A Direct Measurement Method for the Characterization of Corrosion Inhibitors for Quality Metrics in Formulation and New Product Development

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Introduction

Corrosion costs the petroleum industry an estimated $1.3 billion in non-productive time, materials and labor annually. Imidazolines prepared from fatty acids and amines are a widely-used class of chemical corrosion inhibitor, due to excellent performance and ease of handling. However, commercial imidazolines are actually mixtures of several different chemical compounds, and the relative proportions of these species can have a large impact on both corrosion inhibition and product physical properties. The absence of gold standard analytical methods to characterize the active ingredients in imidazoline formulations limits the understanding of the chemistry of these materials. It is for this reason that a SPE-LC-MS method was developed to supplement the chemical information afforded by bulk testing / wet chemistry methods (e.g. titrations, IR spectra etc). A high resolution time-of-flight (TOF) mass spectrometer was selected based on the fast scanning platform. This instrument allows for low level detection and accurate mass characterization. It is anticipated that this method will have significant impact in the formulation of new corrosion inhibitors for oilfield applications as well as the quality control of finished products in manufacturing.

Reaction Chemistry

The preparation of an imidazoline from oleic acid (OA) and diethylenetriamine (DETA) is a two-step process, with several possible byproducts:

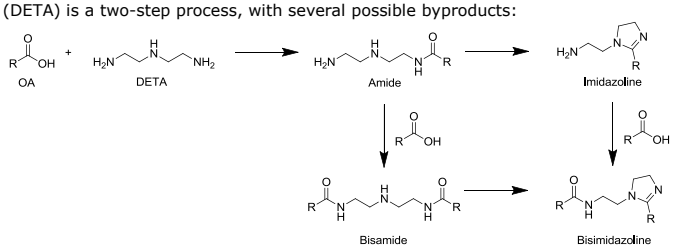

Figure 1. Preparation of Imidazolines and Byproducts

Experimental

Table 1. Summary of Imidazoline Syntheses

Sample	OA:DETA Ratio	Reaction Conditions
1	1:1.5	260 °C for 5 h Purged with N_2 for 4 h
2	1:1.3	160 °C for 3 h 240 °C for 3 h Purged with N_2 for 4 h
3	1.2:1	175 °C for 2 h
4	1:1	165 °C for 2 h Purged with N_2 for 4 h
5	2:1	170 °C for 2 h

Sample Preparation prior to LC-MS Solid Phase Extraction (SPE)

A variety of sorbent chemistries were screened for the selected analytes (ISOLUTE Si, ISOLUTE EPH, ISOLUTE AL-A, ISOLUTE AL-N, ISOLUTE-AL-B). Preliminary data suggested that a no drydown method developed on ISOLUTE Si was the best choice; however, as additional analytes were evaluated, ISOLUTE AL-N and AL-B proved a better choice. Relative recovery was determined to be **>70%** for the analytes of interest. When applied to production quality control, it is anticipated that SPE will extend the life of the LC columns and minimize mass spectrometer downtime.

The method employed was: Biotage 100 mg AL-B 1 mL SPE cartridge was first conditioned with 6 mL of dichloromethane. The SPE cartridge was loaded with a dilution of 0.5 mg of sample in 0.5 mL of dichloromethane. The sample was then eluted with 6 mL of a 5% acetic acid in isopropanol solution. The solvent was then evaporated under low heat and nitrogen and the sample was prepared as described below in the LC-MS section. The optimization of wash steps will ensure consistent throughput for this method.

LC-MS

For the LC-MS, an ~0.3 mg/mL solution of sample in mobile phase A was prepared and analyzed by the following method in Table 2 on an Agilent 1260 Infinity LC with a 6230 TOF LC/MS.

Table 2. Chromatographic and MS Conditions

Column	Agilent Porshell 120 SB-C8 column (2.1 x 100 mm, 2.7 µm)
Column Temperature	50 °C
Mobile Phase A (MPA)	60:40 IPA: H_2O with 0.5% Formic Acid
Mobilie Phase B (MPB)	10:10:80 IPA:H_2O:Butanol with 0.4% Formic Acid
Flow Rate	0.2 mL/min
Injection Volume	1.5 µL
Gradient	Start with 5% MPB at 1 min 5% MPB at 6 min 20% MPB at 7 min 30% MPB at 15 min 50% MPB
Source	Dual ESI
Ion Mode	Positive
Drying Gas Temperature	300 °C
Drying Gas Flow	12 L/min
Nebulizer	35 psig
V_{cap}	4500 V
Fragmentor	175 V
Scan Range	100 – 3000 m/z
Scan Rate	1.00 spectra/min

Five compounds were identified on the LC-MS, the four products in Figure 1, and a imidazoline degradation byproduct illustrated in Figure 2. The relative percentages of each component for samples that had not undergone SPE are shown in Table 3.

Figure 2. Imidazoline Degradation Byproduct

Table 3. Percentages of Each Component as Determined by LC-MS

	HPLC Area (%)				
Sample	Imidazoline (FW 349)	Amide (FW 367)	Imidazoline* (FW 306)	Bisimidazoline (FW 612)	Bisamide (FW 631)
1	79	0	7	14	0
2	53	0	0	47	0
3	20	46	0	15	18
4	57	11	9	17	5
5	11	0	8	74	7

* Imidazoline byproduct from a degradation reaction

Infrared Ratio (IR)

A drop of the sample was placed on the ATR crystal of a Nicolet 6700 FT-IR and a spectrum was collected. The peak intensities in absorbance mode for the amide (1645-1675 cm^{-1}) and for the imidazoline (1604-1612 cm^{-1}) were ratioed according to the equation

$$IR = 100 \times \frac{I_{imidazoline}}{I_{imidazoline} + I_{amide}}$$

The measured IR values were compared to theoretical calculations based on the above equation and the percentages of each component as determined by HPLC Area %, with the results summarized in Table 4.

Table 4. Comparison of Measured and Calculated IR Values

Sample	Measured IR (%)	Calculated IR (%)
1	84.0	83.4
2	60.2	68.6
3	37.0	24.7
4	76.3	66.8
5	41.9	50.2

Total Amine Value (TAV) Titration

An aliquot of the sample was dissolved in glacial acetic acid and titrated with a 0.1 N solution of perchloric acid in glacial acetic acid until a pH of ~1.5 was reached, as measured on a Metrohm 736 GP Titrino. The TAV was calculated using the equation

$$TAV = \frac{V \times N \times FW_{KOH}}{1000 \times m}$$

The FWs and theoretical TAVs of each component, along with the percentages of each component as determined by HPLC Area %, were used to calculate the theoretical TAV according to the equation below, and the results are shown in Table 5.

$$Theoretical\ TAV = \frac{N_G \times FW_{KOH}}{FW_{sample}}$$

Table 5. Measured and Calculated TAV Values

Sample	Measured TAV (mg KOH/g)	Calculated TAV (mg KOH/g)
1	251.1	198.6
2	125.9	169.7
3	288.9	276.4
4	215.3	208.2
5	93.3	129.1

Conclusion

The LC-MS method corresponds well to the traditional analytical methods of testing imidazolines, IR and TAV. Furthermore, the LC-MS method provides more valuable data such as the relative concentrations of OA-DETA imidazolines and byproducts. The LC-MS method also allowed for the identification of an additional byproduct. These results substantiate that the LC-MS method is of great value when tailoring the properties and performance of imidazoline chemistry, optimizing a synthetic scheme, or troubleshooting poor corrosion performance of a particular sample.

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