

Quantitation of a Metal Deactivator Additive by Derivatization and Gas Chromatography–Mass Spectrometry

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Abstract

The quantitative analysis of phenolic and amine-containing petroleum additives can be challenging. One such compound—*N,N*-disalicylidene-1,2-propanediamine, a common metal deactivator additive (MDA)—is thought to inhibit fuel oxidation catalyzed by metals both in the fuel and on surfaces. The ability to measure the concentration of MDA in storage stability tests, thermal-stressing studies, and field samples is important. Quantitating low concentrations of MDA can be difficult because of surface adsorptivity due to the phenol and amine functional groups. This paper describes the shortcomings of direct-injection gas chromatography–mass spectrometry to quantitate MDA as well as a solution to the analytical problem using the common silylation agent BSA to derivatize the MDA. Results demonstrate that the silylation technique is suitable for the determination of MDA concentrations in aviation fuel samples and suggests that the MDA may be readily determined in other petroleum products with a lower detection limit for MDA of 0.5 mg/L. Measurements conducted in heated batch reactors indicate that MDA concentration is reduced as hydrocarbon fuels are stressed. In addition, only free or available MDA is measured by this technique, not MDA that is complexed with metals.

Introduction

Metal deactivator additive (MDA) has been used for over sixty years to prevent metal catalyzed oxidation reactions in petroleum products (1). MDAs are thought to act in two ways: (a) by chelating (binding) dissolved metal ions (as shown in Figure 1) and (b) by passivating active sites on metal surfaces (2). Presently, the US Air Force allows refineries to add up to 5.7 mg/L of a metal deactivator solution (75% active ingredient) to JP-8 fuel to improve thermal stability (the tendency to resist deposit formation under conditions of elevated tem-

perature). Recently, the US Air Force has been treating JP-8 fuel with an additive package that contains as one of its components *N,N*-disalicylidene-1,2-propanediamine (in this study referred to as the MDA), at a treatment rate of 2.0 mg MDA per liter of fuel. The additive package JP-8+100 minimizes deposition when the fuel is used as a heat sink by high-performance aircraft. Because of its surface activity and reactivity, MDA may be reduced in concentration as the fuel is handled or thermally “stressed” (oxidized at the elevated temperatures experienced in flight). It is desirable to be able to measure MDA concentrations in JP-8+100 fuels to verify that the addition was made properly. Furthermore, it would be beneficial to be able to monitor MDA concentrations in thermal stressing and storage stability studies in order to understand the role MDA plays in these processes.

The goal of this work was to develop a simple technique to quantitate JP-8 specification levels of MDA (2.0–5.7 mg/L) without prior concentration in both stressed and unstressed fuels. In addition, this analysis needed to be capable of quantitating lower levels of MDA (0.1–2 mg/L) in stressed aviation fuels from thermal stability studies. Finally, an autosampling technique for analysis was desired using the most common type of autosampler for gas chromatography (GC) (i.e., automatic injection into conventional split/splitless injectors).

Several nonchromatographic techniques for measuring MDA are available (3–5). These techniques typically require an

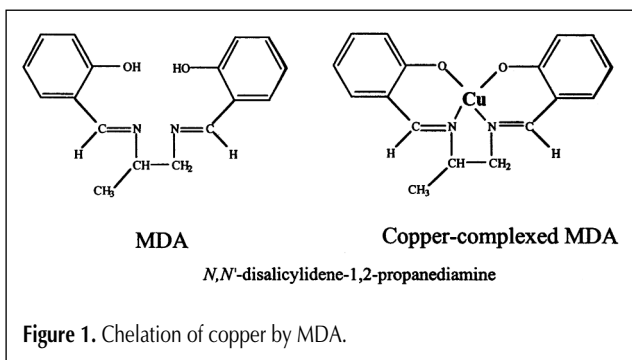


Figure 1. Chelation of copper by MDA.

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extraction of the metal deactivator from the fuel matrix, followed by spectrometric analysis. Many of these techniques do not work properly if the aviation fuel has a high polar content, low level of MDA, or yellow or brown color from thermal oxidation. The tests generally involve a large volume of fuel (10–100 mL) and aqueous extractions. These extractions may not be effective when powerful detergent/dispersant additives such as those used in the JP-8+100 package are present. Consequently, a chromatographic technique with high specificity, good detection limits, and small sample size is desired.

The two main obstacles to overcome in analyzing MDA by GC–MS are the adsorptive nature of the solute molecule and the complex matrix of the fuel. The surface adsorptivity of MDA was investigated by several chromatographic experiments described here as well as by inverse liquid chromatography experiments described elsewhere (6). The complex fuel matrix complexity was addressed mainly by programmed temperature GC, which separated the volatile components of the fuel matrix (less than approximately 226 amu) from the higher molecular weight MDA (282 amu) or its heavier derivatized product.

Surface adsorptivity of MDA

MDA (Figure 1) has a molecular weight of 282 g/mol and contains two amine and two hydroxyl groups. Because of the phenolic and amine functionalities, this compound is extremely adsorptive in both the liquid and gas phase. In liquid-phase adsorption work (conducted in an HPLC configuration), the dispersion and tailing of the solute zone was measured and compared to nonadsorptive solutes (6). The result of these studies demonstrated the importance of liquid-phase adsorption onto both glass and metal surfaces, and that MDA must be handled carefully in the laboratory to prevent adsorption to syringes, filters, sample vials, and other glass and metal surfaces. Gas-phase adsorption of phenolic and amine-containing compounds is well-documented for GC systems (7) and is a common concern for practicing chromatographers. The analysis of these types of compounds usually involves the deactivation of surfaces in order to obtain less adsorption and therefore better quantitation.

Derivatization techniques

The common derivatizing agent BSA (*N,O*-bis[trimethylsilyl]acetamide) was investigated to reduce the adsorptivity of MDA. This silylation reaction decreases the surface activity of phenolic substituents by replacing the phenolic hydrogens with the trimethylsilyl functionality (Figure 2). The decrease in surface activity inhibits adsorption processes that are problematic in low-concentration analyses.

Although there are many different types of silylation agents available, room-temperature silylation reactions with short reaction times were preferred for this application. Other silylation reactions using hexamethyldisilazane work well with phenolic analytes but must be heated to temperatures above 50°C for short periods of time (8,9). Derivatizing agents allow more-common chromatographic columns and conventional injectors and detectors to be used without having to incorporate “base-deactivated” or surface-passivated injector liners

and wool. The resultant silylated MDA complex was much less adsorptive, thus allowing for GC splitless injection and quantitation without solid-phase extraction (SPE) preconcentration.

Experimental

Direct split injection

Initial measurement techniques were conducted using a straight-forward approach of split injection at 300°C of an unsilylated analyte into a silanized glass liner/silanized glass wool using a conventional DB-5 capillary column (0.25-mm i.d., 0.25- μ m film thickness) with a flame ionization detector (FID). Other experiments were conducted using the same column and injector system with a Hewlett Packard (Palo Alto, CA) 5971 mass-selective detector (MSD). MSD experiments were generally conducted in the selected ion monitoring (SIM) mode for the 161- and 282-amu ions.

SPE and preconcentration with split/splitless injection

An alternative technique for the analysis of MDA was also used to increase detection limits and decrease matrix effects (coelution of trace compounds). Normal-phase SPE was used to separate MDA from its matrix. In this technique, each 1-g silica gel cartridge (Baker Chemical, Phillipsburg, NJ) used was treated with an initial wash of 5 mL of methanol, followed by 15 mL of heptane to condition the bed. The sample containing MDA in jet fuel or kerosene solvent was then added, followed by a 15-mL heptane wash to remove the nonpolar matrix. Finally, the MDA was eluted using 1 mL of methanol. After blowing to dryness in nitrogen, the residue was dissolved in toluene (200 μ L), and this final solution was injected into the GC–MS system as previously described.

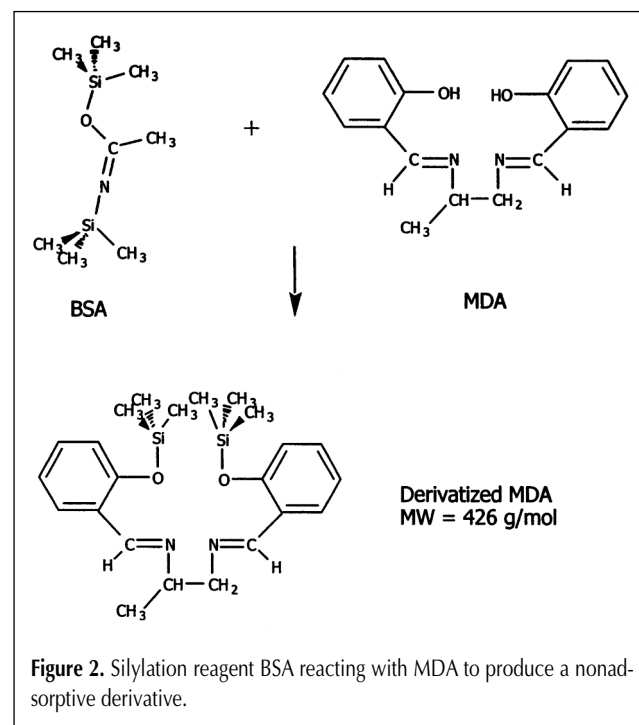


Figure 2. Silylation reagent BSA reacting with MDA to produce a nonadsorptive derivative.

Silylation and quantitative analysis

Standards were prepared by blending MDA (Octel America, Newark, DE) in standard kerosene (Aldrich Chemical, Milwaukee, WI) to produce a stock solution (400–600 mg/L) that was serially diluted to 10, 7, 5, 3, 1, and 0.5 mg/L in kerosene. A 200- μ L aliquot of each standard was pipetted into glass vials with glass or plastic 250- μ L inserts, to which 5 μ L of BSA (Pierce Chemical, Rockford, IL) was added using a Hamilton 701-series syringe. Care was taken to minimize exposure of the BSA to atmospheric moisture, because BSA is highly reactive with water. Each solution was mixed for approximately 10 s on a vortex mixer and analyzed by GC–MS (Table I). Jet fuel samples were handled in a similar manner by pipetting 200 μ L of each fuel into a GC vial/insert. In the case of thermally unstressed fuel samples, 5 μ L of BSA was used to silylate the additive. Thermally stressed fuels from the Isothermal Oxidation Apparatus (IOA) contained more organic alcohols and acids and thus were spiked with 20 μ L of BSA to insure that sufficient BSA was available to react with MDA. All samples were analyzed within one day of adding the derivatizing reagent.

The chromatographic column used was typically a 30-m, 0.25-mm-i.d., 0.25- μ m film thickness HP-5 capillary column (Hewlett Packard), although almost any nonpolar column having a thermal stability greater than 300°C would be suitable. Thin-film columns (0.1- μ m film thickness) may be more desirable for both resolution and analysis time. The mass-spectral patterns of the MDA and silylated MDA are shown in Figure 3. The 220- and 235-amu ions were chosen for quantitation because they were abundant in the silylated MDA but absent in the MDA. The retention time and ratio of the selected ions identified the derivatized MDA from interferences and various reaction products.

Results and Discussion

Direct split injection

Gas-solid adsorption clearly occurs during the analysis of MDA, as with many types of phenolic analytes in similar chromatographic systems (7). The direct analysis of MDA by FID systems for split injectors (clean borosilicate glass liner, silanized or deactivated glass wool, and conventional DB-5 column) is nonlinear with a lower detection limit of approximately 50–80 mg/L (Figure 4). Base deactivation of the injector liner, wool (Restek, Bellefonte, PA), and column (RTX-5 amine, Restek) resulted in a reduction of the detection limit by an order of magnitude, improvement in chromatographic peak shapes, and an increase in linearity.

These deactivation steps improved the analysis, but detection limits were still greater than specification levels (0–5.7 mg/L), presumably because of other surface-adsorptivity factors for MDA. Split injection gave an unexpected improvement in response as compared with splitless injec-

tion, indicating that adsorption effects continued to play a role despite our attempts at surface deactivation. Undeactivated surfaces in the ion source, column tips, and injector or detector components that were not surface passivated may have been

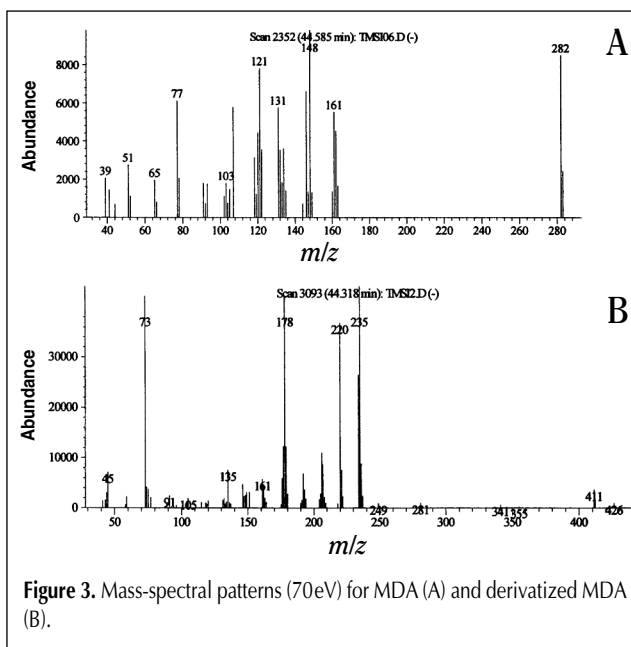


Figure 3. Mass-spectral patterns (70eV) for MDA (A) and derivatized MDA (B).

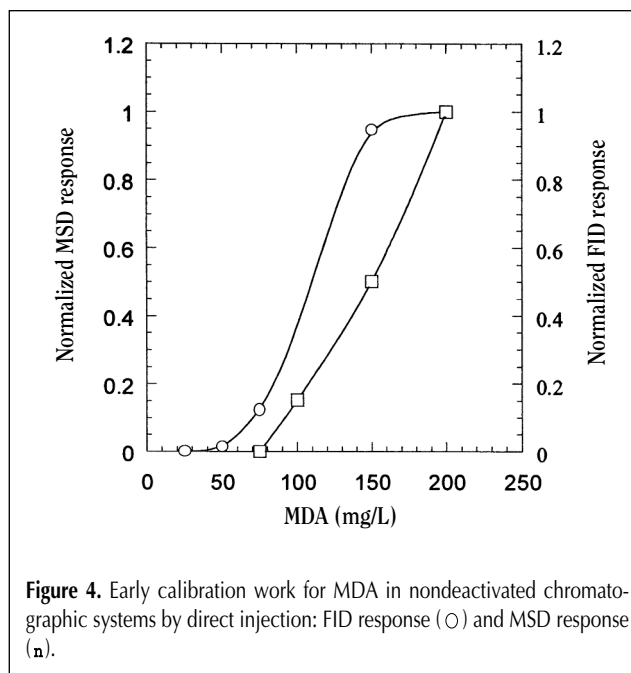


Figure 4. Early calibration work for MDA in nondeactivated chromatographic systems by direct injection: FID response (\circ) and MSD response (\square).

Table I. GC–MS Conditions for Analysis of Silylated Jet Fuels

GC conditions	MS conditions
Splitless injection: 300°C	SIM: 220, 235 amu
Injection volume: 3 μ L	Electron impact ionization: 70 eV
Initial temperature: 150°C (1-min hold)	Dwell time: 100 ms
Temperature program: 10°C/min	
Final temperature: 300°C (5-min hold)	
MS transfer line temperature: 280°C	

detrimental to system performance. "Cool" (ambient temperature) on-column injection was considered but was not desirable because of its limited autosampling capabilities with on-column syringes.

SPE with direct injection

Clearly, detection limits needed to be lowered in order to make this technique effective. SPE successfully increased the concentration of MDA and replaced the complex fuel matrix with the elution solvent methanol. In this work, a 10-mL sample of fuel was concentrated by a factor of 10, and the 1-mL sample was injected into the GC-MS system in SIM mode. The results were similar to previous direct-injection results in that low-level detection was still difficult (detection limits of 2 mg/L were typical). A split ratio of 10:1 provided more response than did splitless operation, presumably because sweeping of the solute through the glass injector liner was more efficient than the splitless process, which may increase contact time with glass or metal surfaces. Also, the accompanying solvent evaporation technique for the injection of the MDA became more time-consuming and tedious.

These steps created an improvement in the analysis, but detection limits were still not acceptable to measure at and below specification levels (2–6 mg/L). Split injection gave improved response as compared with splitless injection, indicating that perhaps adsorption effects continued to play a role in spite of surface deactivation.

Calibration results for derivatized MDA

MDA derivatized with BSA showed detection linearity between 0 and 10 mg/L and low detection limits (Figure 5) in

Table II. Precision and Accuracy of MDA Measurements Using Silylation with BSA

Known values (mg/L)	Measured response (mg/L)		
	Mean	Standard deviation	RSD
0.41	0.38	0.053	14%
2.5	2.5	0.11	4.3%
6.4	6.3	0.060	0.94%

Table III. Effects of Fuel Matrix on MDA Quantitation

Fuel ID	Fuel type	MDA added (mg/L)	MDA measured (mg/L)
POSF-2827	Jet A	2.0	2.8
POSF-2926	Jet A	2.0	2.4
POSF-2962	JP-5	2.0	2.5
POSF-2962	JP-5	6.0	6.0
POSF-2963	JP-5	2.0	2.2
POSF-2963	JP-5	6.0	5.0
POSF-2985	Jet A	2.0	2.0
POSF-3059	Jet A	2.0	2.5
POSF-3084	Jet A	2.0	2.8
POSF-3119	Jet A	2.0	2.7

duplicate analyses. The intercept for the curve is nonzero, indicating a lower detection limit of approximately 0.5 mg/L.

The lower detection limit of the derivatized MDA may be affected by the adsorption of MDA to the glass-vial insert and other surfaces to which the MDA was exposed before it was injected into the GC. If BSA is added to a 10-mg/L solution and the derivatized MDA is then serially diluted with reference kerosene to produce several solutions between 0 and 1 mg/L, the minimum detectable level is greatly improved (Figure 6). This observation is consistent with MDA being adsorbed to active sites in the glass vial that have high surface-to-volume ratios, affecting the lower-level standards more than higher-level standards. The use of plastic inserts did not improve the adsorption of MDA before it could be derivatized.

Method repeatability

Replicate analyses ($n = 5$) were conducted for three levels of MDA in a reference kerosene. The solutions of MDA in kerosene were then spiked with the derivatizing agent and analyzed using the autosampling splitless injection. The results showed good agreement with spiked levels of MDA and reasonable standard deviations for replicate analyses (Table II). Low concentrations of MDA clearly have a higher relative standard deviation (RSD) because of the difficulty of insuring that all of the analyte is successfully transported to the chromatographic detector. Any glass or metal surface may adsorb a small amount of the analyte, making results less consistent. However, this level of RSD is typical of trace analyses at the sub-parts-per-million level, especially for such a surface-active compound.

Effect of fuel matrix on measurement

To explore the effect of the fuel matrix on the quantitation of MDA, a series of Jet-A and JP-5 aviation fuels were spiked with a known amount of MDA. These samples were treated with BSA, and duplicate measurements of each were used to quantitate the level of MDA (see Table III). No history of the origin of the fuel was available. Levels of MDA that may have already

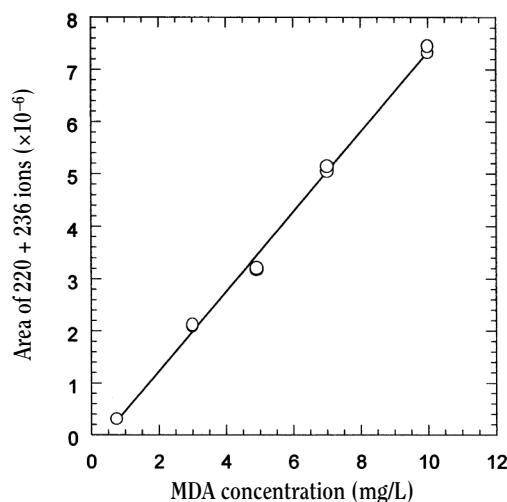


Figure 5. Typical calibration for derivatized MDA in a reference kerosene ($n = 2$).

existed in the fuel were not available.

All of the results obtained were greater than or equal to the amount added to the original fuel. We suspect that some of these fuels may have been doped with MDA at the refinery (up to 5.7 mg/L is allowable for Jet-A and 5.8 mg/L for JP-5). Because the history of each fuel was unknown, all unspiked or fresh-fuel samples were reanalyzed with BSA alone to detect low levels of MDA. With the exception of POSF-2962, all samples showed small amounts of MDA present (less than 0.5 mg/L). Attempts were made to quantitate between 0 and 1 mg/L, but results indicated nonlinearity in this range because of adsorption of the small amounts of MDA on surfaces. Further work needs to be conducted to improve the low-level accuracy (and precision) of this technique.

We suspect that MDA would not be silylated when chelated with a metal in solution. To test this hypothesis, 98-ppb copper, 60-ppb iron, and 14-ppb zinc were added to POSF-2962 and referred to as POSF-2963. Because the mass spectrometer was used to detect a specific mass at a specific retention time, MDA complexed with copper and silylated should not be detected at the same retention time as MDA not complexed with copper. The metal-containing fuel had approximately 1.0 ppm lower level of MDA, indicating that the MDA metal complex was not detected in this chromatographic arrangement (see Table III). In fact, the metal content of 172 ppb (the total for these three metals) would almost account for the 1.0 ppm difference, because 1 mol of each metal would complex with 1 mol of MDA and the mass ratio would be an approximate factor of 4.5 (for copper). These three metals alone account for 0.8 ppm of the MDA; other trace metals were not measured. Therefore, we concluded that the silylation technique is applicable only to uncomplexed or available MDA (i.e., MDA that has not already reacted with trace metals in the matrix).

Measurement of field samples for additive content

An additive package currently being developed for Air Force fuels (JP-8+100) is comprised of several additives including a detergent/dispersant, antioxidant, and MDA. Because the additive package is introduced in the field at the user level, measurements of the level of MDA could provide an important check on the techniques used to deliver and mix the additive package. Four samples were obtained from active air bases currently using the JP8+100 additive and were received in 1-gal metal cans. Results from the four samples indicated levels of MDA below the desired level of 2.0 mg/L. Again, MDA adsorptivity in holding, sampling, and analysis containers may have each had an effect in reducing the level of MDA for the chromatographic detector. Field samples may be more accurately measured by the addition of BSA to small samples taken from larger tanks in the field. These small samples could then be shipped to a laboratory for analysis. Using metal cans with high surface-to-volume ratios (compared to storage tanks) may deplete MDA as a result of adsorption or reaction with surface-bound water. Future work will address the possible deactivation of these surfaces so that field sampling of the additive package will be able to predict or indicate problems in the field.

Tracking additive concentration during stressing tests

The ability to measure MDA concentration as a function of time during fuel testing is of interest to fuel researchers. The time dependence of the MDA concentration can yield information about the chemical and physical mechanisms of MDA action as well as enable the optimization of the MDA concentration for a given system or fuel or both. Figure 7 shows that MDA concentration decreases as a function of time with simulated aircraft fuel-system stressing in an IOA (10). In these experiments, nitrogen was bubbled through the fuel as the fuel was heated to 180°C in an all-glass batch reactor. After reaching the desired temperature, air was introduced and the MDA level was measured as a function of time. The lack of metal exposure and low surface-to-volume ratio would preclude the explanation of the adsorption of MDA in reducing its concentration. Thermolysis (or a unimolecular decomposition) of MDA at 180°C is possible, although the reactor was

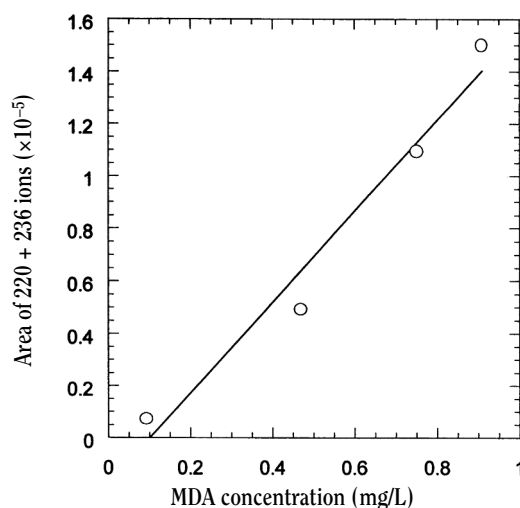


Figure 6. Calibration curve between 0 and 1 mg/L by dilution of the derivatized MDA.

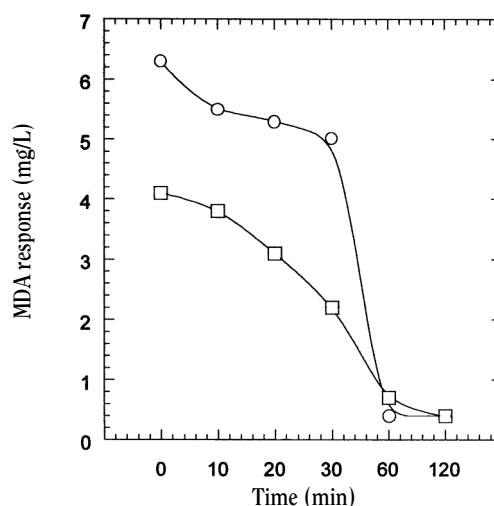


Figure 7. MDA reaction during thermal stressing of neat and copper-doped fuel in the IOA.

heated in a flowing stream of nitrogen as the system was heated. A significant amount of MDA would have degraded during the 60–90 min spent arriving at a thermal equilibrium if thermolysis was important. It would seem that bimolecular reactions involving the phenolic or amine functionality or both would be a more likely route of degradation for MDA. Previous work in a copper-doped fuel also observed MDA consumption during thermal oxidation at 140°C (11). MDA consumption below concentrations required to completely complex the copper resulted in substantial increases in the oxidation rate. It was surmised that MDA consumption could occur by the process of fuel peroxy radical extraction of one of MDA's phenolic hydrogens. In this study, the fuel containing 98-ppb copper showed a lower level of uncomplexed MDA initially, as was expected. Both experiments showed similar rates of decrease for uncomplexed MDA, indicating the probability of the same mechanism for MDA removal in both samples. Future experiments may include investigations of the ultimate fate of the MDA.

Conclusion

MDA can be successfully quantitated by GC–MS at jet-fuel specification concentrations by creating a trimethylsilyl derivative using BSA. The derivative circumvents the problems with accuracy, precision, and detectability of low levels (0–6 mg/L) of the highly adsorptive MDA molecule. Derivatization with BSA can be conducted at room temperature using extremely small samples (200 μ L) with sensitivity sufficient to cover the specification range of the additive (2–6 mg/L). The technique has been applied with reasonable success to the evaluation of additive concentrations in JP-8+100 samples and the tracking of MDA concentrations in thermal-stressing studies.

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