Supporting Information

Effect of Glycerol Concentration on Rate and Product Speciation for Ni and Au-based Catalysts

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Table of Contents

1. Electrochemical Flow Cell Diagram

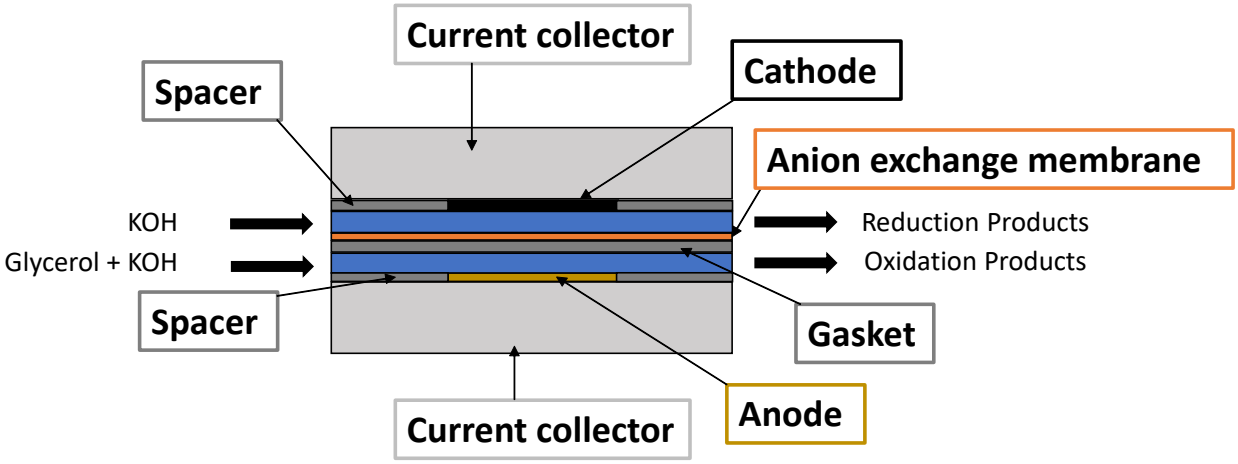

Figure S1. Diagram of Electrochemical Flow Cell Configuration.

Figure S1 describes the flow cell configuration utilized in flow experiments.

2. Electrochemical Activity of Catalysts with Varied Glycerol Concentrations

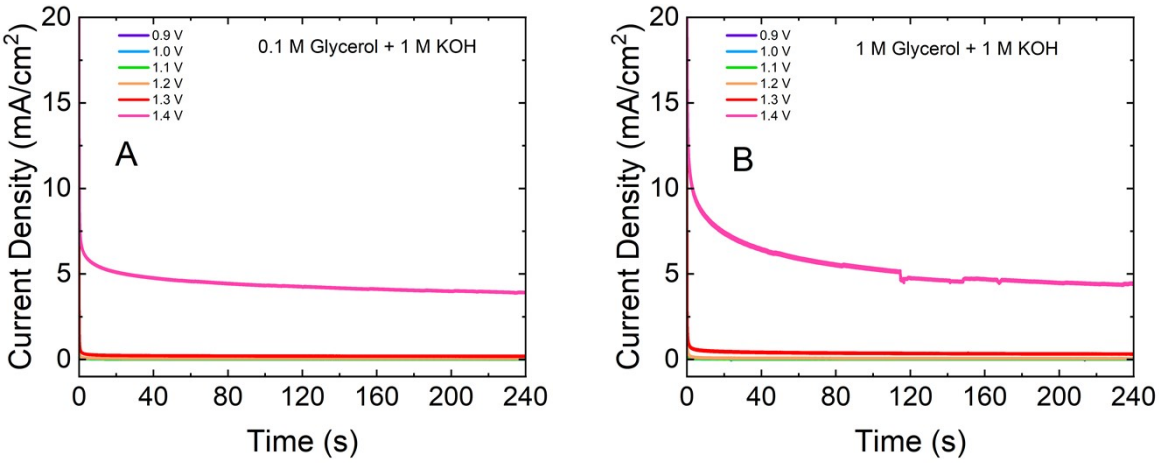

Figure S2. Chronoamperometry of GEOR on Ni foil catalysts at varied potentials in 0.1 M glycerol (A) and 1 M glycerol (B) in 1 M KOH

Figure S2 shows the results of GEOR chronoamperometry on Ni foil catalysts. Significant current density for glycerol oxidation is not observed until 1.4 V vs RHE in both 0.1 M glycerol and 1 M glycerol. Oxidative current is stable between 120 s and 240 s, where product samples were collected for analysis.

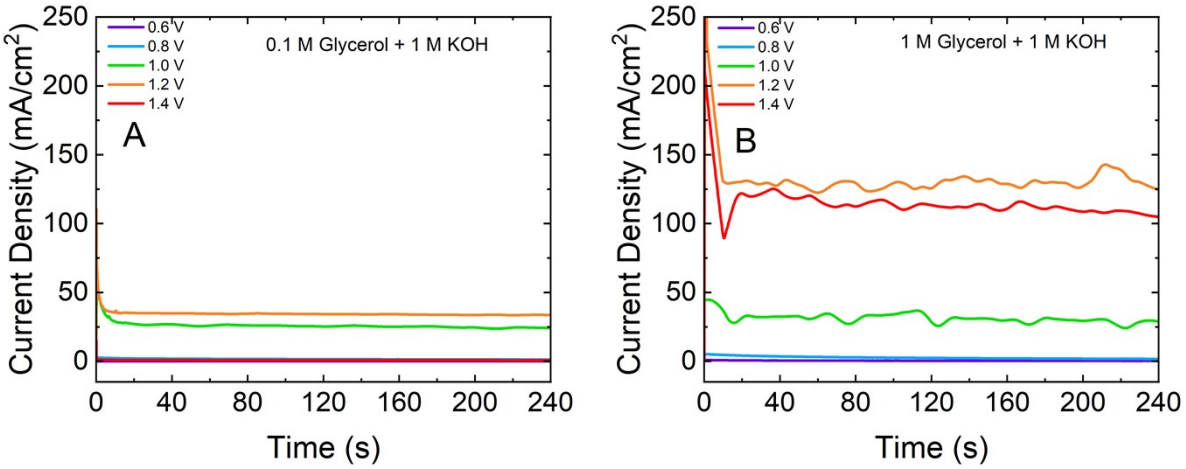

Figure S3. Chronoamperometry of GEOR on Au foil catalysts at varied potentials in 0.1 M glycerol (A) and 1 M glycerol (B) in 1 M KOH

Figure S3 shows the results of GEOR chronoamperometry on Au foil catalysts. In 0.1 M glycerol, oxidative current increases up to 1.2 V and decreases significantly at 1.4 V. In 1 M glycerol, oxidative current increases up to 1.2 V and remains at high (> 100 mA/cm^2) at 1.4 V. Oxidative current is stable between 120 s and 240 s, where product samples were collected for analysis.

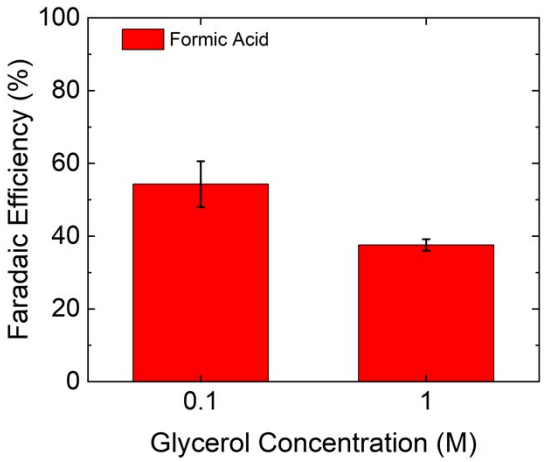

Figure S4. Faradaic efficiency for glycerol oxidation on Ni foil at 1.4 V vs RHE.

Figure S4 shows the faradaic efficiency for GEOR on Ni foil at 1.4 V in 0.1 M glycerol + 1 M KOH and 1 M glycerol + 1 M KOH. Formic acid is the only major product at quantifiable concentrations. The faradaic efficiency for formic acid decreased from 54% to 37% with an increase in glycerol concentration from 0.1 M to 1 M.

3. Product Detection by High Performance Liquid Chromatography

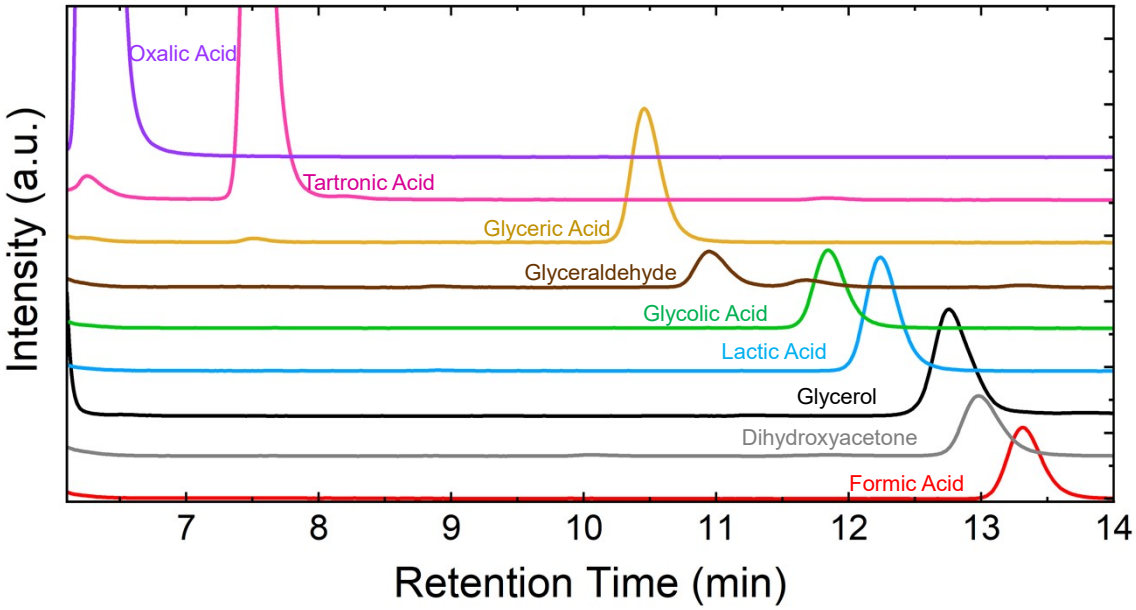

Figure S5. Chromatography of glycerol and glycerol oxidation products

Figure S5 shows the chromatograms for glycerol and the possible glycerol oxidation products of oxalic acid (OA), tartronic acid (TA) glyceric acid (GEA), glyceraldehyde (GALD), glycolic acid (GOA), lactic acid (LA), dihydroxyacetone (DHA), and formic acid (FA). Peak analysis was performed using Origin and MATLAB.

Table S1. HPLC retention times for glycerol oxidation products

Peak Retention Time (min)	Glycerol Oxidation Product
6.2	Oxalic Acid
7.5	Tartronic Acid
10.6	Glyceric Acid
10.9	Glyceraldehyde
11.9	Glycolic Acid
12.2	Lactic Acid
12.7	Glycerol
13.0	Dihydroxyacetone
13.4	Formic Acid

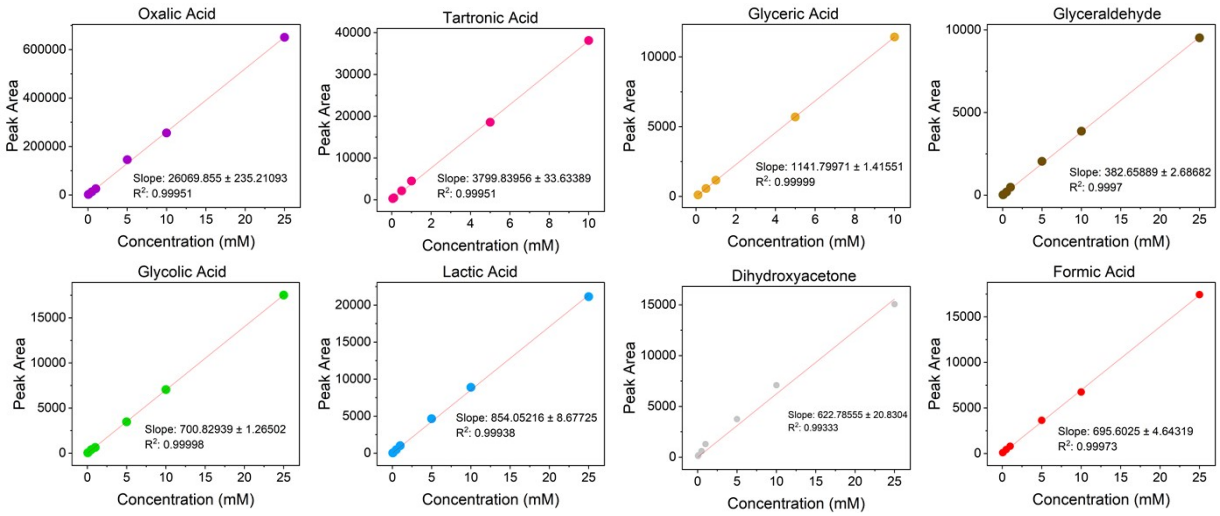

Figure S6. Calibration curves for glycerol oxidation products

Figure S6 shows the calibration curves for oxalic acid, glyceraldehyde, glycolic acid, lactic acid, dihydroxyacetone, and formic acid for a concentration range of 0.05- 25 mM. Tartronic acid and glyceric acid calibrations were made with a concentration range of 0.1– 10 mM.

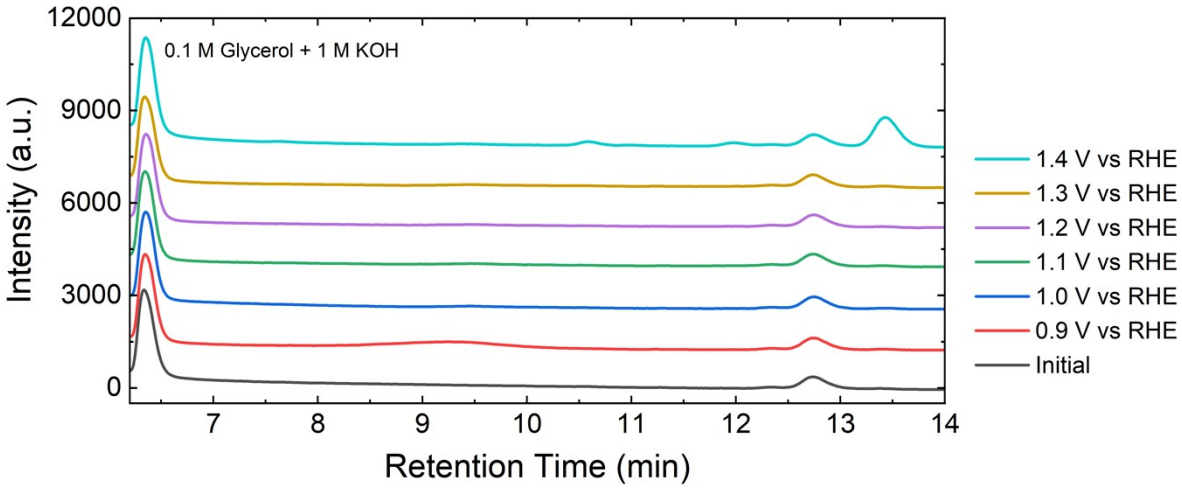

Figure S7. Chromatography of Ni-catalyzed GEOR products at different potentials in 0.1 M glycerol + 1 M KOH

Figure S7 shows the chromatography of product samples collected during chronoamperometry for Ni-catalyzed GEOR in 0.1 M glycerol. Distinct peaks at 6.2 and 12.7 minutes are observed in the initial sample, corresponding to the presence of glycerol and oxalic acid. Oxalic acid was only present in trace amounts (<0.05 mM) and unable to be quantified. These are the only major observed peaks until a potential of 1.4 V is reached, where peaks corresponding to glyceric acid, glycolic acid, and formic acid are observed. Formic acid is the major product for GEOR on Ni foil in 0.1 M glycerol at quantifiable concentrations (>0.05 mM). Other products were only present in trace amounts (< 0.05 mM) and were unable to be quantified.

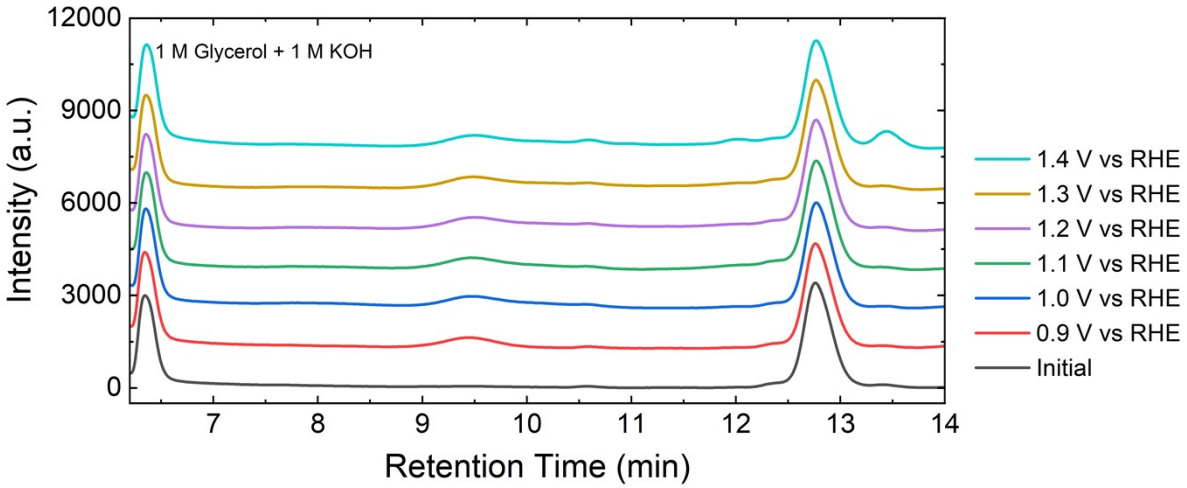

Figure S8. Chromatography of Ni-catalyzed GEOR products at different potentials in 1 M glycerol + 1 M KOH

Figure S8 shows the chromatography of product samples collected during chronoamperometry for Ni-catalyzed GEOR in 1 M glycerol. Distinct peaks at 6.2 and 12.7 minutes are observed in the initial sample, corresponding to the presence of glycerol and oxalic acid. Oxalic acid was only present in trace amounts (<0.05 mM) and unable to be quantified. Similar to chromatography of Ni-catalyzed GEOR in 0.1 M glycerol, these are the only major observed peaks until a potential of 1.4 V is reached, where peaks corresponding to glyceric acid, glycolic acid, and formic acid are observed. Formic acid is the major product for GEOR on Ni foil in 1 M glycerol at quantifiable concentrations (>0.05 mM). Other products were only present in trace amounts (< 0.05 mM) and were unable to be quantified.

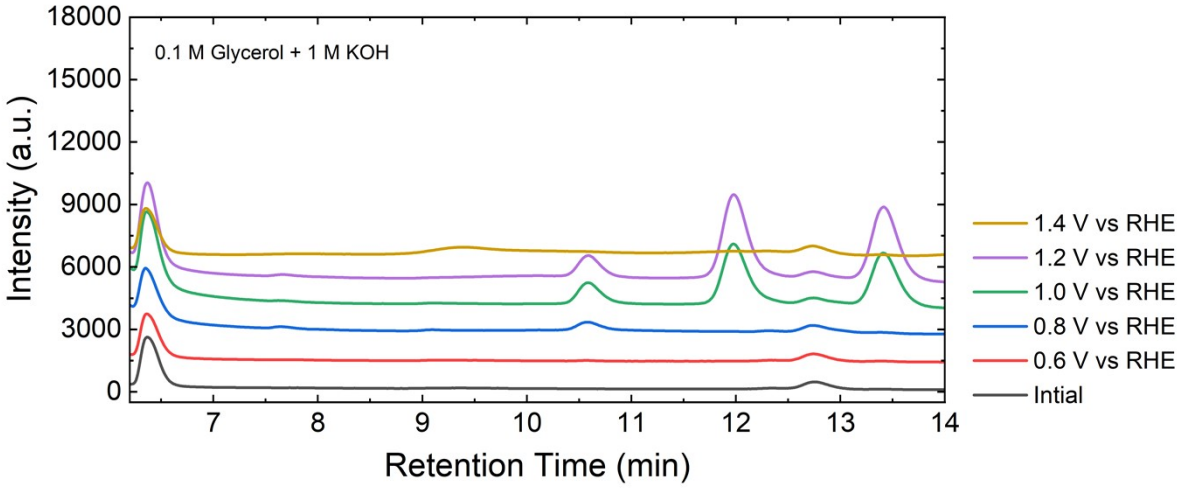

Figure S9. Chromatography of Au-catalyzed GEOR products at different potentials in 0.1 M glycerol + 1 M KOH

Figure S9 shows the chromatography of product samples collected during chronoamperometry for Au-catalyzed GEOR in 0.1 M glycerol. Distinct peaks corresponding to the presence of

glycerol and oxalic acid are observed in the initial sample. Oxalic acid was only present in trace amounts (<0.05 mM) and unable to be quantified. At 0.8 V, a peak corresponding to glyceric acid is observed. Peaks corresponding to glycolic acid and formic acid are observed at 1.0 V and 1.2 V. Formic acid and glycolic acid are the major products at these potentials, with glyceric acid as a minor product. At 1.4 V, glycolic acid, formic acid, and glyceric acid peaks are significantly diminished. In summary, Figure S10 shows that the major products observed on Au foil in 0.1 M glycerol are glyceric acid, glycolic acid, and formic acid. Product formation is observed up to 1.2 V and decreases significantly at 1.4 V.

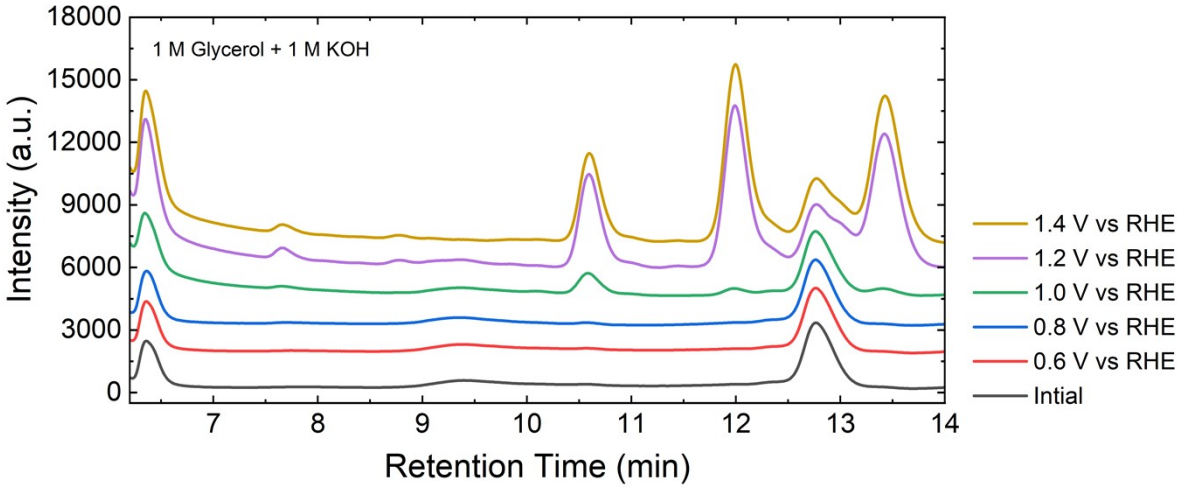

Figure S10. Chromatography of Au-catalyzed GEOR products at different potentials in 1 M glycerol + 1 M KOH

Figure S10 shows the chromatography of product samples collected during chronoamperometry for Au-catalyzed GEOR in 1 M glycerol. Distinct peaks corresponding to the presence of glycerol and oxalic acid are observed in the initial sample. Oxalic acid and tartronic acid were only present in trace amounts (<0.05 mM) and unable to be quantified. Peaks corresponding to glyceric acid, glycolic acid, lactic acid, and formic acid are observed at 1.0 V and increase drastically at 1.2 V and 1.4 V. At 1.2 V and 1.4 V, a peak corresponding to dihydroxyacetone is also observed. Formic acid, glycolic acid, and glyceric acid are the major products at 1.2 V and 1.4 V, with lactic acid and dihydroxyacetone as minor products. All other peaks correspond to products present at trace amounts (<0.05 mM) and were unable to be quantified.

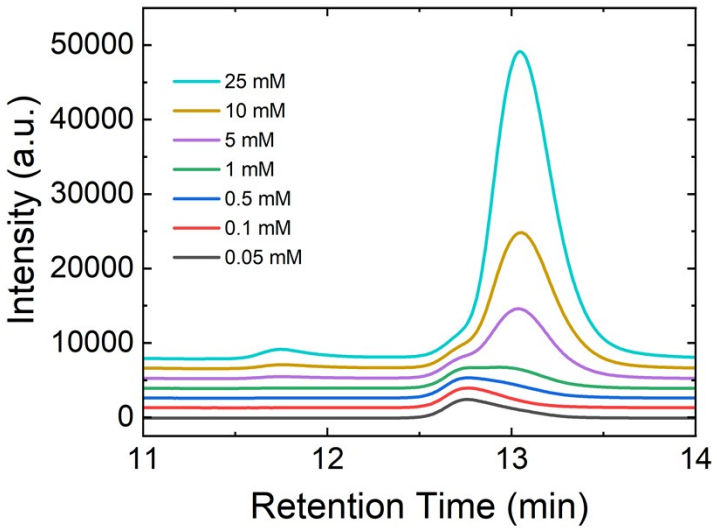

Figure S11. Chromatography of dihydroxyacetone calibration curves in the presence of glycerol

Figure S11 displays chromatography for dihydroxyacetone calibrations in the presence of glycerol, correlating to the linear calibration curve in Figure S6.