Electronic Supplementary Material (ESI) for Analyst
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SUPPORTING INFORMATION

In-Situ Analysis of Corrosion Inhibitors using a Portable Mass Spectrometer with Paper Spray Ionization

*Fred P.M. Jjunju, Anyin Li, Abraham K. Badu-Tawiah, Pu Wei, Linfan Li, Zheng Ouyang, Iman. Roqan and R. Graham Cooks**

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1. Quantitative analysis of the ammonium salts in oil

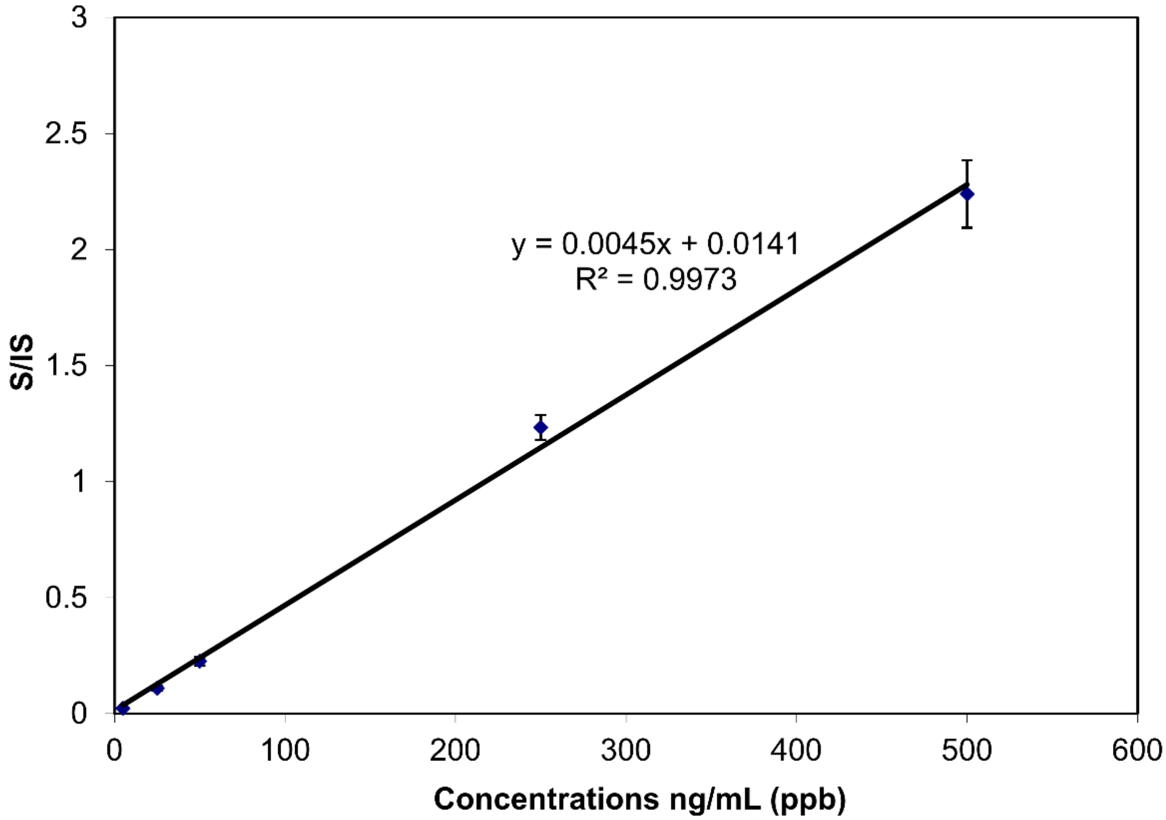

Fig S1. Calibration curve for the quantitative analysis of ammonium salts in oil matrix using a commercial ion trap mass spectrometer

2. Experimental setup for the analysis of corrosion inhibitors using a benchtop commercial mass spectrometer coupled with paper spray ionization

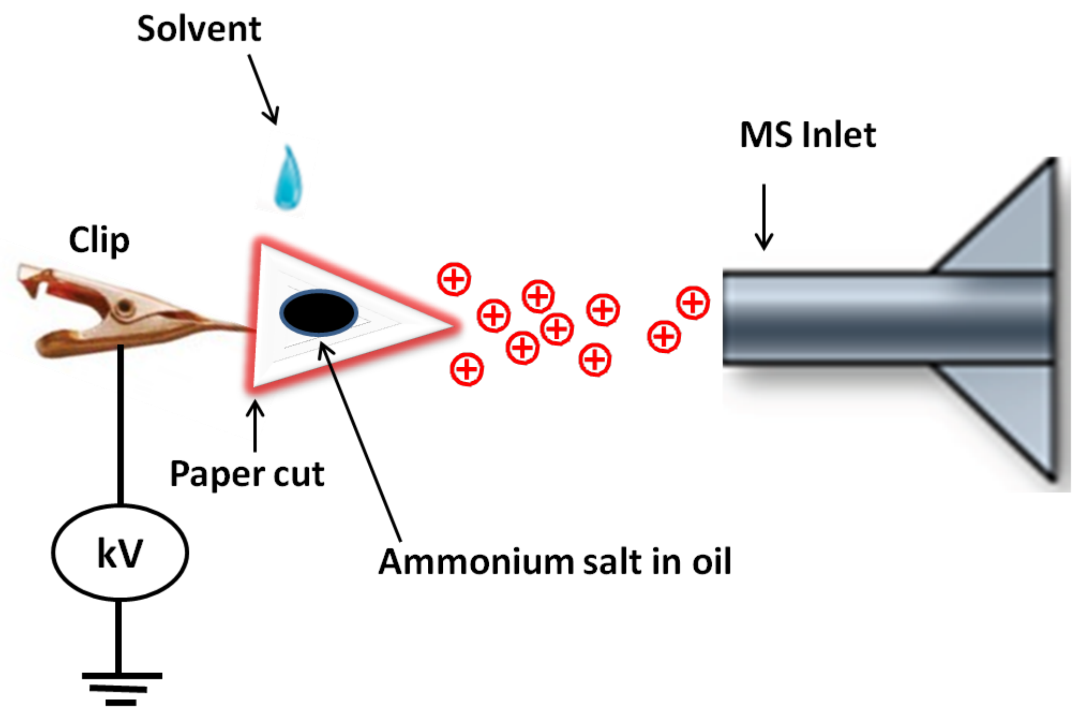

Figure S2. Paper spray ionization mass spectrometry for *in situ* analysis of corrosion inhibitors using a commercial benchtop mass spectrometer

3. Analysis of the corrosion inhibitor model compounds using a benchtop commercial mass spectrometer

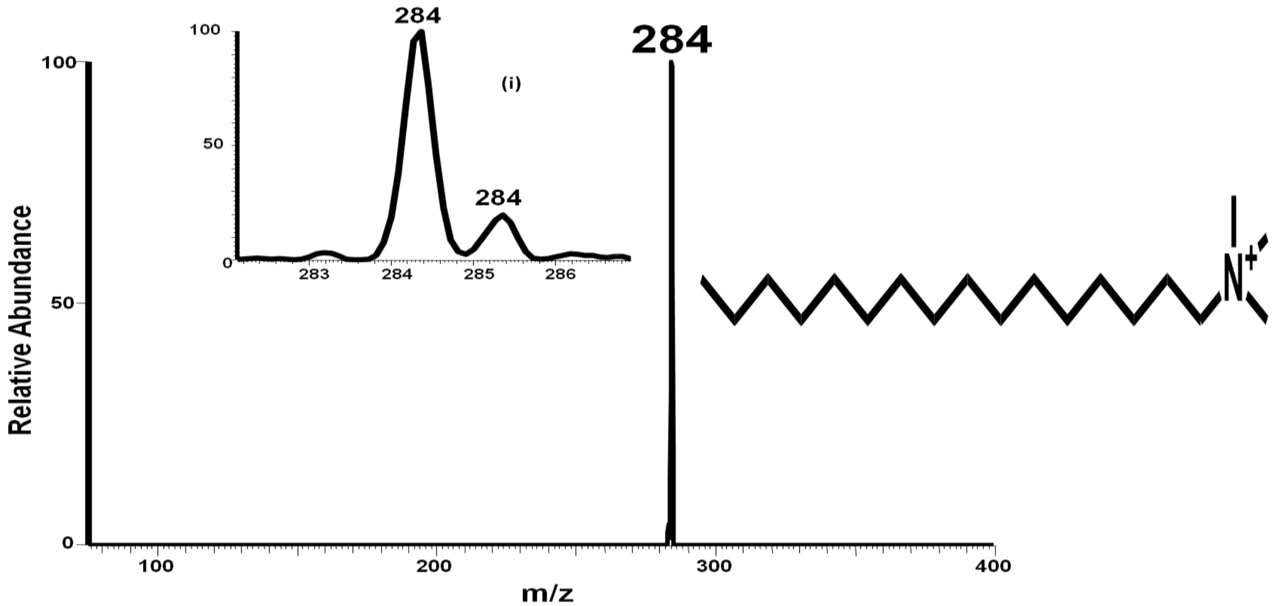

Figure S3. Positive PS-MS mass spectrum of hexadecyltrimethylammonium bromide. Insert (i) shows the isotopic distribution of of the analyte,tandem mass spectrometry (MS/MS) of the hexadecyltrimethylammonium cation at m/z 284.0 was not returning good signal since the expected major fragment is below the low mass cut off the instrument.

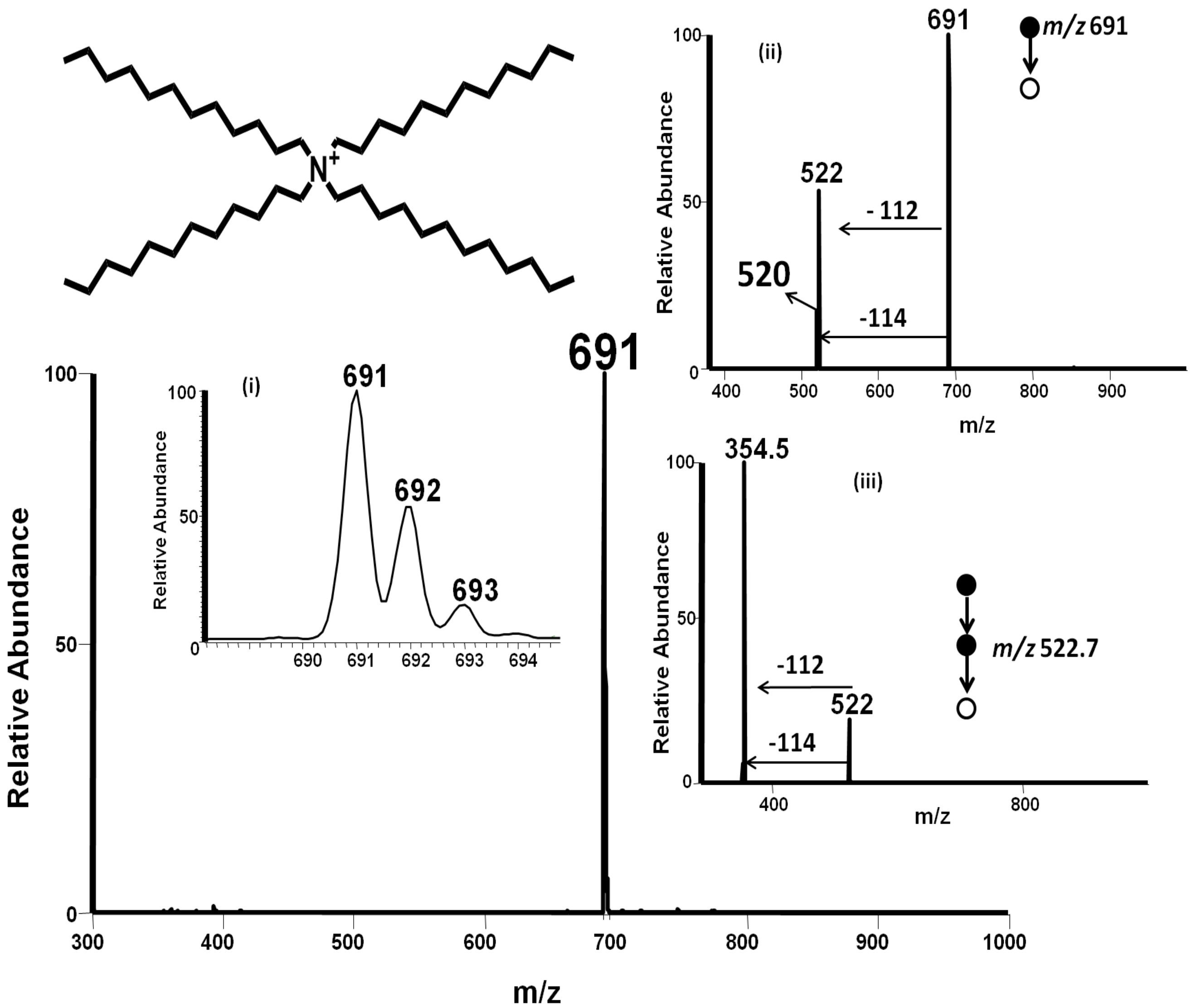

Figure S4. Positive PS-MS mass spectrum of tetradodecylammonium bromide. Insert (i) shows the isotopic distribution of the analyte, (ii) – (ii) Tandem mass spectrometry (MS/MS) of the tetraoctylammonioum cation at m/z 691.0 gives a major fragment ion at m/z 522.0 with a alkene loss of 112.0 and a minor fragment ion at 520.0 with a alkane loss of 114, which confirm the structure. Again (iii) MS/MS/MS of the major fragment ion at m/z 522.0 (major) fragments further to give an ion at m/z 354.5 and ion at m/z 352.5 with a neutral loss of -[112]and –[114] respectively further confirming the identity of the compound

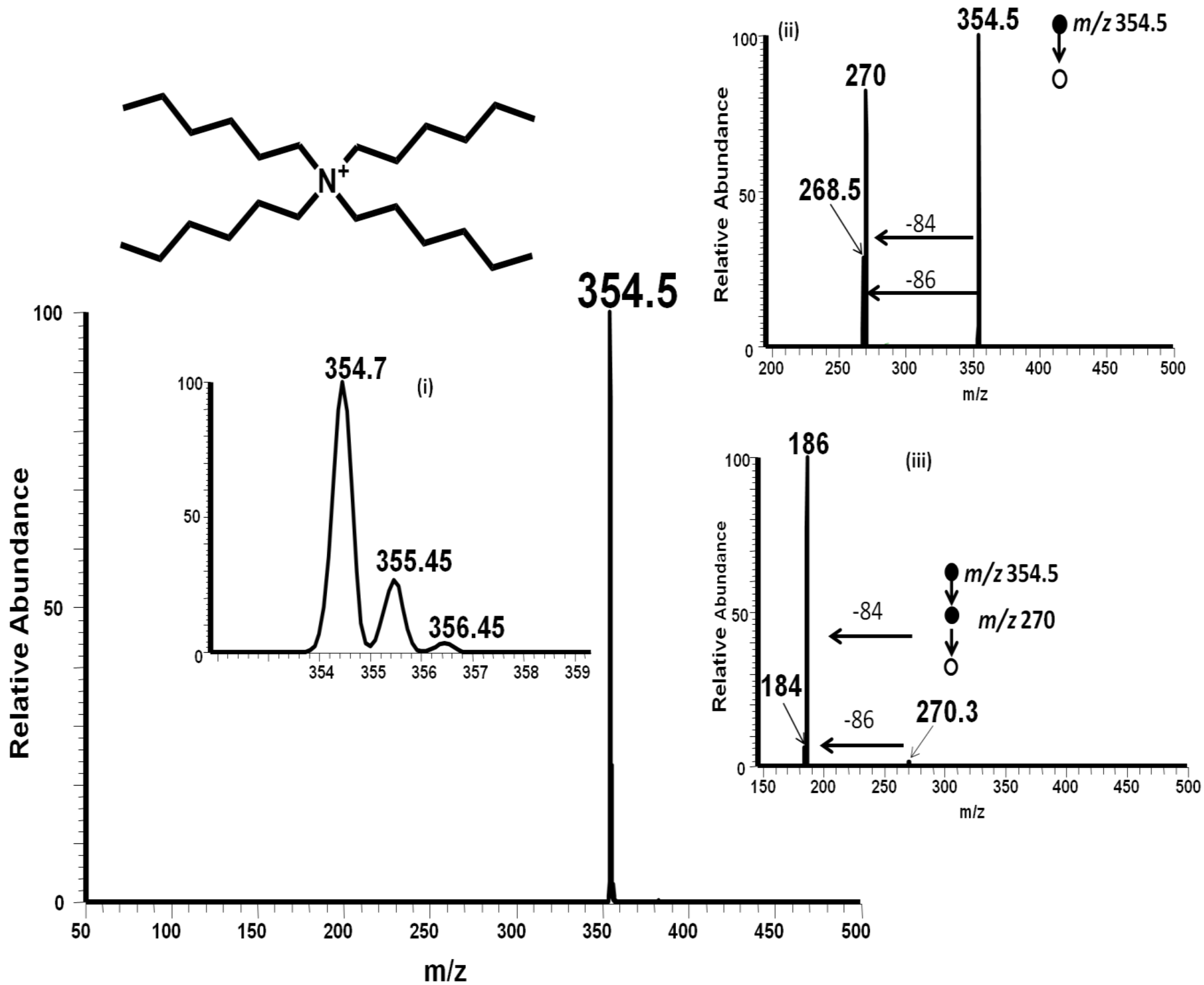

Figure S5. Positive ion PS-MS mass spectrum of tetrahexylammonium bromide. Insert (i) shows the isotopic distribution of the analyte ion, (ii) – (iii) Tandem mass spectrometry (MS/MS) of the tetrahexylammonium cation at m/z 354.7 gives a major fragment ion at m/z 270.0 with a loss of alkene –[84] and a minor fragment ion at 268.5 with a loss of alkane –[86] that confirms the structure. Again (iii) MS/MS/MS of the major fragment ion at m/z 270.0 fragments further to give an ion at m/z 186.0 (major) and ion at m/z 184.0 (minor) with a neutral loss of –[84] and –[86] respectively further confirming the identity of the compound

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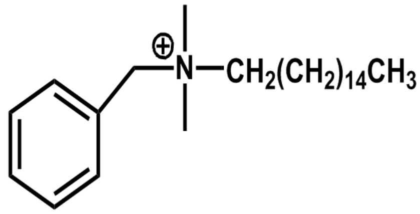

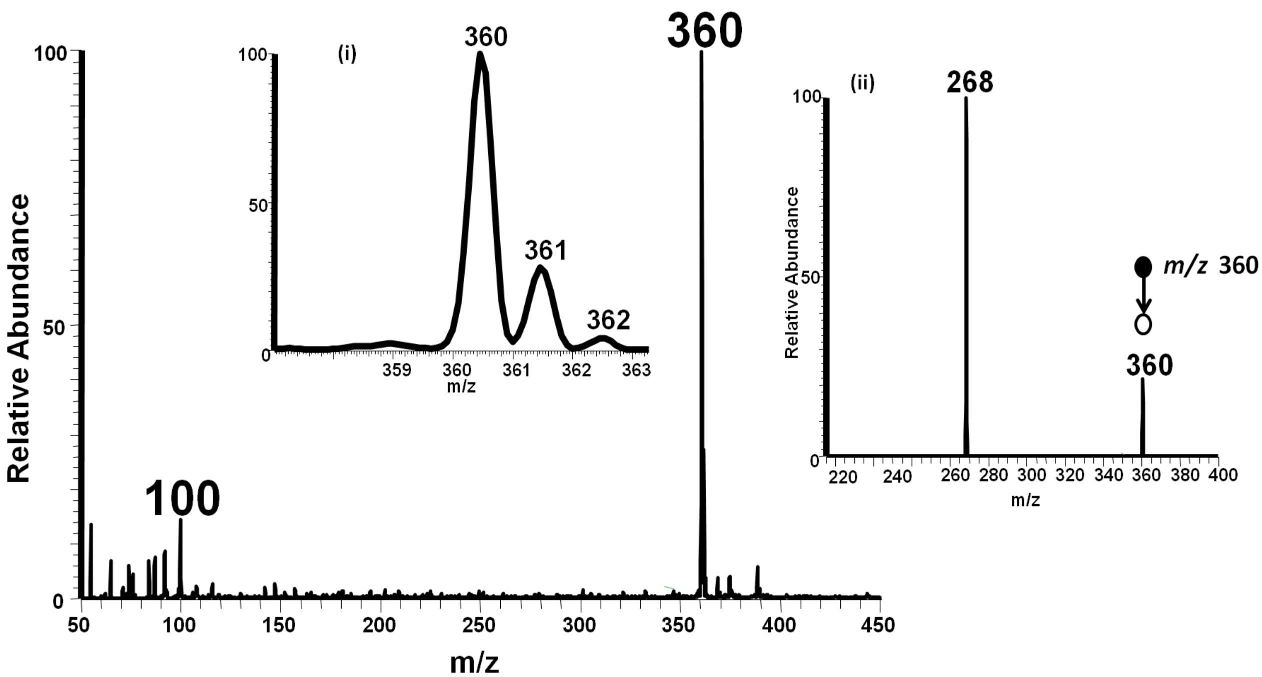

Figure S6. Positive ion PS-MS mass spectrum of benylhexadecyldimethylammonium chloride. Insert (i) shows the Isotopic distribution of the analyte ion, (ii) Tandem mass spectrometry (MS/MS) of the benylhexadecyldimethylammonium cation at m/z 360 gives a major fragment ion at m/z 268 with a loss of alkene –[92] that confirms the structure

4. Analysis of the corrosion inhibitor model compounds in the oil mixture using a benchtop commercial mass spectrometer

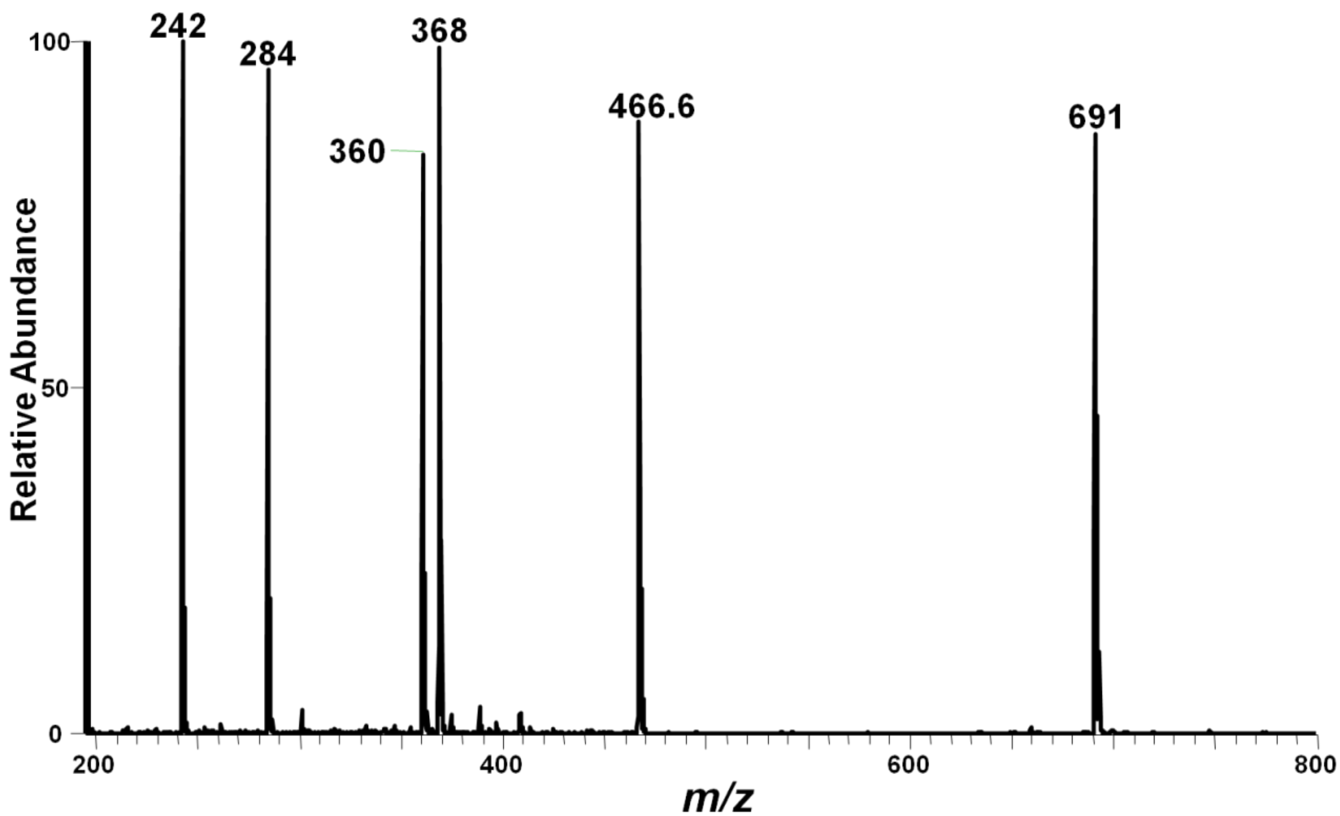

Figure S7. Positive ion mode paper spray mass spectrum for artificial mixtures of model compounds analyzed using a benchtop instrument. Tetrabutylammonium bromide was observed at *m/z* 242.0, hexadecytrimethylammonium bromide at *m/z* 284.0, benzylhexadecyldimethylammonium chloride at *m/z* 360.0, tetraoctylammonium bromide at *m/z* 466.6 and tetradodecylammonium bromide at *m/z* 691.0.

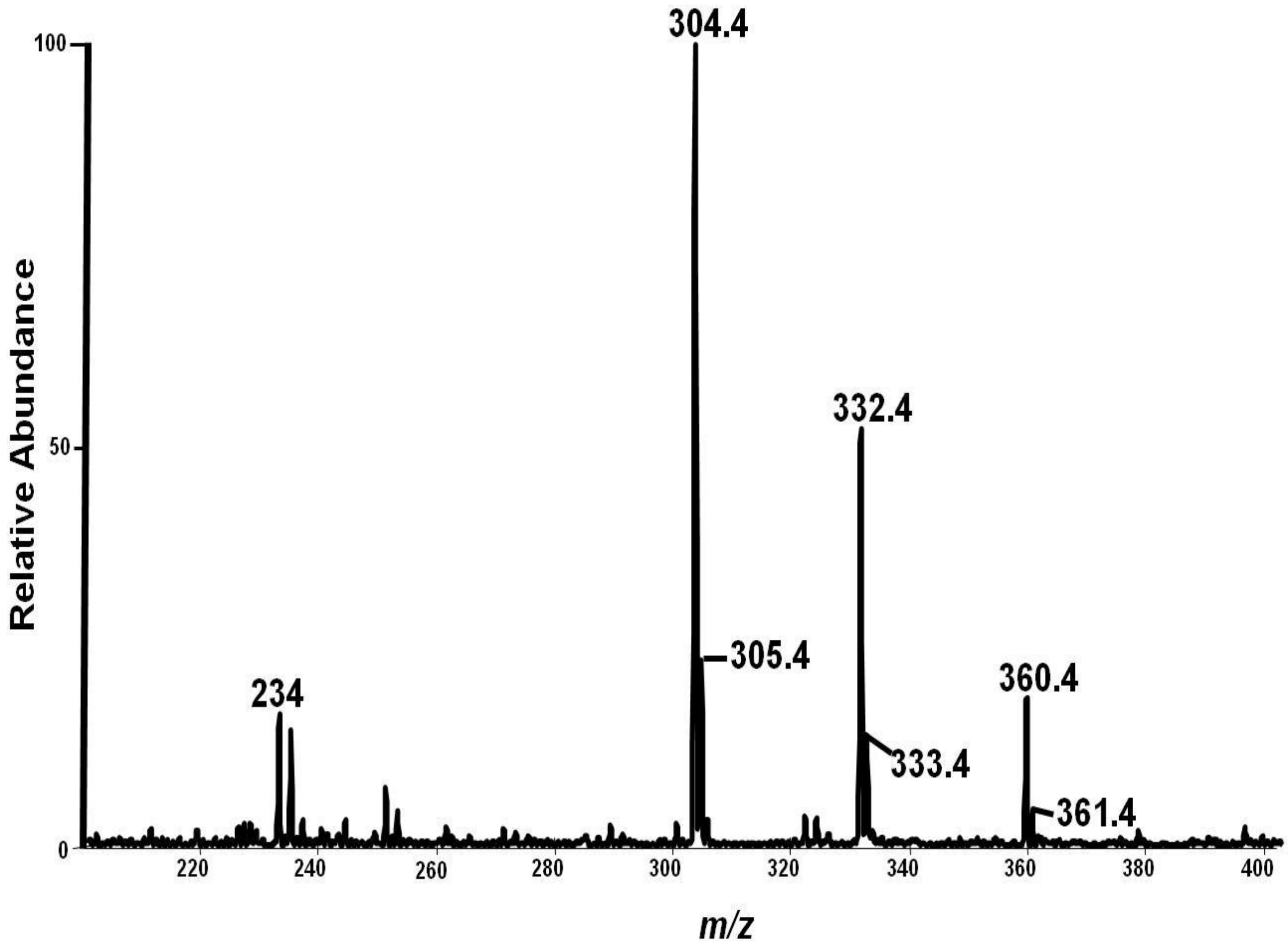

Figure S8. Typical positive ion paper spray mass spectra for a mixture of alkyl dimethylbenzyl ammonium chloride salts $[C_6H_5CH_2N(CH_3)_2R]Cl$ where R is predominantly n-$C_{12}H_{25}$ (also contains small amounts of *m/z* 332 (C_{14}) and *m/z* 360 (C_{16}) homologs) standard analyzed using a benchtop ion trap mass spectrometer. The trace levels of C_{16}homolog, are manifest in the relative abundances compared with other components in the mixture.

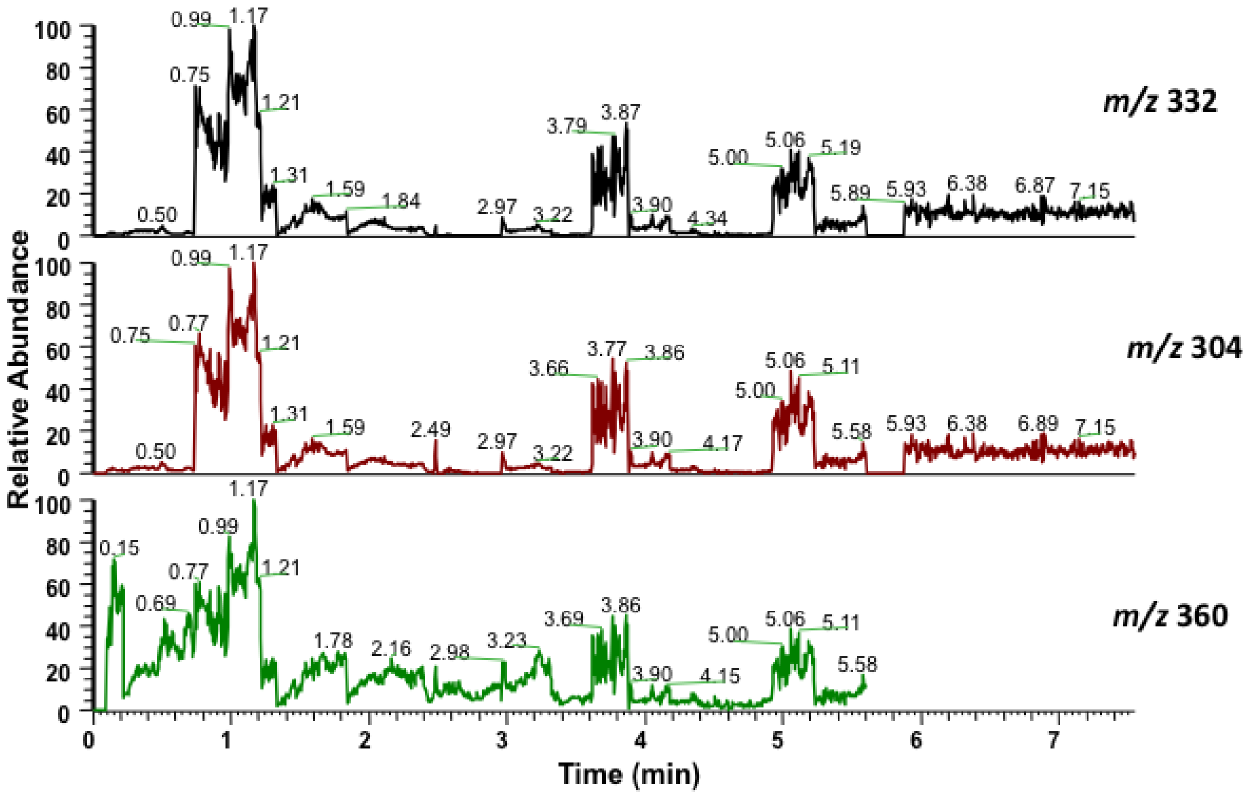

Figure S9. Ion chronograms for the for alkyl dimethylbenzyl ammonium chloride [$C_6H_5CH_2N(CH_3)_2R$]Cl where R is predominantly n-$C_{12}H_{25}$; data for the homologs C_{14} (*m/z*) 332, C_{12} (*m/z*) 304, and C_{16} (*m/z*) 360 are shown.

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Table S1 Structures and Product Ions of CID of the Salt $[C_6H_5CH_2N(CH_3)_2R]^+Cl^-$ Analyzed in Pump Oil by PS-MS using Benchtop and Miniature Instruments

Active corrosion compound	**MW (Cation)**	**MS/MS Transitions**	**Ion Loss**
Quat C_{12}	304	m/z 304 → 212	92
Quat C_{14}	332	m/z 332 → 240	92
Quat C_{16}	360	m/z 360 → 268	92