analytical chemistry

Screening and Quantification of Aliphatic Primary Alkyl Corrosion Inhibitor Amines in Water Samples by Paper Spray Mass Spectrometry

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S Supporting Information

ABSTRACT: Direct analysis and identification of long chain aliphatic primary diamine Duomeen O (*n*-oleyl-1,3-diaminopropane) corrosion inhibitor in a large medium pressure water tube boiler plant water samples at low LODs (<0.1 pg) has been demonstrated for the first time, without any sample preparation using paper spray mass spectrometry (PS-MS). The presence of Duomeen O in water samples was confirmed via tandem mass spectrometry using collision-induced dissociation and supported by exact mass measurement and reactive paper spray experiments using an LTQ Orbitrap Exactive instrument. Data shown herein indicate that paper spray ambient ionization can be readily used as a rapid and robust method for *in situ* direct analysis of polymanine corrosion inhibitors in a large water boiler plant and other related samples in the water treatment industry. This approach was applied for the analysis of three complex water samples including feedwater, condensate water, and boiler water, all collected from large medium pressure (MP) water tube boiler plants, known to be dosed with varying amounts of polyamine and amine corrosion inhibitor components. Polyamine chemistry is widely used for example in large high pressure (HP) boilers operating in municipal waste and recycling facilities to prevent corrosion of metals. The samples used in this study are from such a facility in Coventry waste treatment facility, U.K., which has 3 × 40 tonne/hour boilers operating at 17.5 bar.
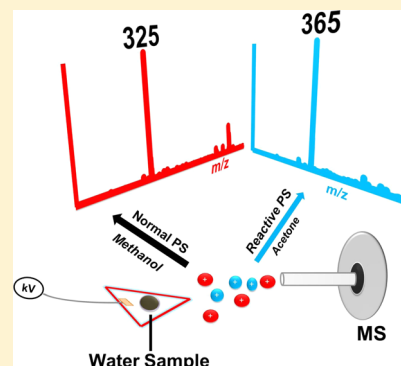
The addition of corrosion inhibitors to corrosive systems is a well-established preventative approach worldwide.[1−4] Neutralizing agents such as aliphatic and aromatic amines, mono, di-, or poly amines and their salts when added in small amounts to a corrosive water boiler system are known to reduce, slow down, or prevent corrosion to metal.[5−9] In agreement with green chemistry aims, new corrosion inhibitor formulations should be less toxic, soluble in aqueous medium, and biodegradable,[10−15] especially when they are to be used in portable water transfer systems. Therefore, toxic aromatic amines and their salts should be avoided and replaced with greener long-chain aliphatic mono-, di-, or polyamines or their salts.[16] Polyamine corrosion inhibitor formulations are widely used in large high pressure (HP) water tube boiler plants, e.g., refineries, power generating plants, steel works, chemical plants where the operating pressure is >45 bar. There is a strong need for analytical methods for on-site analysis and quantification of corrosion inhibitor residues in the large HP water tube boiler plants systems with fast response times, preferably with little or no special sample preparation.[17−25] From such samples, the analytical data obtained should be useful in maintaining the appropriate levels of the inhibitor in the water tube boiler plants. This is useful not only for quality control but in the development of new effective corrosion inhibitors to combat corrosion of the large high pressure (HP) water tube boiler plants.[26−28]

Currently, different extraction procedures based on solid-phase extraction followed by gas chromatography (GC) or high-performance liquid chromatography (HPLC) coupled with mass spectrometry (MS) methods,[29−32] have been successfully used in the identification and quantification of the long-chain aliphatic primary polydiamines in boiler water samples below ppb levels.[31,33,34] These analytical methods are reliable, and low limits of detection (LODs) with high specificity and sensitivity can be achieved. However, direct

identification and quantification of long chain polydiamines corrosion inhibitor formulations is not possible at present using GC/MS or HPLC–MS due to the fundamental instrument characteristics and a large dipole of the polydiamine.[27,35–37] To overcome these challenges, polydiamine corrosion inhibitors are first derivatized and preconcentrated (using either solid-phase or liquid–liquid extraction) to improve the GC/HPLC detection properties.[35,38–40] While these analytical methods have proven successful in the analysis of the long chain aliphatic primary polydiamines corrosion inhibitor formulations in large high pressure (HP) water tube boiler plants, they can be time-consuming. Moreover, these methods are limited by the need for manual transfer of samples to the laboratory before analysis. Therefore, there is a strong interest in rapid screening methods for long chain aliphatic primary polydiamines inhibitor formulations in large HP water tube boiler plants that requires no sample preparation and yet provides specific information regarding the corrosion inhibitor levels in the large HP water tube boiler plant. Such methods would have several important applications in the water treatment industry, energy sector, and for environmental monitoring and hygiene.[19,41,42] As will be shown in this study, ambient ionization mass spectrometry (AI-MS) combined with tandem mass spectrometry (MS/MS) and exact mass measurements can meet such criteria.[43–45]

AI-MS is an experiment in which ion generation is performed from untreated samples, in air outside the vacuum environment of the mass spectrometer. The fact that no sample preparation or prior extraction steps are needed in AI-MS means that experiments are simple, which ultimately reduces the total MS analysis time.[46–51] Ambient ionization methods include desorption electrospray ionization (DESI),[45,52,53] direct analysis in real time (DART),[54,55] laser ablation electrospray ionization,[56] desorption atmospheric pressure chemical ionization (DAPCI),[57–59] nanodesoption electrospray ionization (nano-DESI),[60] and low temperature plasma (LTP)[61] among others. These methods have been successfully applied to the analysis and quantification of a wide range of samples such as environmental pollutants,[62] animal tissues,[60] and in complex mixtures without any sample pretreatment. High molecular specificity and sensitivity have been successfully achieved with AI-MS analysis through MS/MS, in situ ion/molecule reactions, and high resolution mass measurements.[63–66]

Paper spray (PS) ionization is a relatively new AI-MS method, which has been successfully applied in the analysis and quantification of complex molecules, ranging from small organics to large biological molecules including dried blood under ordinary ambient conditions.[67] When using PS, the sample is usually loaded onto paper (or another porous medium) that has been cut to a fine point (tip). The paper is wetted with a solvent and charged liquid droplets are emitted from the paper tip when a high dc voltage (±3.5 kV) is applied. Droplet emission occurs presumably by field emission and/or other unidentified mechanisms.[68–70] Analysis by PS-MS requires little or no sample preparation and the entire experiment can be completed in times on the order of a few seconds (i.e., less than 1 min). In comparison to other ambient ionization methods, PS integrates three analytical steps: sample collection, separation, and ionization into a single experimental step making it more attractive for rapid and direct analysis of analyte(s) in complex mixtures. In addition, no nebulizer gases are required and so the technique can be used with portable MS in the field. Recently the successful application of analysis of aromatic quaternary ammonium corrosion inhibitor formula-

tions in petroleum oil samples using PS with a miniature mass spectrometer (Mini 12) has been reported.[71] Reactive PS-MS is a variant of the normal PS-MS experiment that incorporates rapid chemical reactions into the PS ionization process. Reactions occur at the sampling spot concurrently with mass spectra acquisition to improve sensitivity and selectivity for target molecules present in the complex mixtures by doping a reactive reagent into the spray solvent.[72–75]

In the present article, we use PS-MS as a sensitive and selective ionization method for the rapid detection and quantification of the aliphatic long chain primary polydiamine (n-oleyl-1,3-diaminopropane (Duomeen O)) corrosion inhibitor formulation in a variety of complex sample matrixes including polyamine and amine mixtures collected from a large water tube boiler plant operated at medium pressure (17.5 bar). Reactive PS-MS is also used in which acetone is doped with the spray solvent to aid in characterization and selective detection of the n-oleyl-1,3-diaminopropane (Duomeen O) from a mixture of polyamines and amines. The samples studied include competitor product A, naylamul S11 and ascamine DW BR1 (mixture of polyamine and amines), and three water samples (feedwater, condensate water, and boiler water) collected from a large HP boiler system at Coventry waste treatment facility in the U.K. that was previously dosed by a six-component polyamine and amine corrosion inhibitor.

To successfully characterize and confirm the presence of Duomeen O analyte(s) in crude complex water samples, it was necessary to first analyze a standard with high-resolution MS and tandem MS using collision induced dissociation (CID) to determine the molecular formula and structure, respectively. Sample preparation was reduced to dilution of the standard model compounds in methanol while real water samples were analyzed directly as supplied without any dilution. As shown, PS retains the advantages of high sensitivity and specificity typical of MS experiments, plus short (<1 min) total analysis times with, no sample pretreatment; the ability to identify corrosion inhibitor formulations can be achieved readily at trace levels with a limit of detection (LOD) of 0.1 pg (absolute concentration) with acceptable reproducibility (RSD of <10%) in a variety of untreated, complex samples.

■ EXPERIMENTAL SECTION

Chemicals and Standards. The PS organic solvents; methanol (HPLC grade) and acetone were purchased from Mallinckrodt Baker Inc. (Phillipsburg, NJ). The chromatography paper used as the sample substrate was grade I cellulose Whatman (Whatman International Ltd., Maidstone, U.K.). The standard model compound, n-oleyl-1,3-diaminopropane (Duomeen O), cyclohexylamine, morpholine, diethyl amino ethanol, and the polyamine and amine mixture corrosion inhibitor formulations (competitor product A, naylamul S11 and ascamine DW BR1), used in this study were supplied by B&V Water Treatment Company (Lamport Drive Heartlands Business Park Daventry Northamptonshire, NN11 8YH, U.K.). The crude water samples (i.e., feedwater, condensate water, and boiler water) were collected from a large HP water tube boiler plant at the Coventry waste treatment facility U.K., that was previously dosed by a six component mixture of cyclohexyl-amine, diethyl amino ethanol, mono ethanol amine, methyl ethyl ketonoxime, Duomeen O, and tallow S 11 corrosion inhibitor formulation.

Sample Preparation. Sample preparation was reduced to the dilution of the model compounds to the desired

concentration while no sample preparation was performed for the raw boiler water samples. Each model compound was diluted in methanol (HPLC grade) to a desired concentration. From each solution, 2 μL was deposited using a pipet onto cellulose paper substrate and then analyzed using PS-MS. The boiler water sample mixtures (i.e., feedwater, condensate water, boiler water), and polyamine and amine mixture (i.e., competitor product A, naylamul S11, and ascamine DW BR1), were used as supplied without any modification or preconcentration. A volume of 2 μL of each sample deposited using a pipet onto cellulose paper substrate analyzed using normal PS-MS and *reactive*-PS-MS.

PS-MS Instrumentation. All experiments were performed using a linear ion trap (LTQ) mass spectrometer (Thermo Fisher Scientific, San Jose, CA), tuned for optimum detection of the precursor ion of interest. The temperature of the MS capillary inlet was typically set at 250 °C. The tube lens voltage was set at 65 V and the capillary voltage maintained at 15 V in both positive and negative modes, respectively. The paper spray ion source was placed 3 mm in front of the inlet the LTQ instrument in all the experiments. An electric potential of ±3.5 kV was used for all the PS experiments in both positive and negative mode. It is important to note that in the paper spray experiments no carrier gas is required, instead a plume of ions is generated only with the application of a potential on the paper with the sample and the spray solvent as shown in Figure 1.
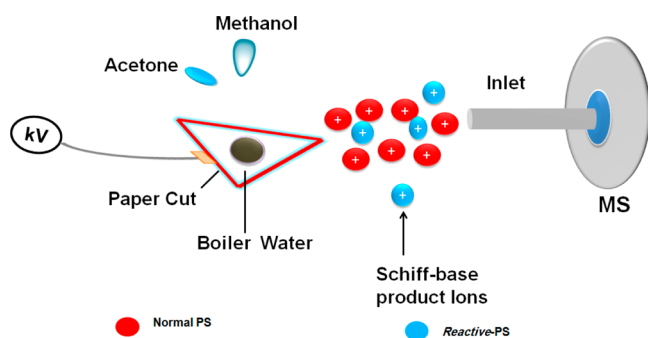
Figure 1. Schematic of the paper spray mass spectrometry experimental setup used in rapid screening of Duomeen O in the boiler system water samples.

Approximately ~2 μL of each sample was deposited on a filter paper surface and analyzed directly without any sample preparation. Tandem mass spectrometry (MS/MS) was used for the structural elucidation, and analyte identification was performed on the molecular ions of interest using collision-induced dissociation (CID). An isolation window of 0.1−1.5 Th (mass/charge units) and normalized collision energy of 15−40% (manufacturers unit) was used. Furthermore, the identities of studied long-chain polyamine and other corrosion inhibitor formulations were confirmed using a high-resolution mass measurement Orbitrap mass spectrometer (Exactive, Thermo Fisher Scientific, San Jose, CA). The experimental conditions on the Orbitrap were as follows: maximum injection time of 50 ms, two microscans, and activated automatic gain control (AGC).

PS-MS. A cellulose chromatography paper (Whatman, Maidstone, U.K. grade I) was used as the paper substrate, and equilateral triangles with ~5 mm sides were cut manually with scissors. The tips of the base angles were cut off and the vertex angle was kept sharp. The paper substrate was held by a copper clip (Figure 1) so that the vertex was ~3 mm away from the inlet capillary of the mass spectrometer with an atmospheric pressure interface that transports the spray plume of ionized analyte(s) into the vacuum system of the mass spectrometer for analysis. The sample solution was applied to the paper triangle followed by application of a high voltage. The typical experimental parameters used were as follows: paper spray solvent 10 μL of acetonitrile; and the voltage applied to the paper was in the range of +3.5 kV in positive and −3.5 kV in negative modes. In all experiments (unless noted) the instrument was set to record spectra in the AGC mode for a maximum ion trap injection time of 100 μs and 3 microscans were combined per spectrum. Figure 1 shows the experimental protocol that was followed in this study; first, a blank spectrum of 10 μL of methanol was taken before sample was applied onto the paper substrate. The analysis was performed in both full MS mode for analyte identification and tandem MS mode for structure elucidation.

Reactive-PS-MS. In the *Reactive*-PS-MS experiment of Schiff-base reaction, pure acetone was utilized to enhance the selectivity and specificity of the long chain *n*-oleyl-1,3-diaminopropane in a variety of sample matrixes. In this experiment, 10 μL of the pure acetone reagent was added to cellulose paper with long chain *n*-oleyl-1,3-diaminopropane using a pipet. All the *reactive*-PS-MS experiments were performed using a commercial LTQ instrument (as shown in Figure 1) following the same settings and procedures as used in the normal PS-MS experiment described above.

■ RESULTS AND DISCUSSION

In this article, we aimed at direct identification, structure characterization, and confirmation of the presence of long chain *n*-oleyl-1,3-diaminopropane (Duomeen O) corrosion inhibitor in water samples using chemical reactions, PS-MS(/MS), and exact mass measurement. We present the characterization of purified Duomeen O samples first, followed by quantitative/analytical performance measurements, and finally the analysis of a variety of complex water boiler samples collected from large HP water tube boiler plant (Coventry Waste Treatment facility U.K.). We chose to examine the long chain Duomeen O corrosion inhibitor formulation in crude water samples because its identification and quantification is essential in the optimization of the corrosive system,[9,14,36] and current efforts have focused on developing new, green, and efficient corrosion inhibitors for water treatment plants.[76−78] There is also the need to monitor the level of residual corrosion inhibitors to prevent run away reactions. Water transfer pipelines are often carbonated to remove dissolved carbon dioxide species, but the process in turn generates carbonic acid that leads to reduced pH and consequently corrosion. Corrosion inhibitor formulations when added in small amounts to a corrosive water boiler system neutralize the carbonic acid and bring the pH to a normal value.

PS-MS Analysis and Characterization of Duomeen O Using Positive Ion Mode. The positive ion PS-MS molecular analysis of Duomeen O, using 2 μL of samples deposited on the chromatography paper triangle was achieved after the application of 10 μL of methanol as the PS spray solvent. The resultant mass spectrum is as shown in Figure 2, which is dominated by intact protonated molecular ion $[M + H]^+$ at m/z 325 in the mass range of 100−1000 Da, with little or no fragmentation (Figure 2a). The insert (i), in Figure 2a shows the isotopic distribution at m/z 325, and the high proton
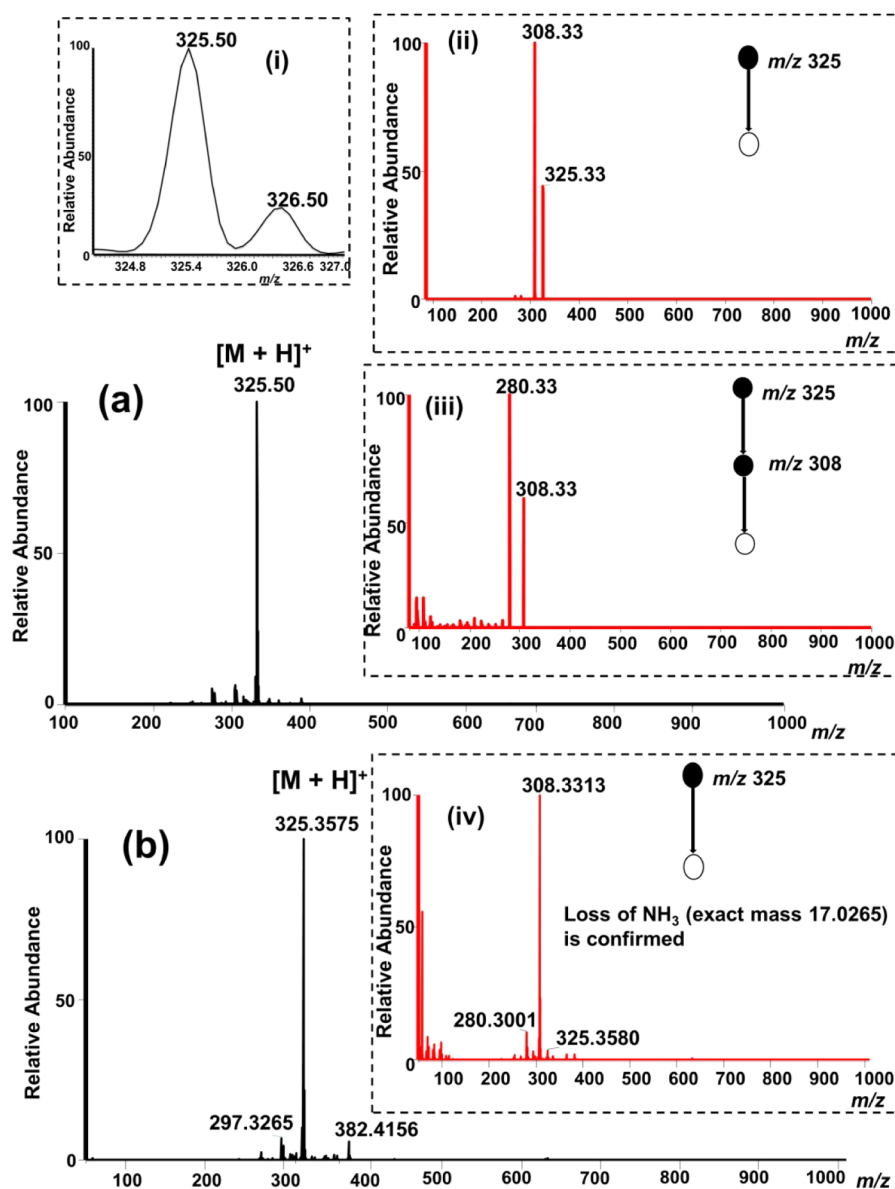
Figure 2. Positive ion mode paper spray mass spectrum for Duomeen O corrosion inhibitor model compound analyzed using a benchtop ion trap mass spectrometer. Absolute amounts of analyte were spotted onto filter paper and ionized in the open air by application of an electric potential, 2 μL, viz., 10 ppb: (a) Duomeen O (MW 324) in methanol solution and (b) exact mass measurement of Duomeen O. Insert (i) shows the isotopic distribution of the Duomeen O protonated molecular ion [M + H]⁺ at m/z 325, and inserts (ii) and (iii) show the MS/MS CID data for the selected ions. Insert (iv) shows the corresponding exact mass MS/MS CID data.

affinity of n-oleyl-1, 3-diaminopropane (Duomeen O) allows for its protonation. The remarkable absence of signal due to the paper spray ionization background is consistent with the high proton affinities of diamine compounds, a well-known ionization feature of many chemical ionization methods.

Structure Characterization and Confirmation of Duomeen O. Tandem MS via multistage CID was employed for the initial structural characterization of the intact protonated [M + H]⁺, Duomeen O cation at m/z 325. The insert (iii) in Figure 2 shows the product ion scan MS² mass spectrum obtained in the positive ion mode using PS-MS where the CID dissociation leads to a single fragment ion at m/z 308 owing to ammonia (MW 17 Da) neutral loss as a result of heterolytic cleavage of the low energy C−H−NH₂ bond. The stability and abundance of the product ion allows three stage (MS³) tandem MS experiments to be performed. In this particular case, CID of the product ion at m/z 308 yielded further fragment ions at m/z 280 through the loss of ethylene (MW 28 Da) neutral molecule as shown in insert (iii) of Figure 2a.

With the molecular weight of 324.6 Da, a major concern about Duomeen O in paper spray was the actual ion type generated (i.e., protonated or radical molecular cation). Nominal mass measurement produced 325.5 Da as the molecular ion (Figure 2a). The MS/MS experiment described above was useful but further verification was needed to confirm the structure of this long chain C₈−Duomeen O compound. For this, tandem MS was combined with exact mass measurements, which provided the chemical formula assignment in the Xcallibar 3.1 software. The use of 50 000 resolution and lock mass proved to be sufficient to determine the molecular formula of Duomeen O with error considerably below 1 ppm (Figure 2b). The proposed molecular formula
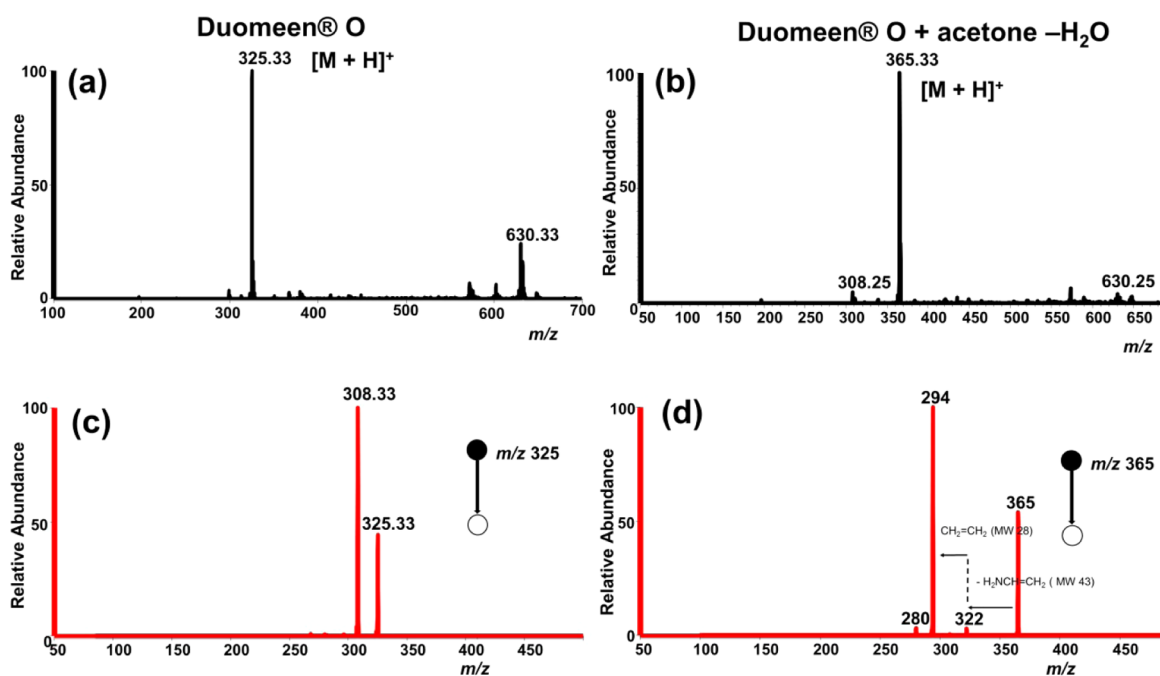
Figure 3. Positive ion mode *reactive*-PS mass spectrum Duomeen O analyzed using a benchtop instrument: (a,b) typical Duomeen O mass spectrum analyzed without the acetone reagent and MS/MS CID data, respectively, while parts b and d show the product of the Duomeen O reaction with acetone detected in open air.

based on the exact mass measurement confirmed that the detected long chain Duomeen O formed a protonated molecule $[M + H]^+$ upon ionization by paper spray ionization, exact mass of CID fragments and neutral loss (insert (iv), Figure 2b) all confirm this assignment which is consistent with the CID data interpretation described in insert (iii) Figure 2a. Other corrosion inhibitor formulation model compounds analyzed by the PS-MS method included cycloxylamine (MW 99), morpholine (MW 87), and dethyl amino ethanol (MW 117). These compounds also gave intact protonated molecules $[M + H]^+$, and their identities were confirmed using their MS/MS CID fragmentation patterns (see Figure S1, Supporting Information, for detailed characterization).

The Duomeen O showed a limit of detection (LOD) of 0.1 pg (absolute concentration) when analyzed using PS-MS. The LOD was determined as the concentration that produces a signal more than three times greater than the standard deviation plus the mean value of the blank, in MS/MS mode. The signal intensity ratios of the most abundant MS/MS transitions (at m/z 325.5 → 308) were found to be linear (regression parameters, $y = 0.0056x + 0.001234$, with R^2 value 0.999; see Figure S2, Supporting Information) in the range of absolute amounts from 0.1 to 1000 ppb and showed good reproducibility (relative standard deviation, RSD < 10% for 1 pg samples deposited on the paper substrate).

Reactive-PS-MS: Duomeen O Detection Using Schiff-Base Reaction with Acetone. In addition to exploring the direct detection of Duomeen O using PS ionization, chemical reactions that form stable adducts can be used in conjunction with PS-MS to enhance the selectivity and detection of analyte(s) in complex mixtures. As such, experiments of this type (reactive-PS-MS) were employed in this study to improve the analysis of Duomeen O in complex water samples. A volume of 10 μL of acetone was spotted *in situ* onto the paper simultaneously with application of 10 μL of methanol solvent as shown in Figure 1. Intense mass spectra containing protonated

molecular ion $[M + H]$ of Duomeen O at m/z 325 were observed (Figure 3a) when only methanol was applied on a filter paper to which Duomeen O had previously been applied. In contrast, applying acetone in tandem with methanol resulted in a completely different mass spectrum (Figure 3c) where the nucleophilic attachment of the carbonyl group in acetone by the primary amine group in Duomeen O yielded a reaction product with MW 364 Da and concomitant loss of water (Scheme 1). The protonated ion of the reaction product is subsequently detected at m/z 365. Collisional activation of the ion at m/z 365 in CID affords product ions m/z 322 (minor) and m/z 294 (major) through sequential elimination of ethenamine (MW 43 Da) and ethylene (MW 28 Da),

Scheme 1. Schiff-Base Condensation Reaction of the Primary Amines[a]
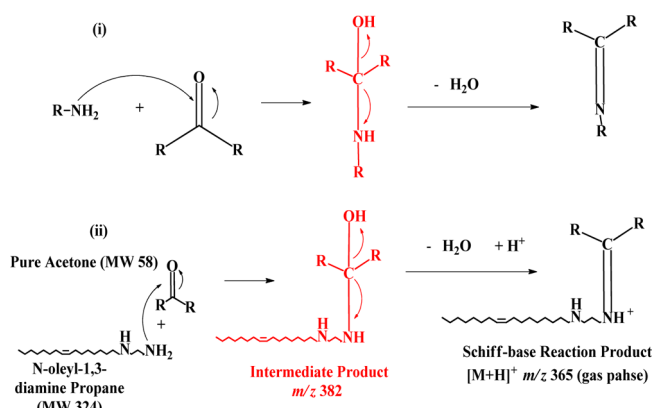
[a](i) Nucleophilic reaction between the primary amine and ketone and (ii) reaction between Duomeen O (*n*-oleyl-1,3-diamine propane) (MW 324) and acetone in gas phase under ambient conditions using *Reactive*-PS-MS.
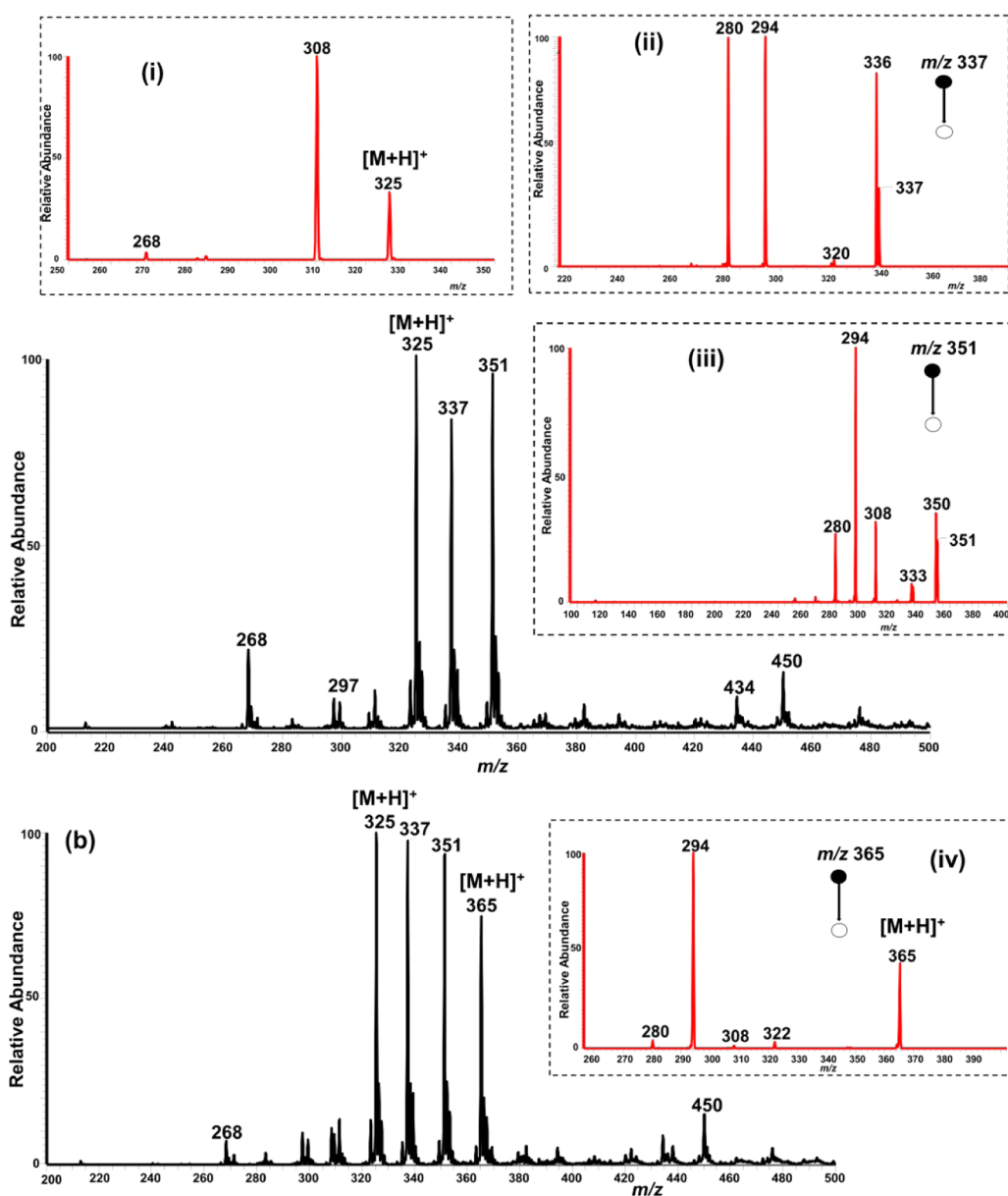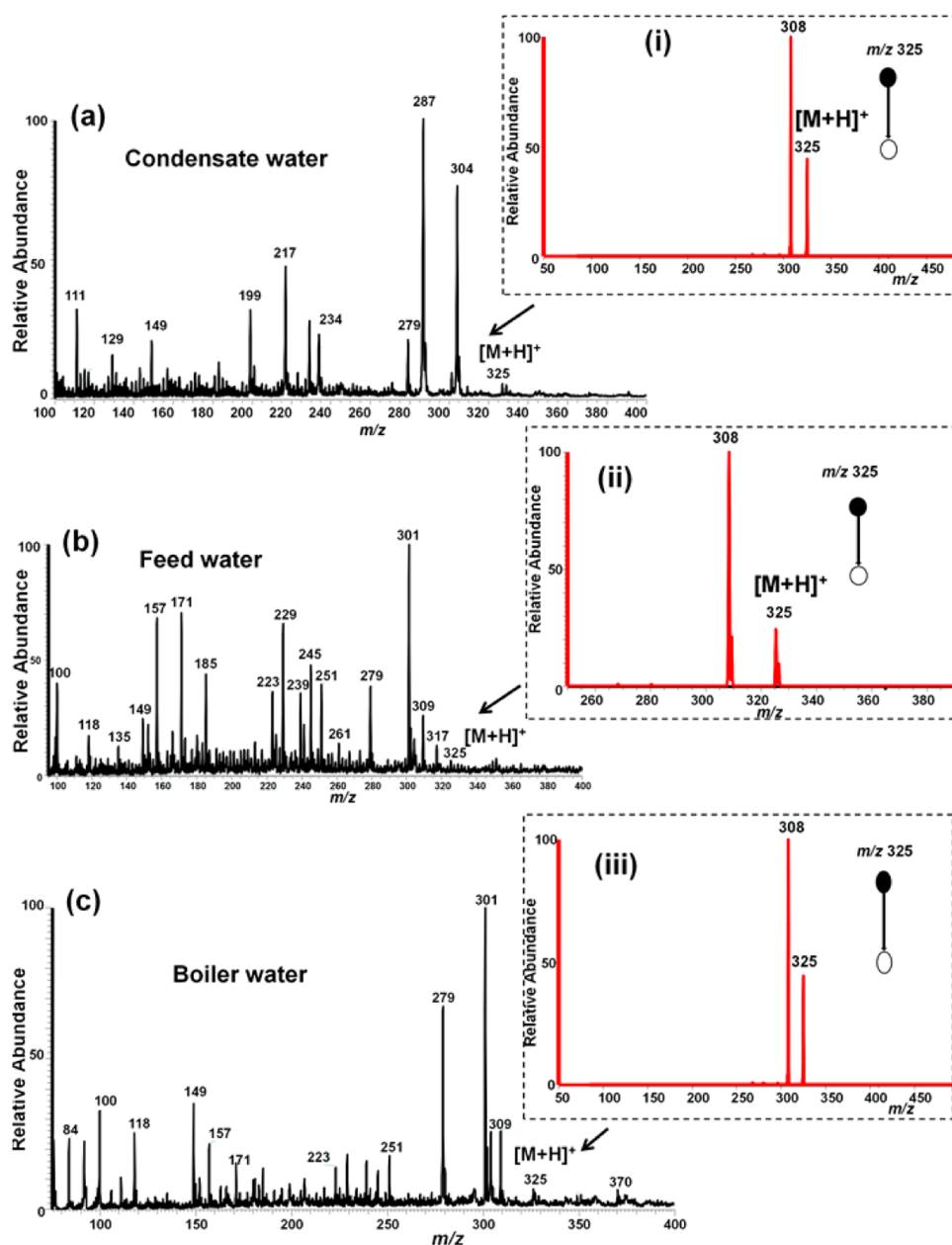
Figure 4. Positive ion mode paper mass spectrum for polyamine and amine corrosion inhibitor formulation complex mixture (competitor product A) analyzed using a benchtop mass spectrometer. (a) Mass spectrum of competitor product A corrosion inhibitor mixture analyzed without acetone reagent. A volume of 2 μL of the corrosion inhibitor mixtures was deposited onto the surface and ionized and analyzed in the open air by application of an electric potential of +3.5 kV positive ion mode. Insert (i)−(iii) are the MS/MS CID mass spectra for the m/z 325, m/z 337, m/z 351, respectively. (b) Mass spectrum of competitor product A corrosion inhibitor mixture analyzed with acetone reagent. The protonated ion of the reaction product is subsequently detected at m/z 365. Insert (iv) is the MS/MS CID mass spectra for the m/z 365.

379 respectively, as shown in Figure 3d. This reactive PS
380 experiment provides reliable complementary chemical informa-
381 tion which facilitates polydiamine and amine corrosion
382 inhibitor formulation identification in complex matrixes with
383 enhanced selectivity.

384   The introduction of reagents in normal PS-MS experiments
385 produce selective detection; when used in combination with
386 tandem MS, this approach provides the confirmation needed to
387 identify the presence of a particular substance. From these
388 experiments, two reactions occurred on the surface in open air:
389 (1) the nonspecific proton transfer reaction forming protonated
390 molecules $[M + H]^+$ (Figure 3a), and (2) the Schiff-base
391 reaction (Figure 3b). It is interesting to note that this
392 condensation reaction between acetone and the amine

393 proceeded rapidly (in less than 5 s) to enable analysis in real
394 time. This reaction time scale is consistent with accelerated
395 reaction rates observed for thin film/charged microdroplet
396 reaction conditions.[79,80]

397   Paper spray ionization is a particularly simple ambient
398 ionization technique which can be employed in the field to
399 measure trace constituents of complex mixtures. Although
400 analysis in MS/MS mode adequately removes matrix effects, a
401 decision needs to be made as to what analyte ion within the
402 mixture should be subjected to collisional activation. In this
403 respect, preforming real time chemical reactions onsite will
404 offer an efficient means to eliminate unrelated matrix ions. The
405 generation of a charged product is expected to improve
406 ionization efficiency in a process once known as "reverse

Figure 5. Positive ion mode paper spray mass spectrum for rapid detection of Duomeen O corrosion inhibitor boiler system water samples: (a) condensate water, (b) feedwater, (c) boiler water. A volume of 2 μL of the sample was deposited onto the surface and ionized in the open environment by application of an electric potential of +3.5 kV positive ion mode. Inserts (i)−(iii) are the MS/MS CID mass spectra for the protonated Duomeen O at m/z 325 detection from each sample.

derivatization".[73] The combined derivatization/ionization process is tested in this study for the analysis of Duomeen O. As such both ionization efficiency and molecular selectivity can be improved by chemical derivatization such as the Schiff base reaction.

PS-MS Analysis of Duomeen O in a Mixture of Polyamine Corrosion Inhibitors. Direct analysis of the long chain Duomeen O in complex polyamine and amine mixtures using PS-MS was investigated without any sample preparation. Polyamine and amine complex mixtures including competitor product A, naylamul S11, and acsamine DW BRI were analyzed as supplied without further pretreatment. A volume of 2 μL from each sample was deposited onto the paper triangle and analyzed using a commercial benchtop mass spectrometer in positive ion mode as described in Figure 1.

Figure 4a shows the recorded mass spectrum for the competitor product A (polyamine and amine mixture) (mass range 200−500) using only methanol as the PS spray solvent. Intense protonated molecular ions of Duomeen O [M + H]$^+$ at m/z 325 were observed and confirmed by MS/MS CID experiments (insert (i) in Figure 4). Two unidentified peaks at m/z 337 and 351 were also observed, and MS/MS experiments (inserts (ii) and (iii), Figure 4) showed that they are unrelated to Duomeen O. This decision was supported by reactive paper spray experiments in which only the peak corresponding to Duomeen O (m/z 325) was observed to be affected by the presence of acetone, with the concomitant appearance of an ion at m/z 365 (Figure 4b). This product ion has previously been identified as coming from a reaction between acetone and Duomeen O (Figure 3b) using purified samples. Similarly, the remaining

polyamine and amine corrosion inhibitor mixtures (i.e., naylamul S11 and ascameen) were analyzed using PS-MS and Duomeen O was detected and characterized (Figure S3, Supporting Information).

The ability to detect and characterize Duomeen O in a variety of different raw crude boiler water samples collected from a water tube boiler plant waste treatment facility (Coventry, U.K.) has been demonstrated. In this experiment 2 μL from each sample was deposited on the paper substrate and analyzed using PS-MS. Figure 5 shows the recorded mass spectra for (a) condensate water, (b) feedwater, and (c) boiler water. Moderately intense protonated molecular ions $[M + H]^+$ of Duomeen O were observed and confirmed using MS/MS CID data as shown in Figure 5, inserts (i)−(iii) in condensate, feed, and boiler water samples. The identification of the Duomeen O molecule in a variety of crude water samples collected from a large HP water tube boiler plant demonstrate the utility of the PS-MS method for direct, rapid screening with little or no sample preparation. It is important to note that other protonated molecules for amine compounds such as cyclohexylamine (MW 99), diethyl amino ethanol (MW 117), were also detected and confirmed using MS/MS CID data (Figure S5, Supporting Information) in the feedwater and boiler water at m/z 100, 118 (Figure 5b,c).

One advantage of ambient ionization methods is their compatibility with high-throughput rapid screening. To implement successful screening experiments, the analytes of interest need to be carefully evaluated with respect to the matrix due to possible complications of ionization suppression and isobaric ion interference. In our experiments Duomeen O was among the low-abundance ions detected in the full mass spectra from the water samples (Figure 5). The same analyte concentrations were sensitively detected in MS/MS mode in which matrix effects are completely eliminated. As demonstrated in other PS-MS experiments,[45,48] the porous cellulose paper substrate used for ionization reduces/filters a large proportion of the particulate present in complex samples and reduces ion suppression effects without extensive sample preparation.

Direct analysis of Duomeen O at very low concentrations (<0.5 pg absolute) in complex mixtures has been demonstrated using paper spray mass spectrometry. The MS/MS experiments, complimented by the reactive PS-MS method, provide a powerful means of qualitative analysis with little or no sample preparation. As demonstrated above, either tandem MS or reactive PS-MS can be used to analyze Duomeen O in complex mixtures. Since quantification was carried out in MS/MS mode, it was required to establish the fragmentation pattern of Duomeen O in collision-induced dissociation experiments. For complex mixtures, it is often difficult to identify species of interest; to improve the efficacy of the identification process for Duomeen O, we implemented a reactive paper spray approach in which acetone was added to the methanol/water spray solvent. Any mass shifts observed after the in situ reaction with acetone signified the presence of an amine functional group, potentially from Duomeen O analyte in water, which can then be quantified in subsequent MS/MS experiments.

■ CONCLUSION

Direct analysis of long chain aliphatic primary polydiamines by PS-MS has been demonstrated in a variety of boiler water samples with little or no sample pretreatment in open air. The use of tandem mass spectrometry analysis assisted in confirming the identity of aliphatic primary amine (Duomeen O) in various boiler system water samples. Exact mass measurements using LTQ-Orbitrap further confirmed the Duomeen O molecule formula observed within 1 ppm mass accuracy. PS-MS ambient ionization is both sensitive and selective for the analysis of corrosion inhibitor formulations in boiler water samples. Linear signal responses with a dynamic range of 5 orders of magnitude were obtained. The LOD of 0.1 pg (absolute concentration) with reproducibility of RSD of <10% is noteworthy for the direct analysis of aliphatic primary polydiamine and amine corrosion inhibitor formulations in crude large medium pressure (MP) water tube boiler plant samples. Furthermore, the Schiff-base reaction between the aliphatic primary polydiamine (Duomeen O) and acetone complements the usefulness of PS-MS analyte molecules in complex sample mixtures. The simplicity of paper spray ionization and the ability to analyze raw boiler water samples without sample preparation further enhances the potential for coupling to a portable or miniaturized mass spectrometer for on-site analysis. Such a system in operation would be of great value in the water industry for quality control. Future work will consider PS ionization coupled to a portable miniature mass spectrometers for in-field characterization of different boiler water samples under ambient conditions. Online *in situ* with online monitoring of the water boiler system is the ultimate aim.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.5b03992.

> PS-MS analysis and identification of amine corrosion inhibitors model compound, semi-quantitative analysis of the Duomeen O using paper spray mass spectrometry, and PS-MS analysis of Duomeen O in a multicomponent mixture of polyamine and amine corrosion inhibitor mixtures using paper spray ionization (PDF)

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Notes

The authors declare no competing financial interest.

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