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Amino acid hydrolysis for analyses in degraded piperazine

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Abstract

Amino acids analyses were performed on lean samples collected during a pilot campaign conducted at the National Carbon Capture Center (NCCC) in 2023. That campaign used 30 wt % aqueous piperazine (PZ) with the objective of demonstrating mitigation of amine oxidation. Samples were hydrolysed with NaOH to reverse the formation of amides and quantify "total" amino acids. Three methods for performing sample hydrolysis were tested and are compared in this talk. All three methods use NaOH and sample dilution before injection on a ThermoFisher ICS-6000 instrument utilizing high performance anion exchange pulsed amperometric detection (HPAE-PAD) for amino acid detection and quantification. Using calibration standards for amino acids and amides and HPAE-PAD sample analysis, comparisons were made of the three hydrolysis methods with respect to the extent of amide conversion, measured as amino acids concentration following hydrolysis. The importance of sample hydrolysis lies in the overall concentration of amino acids and their respective amides in degraded solvents. After ~4,000 hours of continuous operation at NCCC 2023, the aggregate concentration of the total amino acids was 100 mmol/kg, which is sufficient to impact solvent performance.

Keywords: Hydrolysis, amino acids, amides, piperazine, oxidation.

Hydrolysis methods

Three different hydrolysis methods were tested and compared using NCCC 2023 samples. Figure 1 presents a comparison of those tests. The methods are briefly described as follows:

Method 1:

(1) Dilute samples one-to-one mass ratio with 12 N NaOH and let sit for eight hours;
(2) Add 5 gm 250 mmoL NaOH and let sit for 5 hours; and
(3) Dilute 100X with 250 mmoL NaOH and inject on HPAE-PAD instrument.

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Method 2:

(1) Dilute samples one-to-one mass ratio with 12 NaOH and let sit for eight hours;
(2) Add 5 gm deionized (DI) water and let sit for 5 hours; and
(3) Dilute 100X with DI water and inject on HPAE-PAD instrument.

Method 3:

(1) Add 10 uL sample to 10 mL 250 mmoL NaOH; and
(2) Inject sample on HPAE-PAD instrument.

A comparison was performed of hydrolyzation Methods 1 through 3 on a unrelated field sample as depicted in Figure 1. The Quality Control sample for each was a single standard comprised of purchased reagent grade amino acids. The unhydrolyzed data (bottom row) represent the free amino acids whereas Methods 1 through 3 represent the "total" amino acids, measured after hydrolysation using each of the methods.

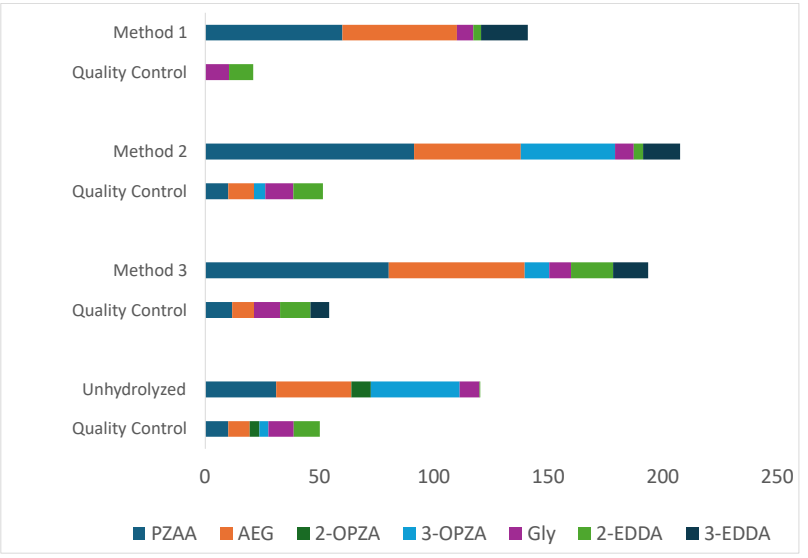

Figure 1. Comparison of hydrolysis methods with a field sample; sample concentrations in mmol/kg.

Seven different amino acids were identified in the field sample. These include glycine (Gly), aminoethyl glycine (AEG), piperazine acetic acid (PZAA), 2-ethylene diamine acetic acid (2-EDDA), 3-ethylene diamine acetic acid (3-EDDA), 2-oxopiperazine acetic acid (2-OPZA), and 3-oxopiperazine acetic acid (3-OPZA). The presence of these amino acids can be explained through oxidation mechanisms in degraded PZ. The amino acid PZAA (dark blue) was detected at the greatest concentration in hydrolysed samples using all three methods whereas 3-OPZA was detected at the greatest concentration in the free amino acid sample. PZAA concentration was at least 2X using all hydrolysed methods compared to the free amino acid analysis (unhydrolysed sample). This indicates that one or more amides of PZAA are being readily hydrolysed to PZAA. A likely amide of PZAA is N-formyl PZAA. AEG (orange) also increased using all hydrolysation methods, indicating that one or more amides are being hydrolysed to this amino acid. Other work has determined that oxopiperazine (OPZ), a lactam of the amino acid AEG, is being hydrolysed to AEG.

Comparison of hydrolysis methods

Due to the use of 12 N NaOH in the first step, Methods 1 and 2 tended to result in the formation of solids. These solids can be dissolved through dilution with DI water in the sample preparation process. Method 1 tended to neutralize or lower the pH of the samples, shifting equilibrium towards the amide from the acid; this method under-measured the amount of all amino acids and provided the lowest level of overall hydrolysis of the three. Method 2 failed to sufficiently hydrolyse 3-OPZA as evidence by the large concentration (~40 mmol/kg) following the

hydrolysation step (blue in bar chart). Method 3 worked well with diacids, as evidenced by the amide 3-OPZA being nearly completely hydrolysed. Finally, although not evident in Figure 1, the retention times of monoacids on the HPAE-PAD instrument were affected by all hydrolysation methods, with Method 3 having the least impact.

Pilot campaign results

The NCCC 2023 samples were hydrolysed using Method 2 (Figure 2). Those data indicate that AEG and PZAA are the species present at greatest concentration in hydrolysed samples, and support the conclusion that amides/lactams of these compounds are hydrolysed and quantified using this method. The lactam OPZ is readily hydrolysed to AEG while N-formyl PZAA and PZ amides of PZAA will be hydrolysed to PZAA. The data in Figure 2 indicate that the major amino acids of oxidized PZ can be accounted for using the HPAE-PAD method, but 3-OPZA will not be completely hydrolysed; a concentration of >10 mmols/kg was reported in samples collected after 4,000 hours during the NCCC campaign. After 3,600 hours of pilot operations at NCCC, the concentration of AEG starts to decrease with a resulting increase in the Gly concentration. It is likely that Gly is a degradation product of one or more amino acids including AEG, with its formation accelerated due to corrosion in process systems.

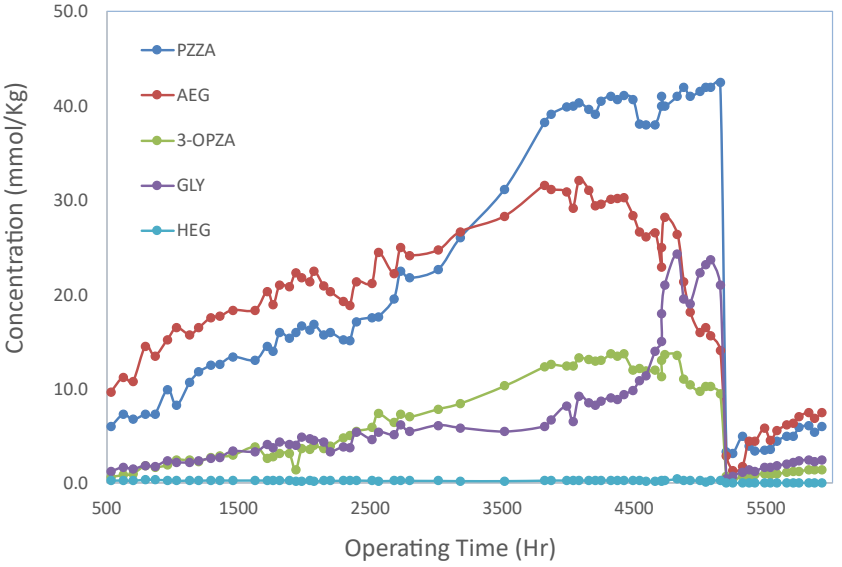

Figure 2. Hydrolysed NCCC 2023 sample analysis.

In conclusion, Method 3 has been selected as the hydrolysation method of choice for future work with amino acid measurements because of its ability to hydrolyse mono and diacids and have the least impact of RT shifts with the HPAE-PAD instrument.

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