psi. Mass spectra were scanned from m/z 30-250 with the electron impact ionization energy of 70 eV. Identification of various peaks was carried out by comparison of the obtained retention time and MS spectra with those of standard compounds available in the library.

(ii) Attenuated Total Reflection – Fourier Transform Infrared (ATR-FTIR) spectral analysis

A known volume of the extracted ether layer obtained above was placed over the diamond ATR plate of the FTIR spectrometer and quickly scanned in the range 4000-400 cm^{-1} . The peaks were assigned by referring to the NIST catalogue.

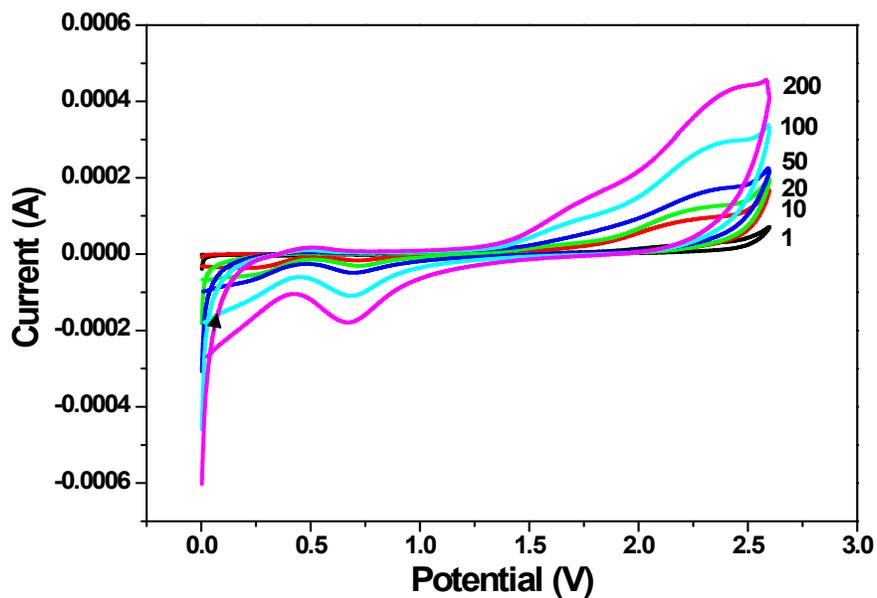


Fig. S1 Cyclic voltammograms of N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide containing 0.05 mmol CoCl_2 at various scan rates (1, 10, 20, 50, 100 and 200 mV/s) at 25 °C.

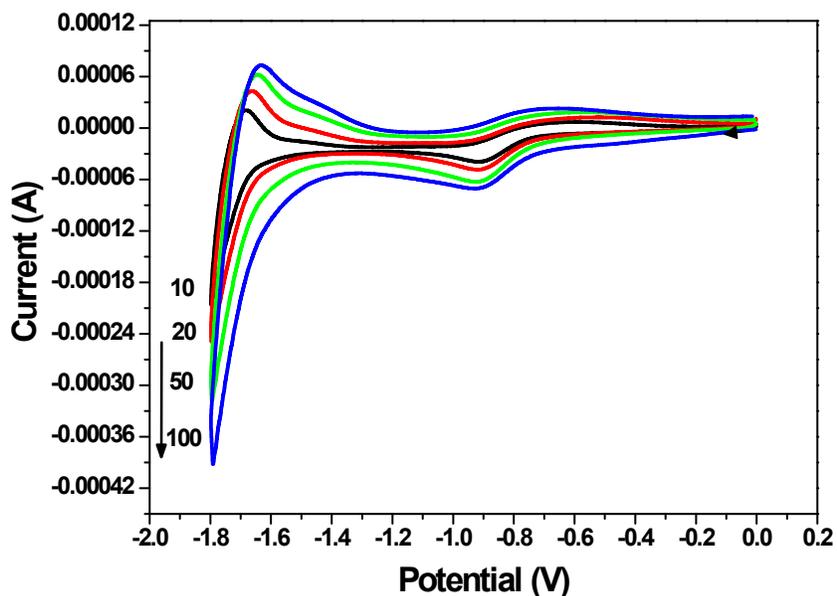


Fig. S2 Cyclic voltammograms (in the cathodic sweep) of N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide containing 0.05 mmol CoCl_2 at various scan rates measured at 25 °C with Ag wire as quasi reference electrode (working electrode: Pt disc (5 mm) and counter electrode: Pt rod (2 mm)).

Foot Note: Co(II) is known to form complexes with ligands and so expected to form a complex with (NTf_2) anion (acts as a ligand with metal ions). Also it has been reported in literature that in the complexed state Co(II) complex undergoes reduction to form Co(I) complex (*Refs. (1) Journal of Electroanalytical Chemistry 543 (2003) 143 – 151; (2) Int. J. Electrochem. Sci., 4 (2009) 717 - 729*).

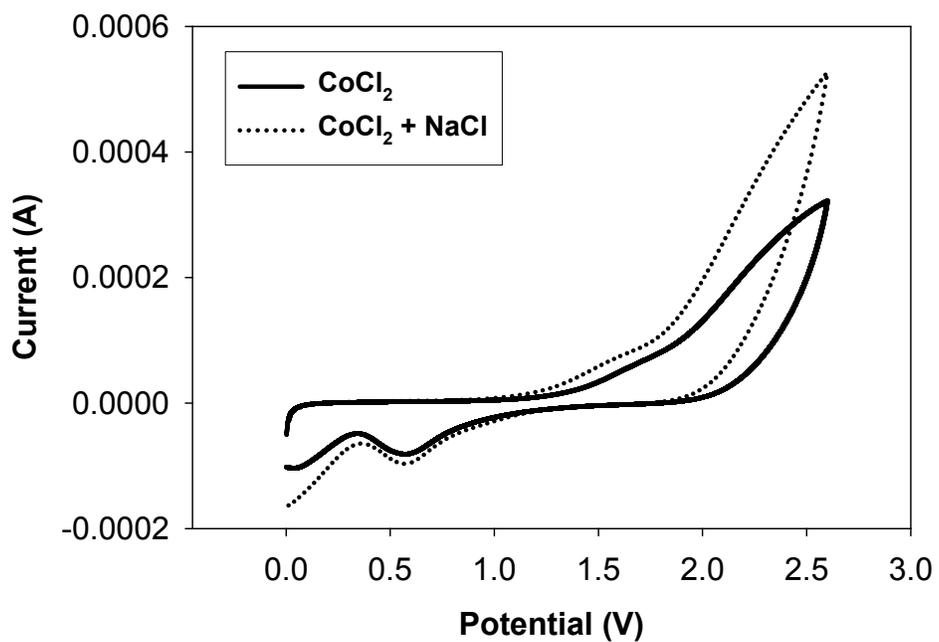


Fig. S3 Cyclic voltammograms of (a) CoCl₂ in [bmpyr]⁺[NTf₂]⁻ and (b) 20 mM CoCl₂ + 0.03 mmol NaCl in [bmpyr]⁺[NTf₂]⁻ at the scan rate of 100 mV/s at 25 °C.

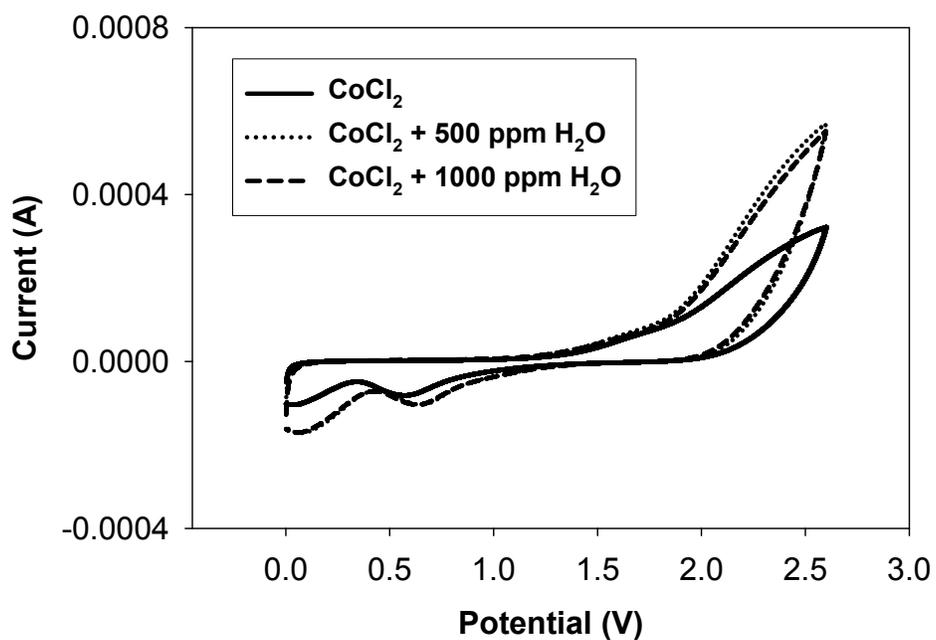


Fig. S4 Cyclic voltammograms of (a) 20 mM CoCl₂ (b) 20 mM CoCl₂ + 500 ppm water and (c) 20 mM CoCl₂ + 1000 ppm water in [bmpyr]⁺[NTf₂]⁻ at the scan rate of 100 mV/s at 25 °C.

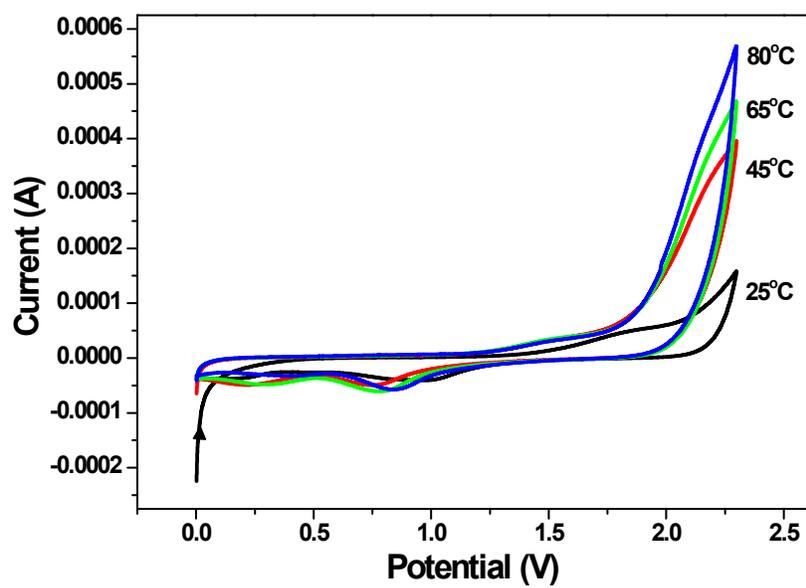


Fig. S5 Cyclic voltammograms of toluene direct oxidation over Pt disc electrode in N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide at the scan rate of 50 mV/s at various temperatures.



Fig. S6 Optical images of 20 mM CoCl_2 dissolved in $[\text{bmpyr}]^+[\text{NTf}_2]^-$ **(a)** before and **(b)** after galvanostatic electrolysis. Co(II) electro-oxidation to Co(III) is indicated by a distinct color change from pale pink to light green (*Galvanostatic electrolysis with Pt disc (5 mm dia.) anode and Pt rod (2 mm dia.) cathode with applied current density of 2.75 mA/cm^2 , duration 5 h*).

Fig. S7A

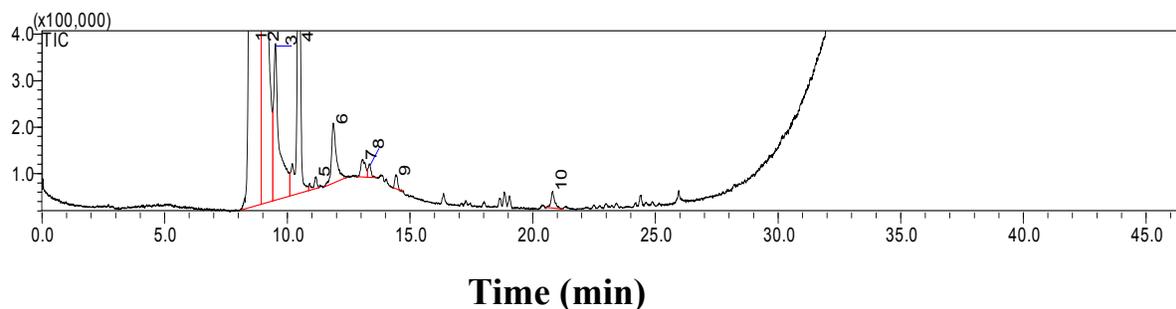


Fig. S7B

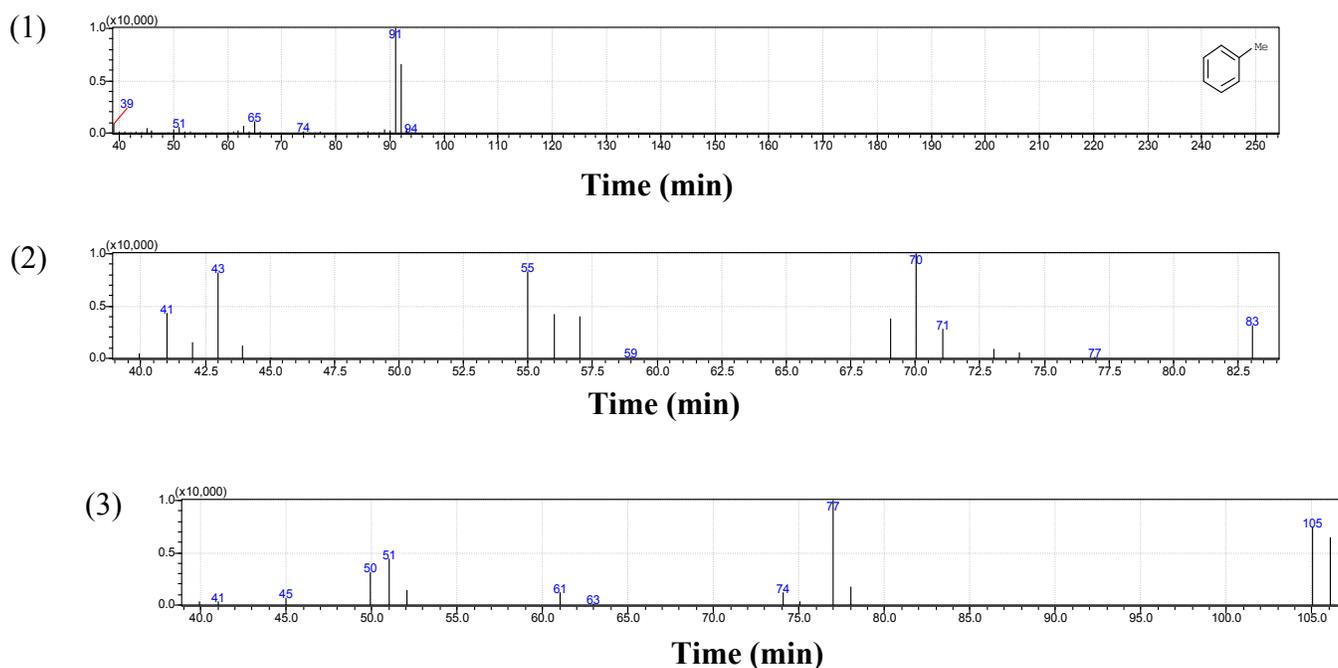


Fig. S7A Total ion chromatograms of diethyl ether extract sample (Peak identification and retention time - *Peak 1*: diethyl ether solvent peak (RT: 8.6); *Peak 2*: ethyl acetate (RT: 9.09); *Peaks 3&4*: toluene (RT: 9.53&10.48); *Peak 5*: 3-methyl-1-hexanol (RT:11.17); *Peak 6*: Thio containing organic residue from NTf_2 anion of the ionic liquid (RT: 11.89); *Peak 7*: Benzaldehyde (RT: 13.08); *Peaks 8-10*: Organic impurities from ionic liquid).

Fig. S7B Mass spectra of **(1)** toluene, m/z: 92 (*peak no. 4 of Fig. S7A*); **(2)** 3-methyl-1-hexanol, m/z: 83 (*peak no. 5 of Fig. S7A – m/z of alkyl chain showing M-33*); and **(3)** benzaldehyde, m/z: 106 (*peak no. 7 of Fig. S7A*).

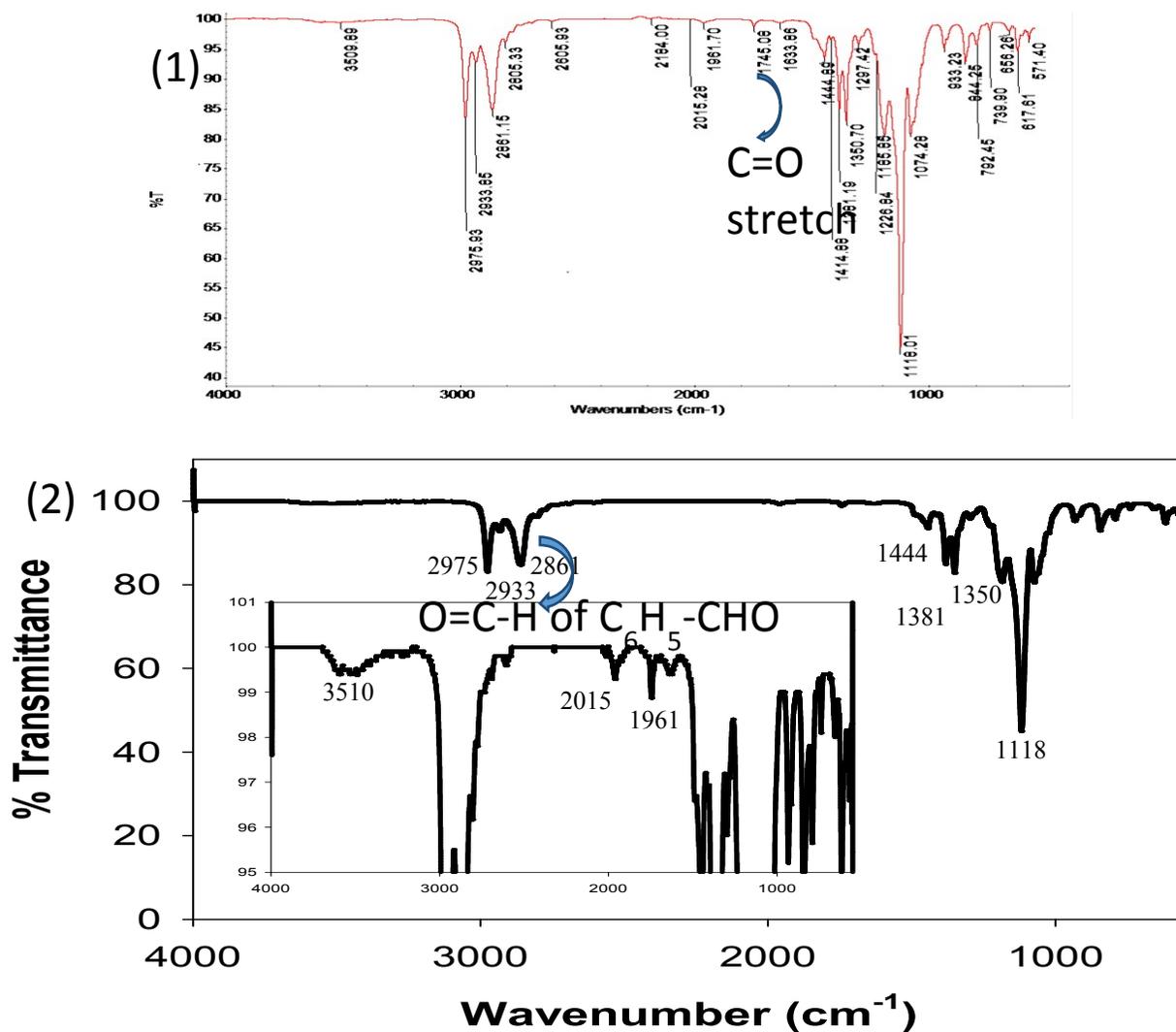


Fig. S8 (1) As obtained ATR-FTIR transmission spectrum of diethyl ether sample; (2) zoom in spectrum for magnifying the smaller intensity peaks (*Ether sample was obtained after extraction from a mixture of equal volume of (3 ml) diethyl ether & [bmpyr]⁺[NTf₂]⁻ containing 20 mM Co(II) and 0.05 mmol of Toluene after galvanostatic electrolysis*).

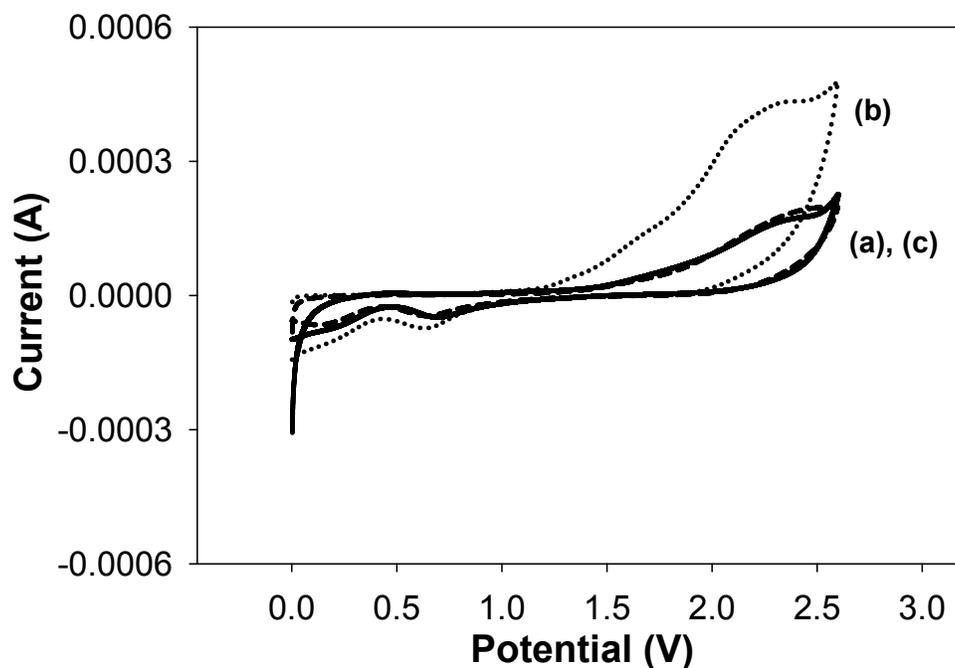


Fig. S9 Cyclic voltammograms of **(a)** 20 mM CoCl_2 (solid line) **(b)** 20 mM CoCl_2 + toluene before electrolysis (.....) & **(c)** 20 mM CoCl_2 + toluene after electrolysis (---) at the scan rate of 50 mV/s at 25 °C (*After electrolysis the toluene oxidation products were recovered by three successive extraction steps using double distilled water and finally the ionic liquid was separated using a separating funnel after centrifugation and stored under vacuum for 1 hour before CV measurements*).