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Field Method for Detection of Metal Deactivator Additive in Jet Fuel

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Air Vehicles Division
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ABSTRACT

Jet fuel may contain a range of additives to improve its thermal and storage stability. One additive is a Metal Deactivator Additive (MDA) which reacts with metal in the fuel to form a stable metal chelate. This metal-MDA chelate is no longer chemically able to catalyse degradation reactions in the fuel. A thermal stability additive used within NATO, designation S-1749, also contains MDA as an integral component. A method, suitable for use in the field or in RAAF fuel testing laboratories, was required to assist fuel management procedures by allowing qualitative assessment of the presence of the additive in fuel. A colourimetric technique was developed using copper dosed silica gel which forms a strong coloured reaction product when exposed to MDA. The test method was found capable of detecting MDA in fuel at concentrations down to 0.5 ppm. The method was suitable as a field technique as it requires only the test tube and a disposable syringe.

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Field Method for Detection of Metal Deactivator Additive in Jet Fuel

Executive Summary

Jet fuel may contain a range of additives to ensure it meets stringent aviation specifications for storage and thermal stability. One such additive is a Metal Deactivator Additive (MDA). The purpose of the MDA is to react with trace metal in the fuel which may otherwise catalyse oxidation and degradation reactions reducing its storage and thermal stability. The new thermal stability additive, often called JP8+100 or S-1749, also contains MDA. The S-1749 additive contains components that may disarm fuel farm filter-colasecers elements, rendering them ineffective. Current fuel management procedures for defuelling aircraft with the S-1749 additive require the fuel to be diluted at a ratio of 100:1 with non-additised jet fuel. To determine if aircraft, especially visiting USAF and Canadian aircraft, have fuel with the S-1749 additive RAAF fuelling staff required a rapid in-field technique to qualitatively assess the fuel for the presence of S-1749.

Current methods for detection of the additive are laboratory based and require expensive instrumentation, trained staff and complex chemical modification of the additive.

DSTO have developed a colourimetric technique to qualitatively asses the presence of the MDA additive. The method is based on a visual colour change in a silica test tube when fuel containing MDA is passed through the tube. The silica powder is chemically modified by adsorbing and immobilising copper salts as a solid stationary phase which react with the MDA in the fuel to form a strongly red-purple coloured copper-MDA chelate. The method was optimised to obtain the most intense colour change by modifying the silica gel and the copper salt thus allowing identification of low concentrations of MDA.

The method is suitable for use at all RAAF base fuel laboratories and offers a rapid, simple, reliable and reproducible method of visually assessing the presence of the MDA and S-1749 additive in fuel.

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1. Introduction

The most significant difference between military jet fuel, AVTUR, and commercial JetA/ A1 is its additive package. One of the allowable additives in AVTUR is a Metal Deactivator Additive (MDA) which is added to counteract the affect of trace metals in the bulk fuel. Trace metals such as copper, cadmium, iron, cobalt and zinc [1] may have an adverse effect on the fuels thermal and storage stability as they can catalyse oxidation reactions which lead to degradation of the fuel. MDA is not normally added to AVTUR and is only included to correct thermal stability problems associated with high metal contents in fuel. This is done by the fuel refiner.

The recently developed GE Betz Spec Aid 8Q462 thermal stability additive package, NATO code S-1749, contains MDA as an integral component of the additive. Therefore any fuel containing the S-1749 thermal stability additive will contain MDA. Other additives are potentially being produced to meet this specification but at this time only the Betz additive is approved for use in aircraft. The ADF does not currently use the S-1749 additive, however, as part of the additive approval process a method to assist refuelling staff to assess the additive content of aircraft fuel was required. The test requirement is to assist with management of fuel during defuelling operations. Current management procedures require fuel containing S-1749 not be remixed back into bulk fuel storage unless it has undergone a 100:1 dilution with non-additised fuel. The additive is known to disarm filter-coalescer units and this dilution procedure is required to dilute the active components of the additive to below levels at which they will degrade the performance of filter-coalescer units.

Current laboratory methods for quantification of the MDA additive are complex and require significant laboratory work up and skilled analysts. They are unsuitable for deployment to field laboratories and are too slow to provide fast response results to assist field and base defuelling operations.

A range of simple field tests have been developed by a number of military laboratories including USAF, DERA and QETE_[2-4]. These methods have proven successful when fresh fully additised fuels are examined but are not suitable for rapid in-field qualitative assessment. The methods are unsuitable for field detection of fuels that have been blended with fuel that does not contain the additive or have been deliberately diluted as part of fuel management procedures. The QETE method offers a field level quantitative test, however, it also requires the use of solvents and a portable spectrophotometer.

It is known that metal complex's of some Schiff bases, such as the MDA, form strongly coloured chelates[5]. A qualitative method was developed based on the formation of coloured MDA-metal chelates when fuel dosed with MDA is passed over metal bound onto a stationary silica support media. The technique was found suitable to qualitatively assess the presence of MDA in fuel at levels down to 0.5 ppm MDA.

2. Metal Deactivator Analysis

2.1 Metal Deactivator Additive

Currently only one compound is approved as a MDA for jet fuel. The approved additive is N, N'-disalicylidene 1,2-propane diamine. This compound is a symmetrical Schiff's base or imine which is formed by condensation of salicylaldehyde and alkylene diamine. It forms a tetradentate ligand complex with metal compounds, Figure 1.

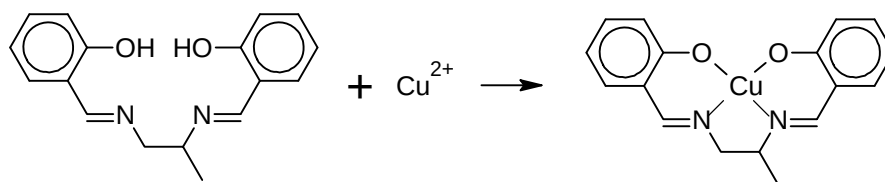


Figure 1: MDA reaction with copper to form MDA copper chelate

Other compounds have been used as MDA's in gasoline and other distillate fuels, however, they have all been discarded due to solubility issues or have not been approved for use in aviation fuel. These compounds include Schiff's bases, hydrazides, oxalyl amides, oxalohydrazides and mannich bases[6].

The MDA compound must meet a range of requirements as well as performing the role of deactivating metals in the fuel. Its primary role is to 'trap' active metal ions that would otherwise catalyse degradation reactions in fuel. The deactivating process is accomplished by chelation of free metal ions which binds the active sites of the metal into the chemical structure of the MDA-metal chelate. The resultant MDA-metal chelate must be soluble in the fuel and not form insoluble precipitates which may block filters and nozzles. The previously approved additive N,N'-disalicylidene-1,2-propylene diamine was withdrawn from service when it was found to produce solid deposits in fuel which resulted in filter blockage in the fuel system of aircraft[7].

MDA is added to fuel at low concentrations (i.e. 2.0 ppm MDA) in the thermal stability additive package or up to 5.7 ppm allowable in fuel. A field test based on colour formation requires the formation of a distinct colour that does not undergo interference from naturally occurring colour bodies in the fuel and the colour intensity is strong enough to detect the metal-MDA chelate formation at very low concentrations.

2.1.1 Current laboratory quantification techniques

As part of the DSTO test method evaluation a reference method was required to quantify levels of MDA in fuel. A method based on gas chromatography-mass spectrometry was used. The method requires chemical derivatization of the MDA before it can be analysed[8].

During test method development it was observed that samples of low concentration standards (i.e. 1 ppm of MDA in jet fuel) would not react to the test method indicating no MDA was

present in the standard. Rigorous testing using the GC-MS method found that the surface active MDA was adsorbing onto the transfer glassware (eg pipettes) and the volumetric glassware used in production of the standards. Significant effort is required to ensure glassware used in MDA testing is deactivated so it will not adsorb the MDA. Silating compounds may be used to achieve the desired level of glassware deactivation.

Once issues of loss of additive had been overcome the GC-MS method was found to be a suitable referee method.

2.1.2 Current field techniques

A range of test methods have been proposed for field assessment of the S-1749 additive in jet fuels. They can be grouped into three main categories based on the property of the additive they are detecting. The categories are the;

- a. Dispersant capacity method
- b. Coloured metal chelate formation method
- c. Conductivity method (not discussed in this paper)

None of the methods are entirely satisfactory as rapid field techniques especially when the S-1749 additive is diluted.

Dispersant Capacity Method. Methods that rely on the additives dispersant capacity are effective when the fuel is fully dosed with the additive but tests at DSTO using erythrosine red indicator dye, Figure 2, found difficulty in correctly identifying the presence of the additive when it was diluted from 256 ppm to 100 ppm. A range of dispersant capacity techniques have been trialed and all have the same limitation. The dispersant capacity tests differ in the material they are dispersing, ranging from fine metal oxide powders to food dyes. The dispersant capacity tests offer some capability to detect diluted additive, however, detection is very subjective and any change in sample conditions may affect the result. The dispersant capacity tests are not suitable when testing for MDA only.



Figure 2: Erythrosine red dye dispersant test for +100 in jet fuel Samples from left to right are 0 ppm, 100 ppm and 256 ppm of S-1749 additive. A colour change of the top phase indicates the presence of the additive.

Coloured Metal Chelate Formation Method. Field test methods that involve formation of coloured MDA-Metal chelates react the MDA with a fuel soluble organo metallic compound, such as iron caprate, to form a coloured solution. The colour intensity is measured at specific wavelengths in the visible range using portable or laboratory based UV-Vis spectrophotometers. This type of test also allows for diluted levels of MDA in the fuel by adding an extraction step to the method. The extraction technique is more suited to laboratory conditions than field analysis.

A method using iron chloride extraction was examined and was found to give a strong colour indication of MDA at 5 ppm, however, it was found difficult to estimate MDA concentrations at 2 ppm given the subjective nature of the colour change, Figure 3. It was also observed that if left to sit the yellow iron chloride solution would tend to darken to a brown colour similar to the iron-MDA chelate. This brown colour was due to hydration of the iron salt to form a rust coloured solution.



Figure 3: Iron chloride solution technique. In order from left to right – 5 ppm MDA, 0 ppm MDA, 2 ppm MDA.

2.2 DSTO Silica Tube Technique

A method was developed at DSTO in an attempt to overcome some of the short comings of the available field tests. The fundamental requirement of the test method was to develop a technique suitable for use at RAAF base fuel laboratories using existing equipment within the laboratories and a complete field deployable test kit that didn't require the use of portable spectrophotometers, solvents or reagents.

The method chosen was based on open column chromatography using a small column of silica gel that was coated with a copper salt. The indicator for the presence of MDA is a colour change in the silica gel. The copper salt bound onto the silica gel forms a tetradentate ligand compound that has a strong red-purple compound at low concentrations.

Using the open column system the volume of fuel passed through the column could be increased to ensure sufficient MDA contact with the stationary copper salt. The MDA is concentrated when it reacts with the metal salt forming a metal chelate of low solubility in the bulk fuel. This technique required no solvents or reagents other than the precoated copper doped silica test tube. A disposable syringe and prefilter can be used to pass fuel through the tube.

Initial attempts were made using iron salts however the colour change was not distinct at low MDA concentrations. The iron salts tended to darken on the column as they reacted with moisture in the air to form hydrated iron oxides (rust), Figure 4, potentially giving a false positive result.

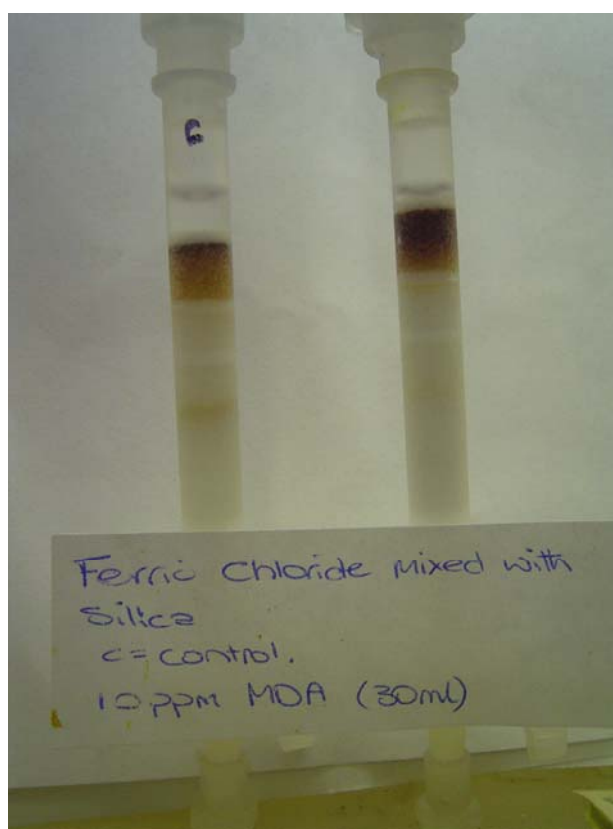


Figure 4: Iron chloride supported on silica showing darkening of the control (left)

2.2.1 Stationary phase

To optimise colour formation and compound retention a range of stationary phases were examined. They included silica gel of various size grades, aluminium oxide and cation exchange resins. All preliminary work was done using silica gel 100 – 200 mesh (0.07 – 15 mm) grade and 1 cm i.d. glass columns. Development of the stationary phase lead to an optimised system of silica gel 200 – 425 mesh (0.07 – 0.037 mm) with a pore size of 60 angstrom grade and disposable solid phase extraction tubes.

In an attempt to concentrate more copper and thus the intensity of the indicating colour reaction cation exchange resins were examined. Bond Elute strong cation exchange resin (SCX) was used as a stationary phase to bond the copper salt and potentially increase the copper loading per cm³ of silica. The SCX stationary phase was found unsuitable as it formed coloured bands when fuel with no MDA was eluted through it, Figure 5. The formation of coloured compounds is possibly due to basic compounds in the fuel reacting with the sulphonic acid on the silica support. The SCX stationary phase is a silica gel with propylbenzenesulfonyl groups bound to the silica, Figure 6.



Figure 5: SCX tube

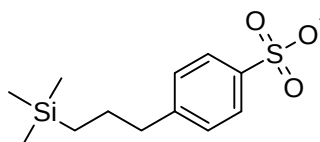


Figure 6: Propylbenzenesulfonyl stationary phase on silica

2.2.2 Metal salt doping of stationary phase

The choice of metal salt to dope the silica gel was found to be important. A range of copper, iron and one nickel salt were examined. Those soluble in fuel were found not to be suitable as they eluted from the column with the fuel rather than being retained, Table 1. Ideally the salt needed to be completely retained on the column to allow formation of the MDA complex from the low concentration of MDA in the fuel. Large volumes of fuel were required to pass through the column to allow sufficient MDA –salt interaction to form the coloured metal complex.

The concentration of metal salt was also found to be important. Experiments were conducted where increasing concentrations of copper salts were dosed onto the silica. It was observed there was both an upper and lower effective limit.

If too high a concentration of metal salt was used, the doped silica gels colour was too strong to observe the colour change on formation of the MDA complex. If the metal concentration was too low then there was insufficient available metal to form sufficient quantity of metal complex to be observed visually.

The polyvalent metal ions were doped onto silica gel through a process of adsorption where the metal ion reacts with the surface silanol groups in the bulk silica gel[9].

Table 1: Metal salt characteristics

Copper Salt	Retention characteristics	Colour change with addition of MDA
Copper naphthenate	Complete elution with fuel front	
Copper acetate $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$	Some elution	Blue – red/purple
Copper sulfate	Suitable retention	Blue – purple
Copper acetylacetonate $[\text{CH}_3\text{COCH}=\text{C}(\text{O}-)\text{CH}_3]_2\text{Cu}$	Not suitable, salt eluted with fuel	
Copper metal (powder)	No visible colour formation	
Iron chloride FeCl_3	Good retention. Gave false positives	Yellow – dark brown
Iron caprate	Complete elution with fuel front	
Nickel chloride	Suitable retention.	White – yellow (low concentration MDA Yellow – red high concentration MDA

2.2.3 DSTO open column silica tube

A small diameter open column tube was filled with alternating bands of metal doped and undoped silica gel. The open column tubes were 1.5 ml polypropylene solid phase extraction reservoirs with frits to contain the silica at top and bottom of the tube, Figure 7. The polypropylene tubes were not completely transparent. The alternating bands were used to assist with observing the colour formation of the MDA complex by contrasting it against the white of the non reactive undoped silica. It was noted that high concentrations of MDA would tend to display colour formation in the lower band, while lower concentrations would only form colours in the top band. These observations lead to a useful semi-quantitative assessment technique.

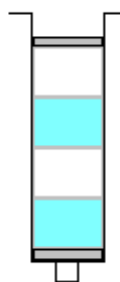


Figure 7: MDA test tube showing alternating layers of metal dosed vs. normal silica

To ensure sufficient MDA was passed through the column to allow formation of visible colours the method was developed based on 100 ml aliquots of fuel. Tubes showing the elution of 100 mls of fuel with varying concentrations of MDA are given in Figure 8. For dilute concentrations of MDA multiple 100 ml aliquots could be passed through the column. It was observed that for 0.5 ppm MDA a visually detectable colour formation occurred after 400 mls of fuel had been passed through the column, Figure 9. It was found that the best colour definition was obtained when observing the column still fuel wetted.

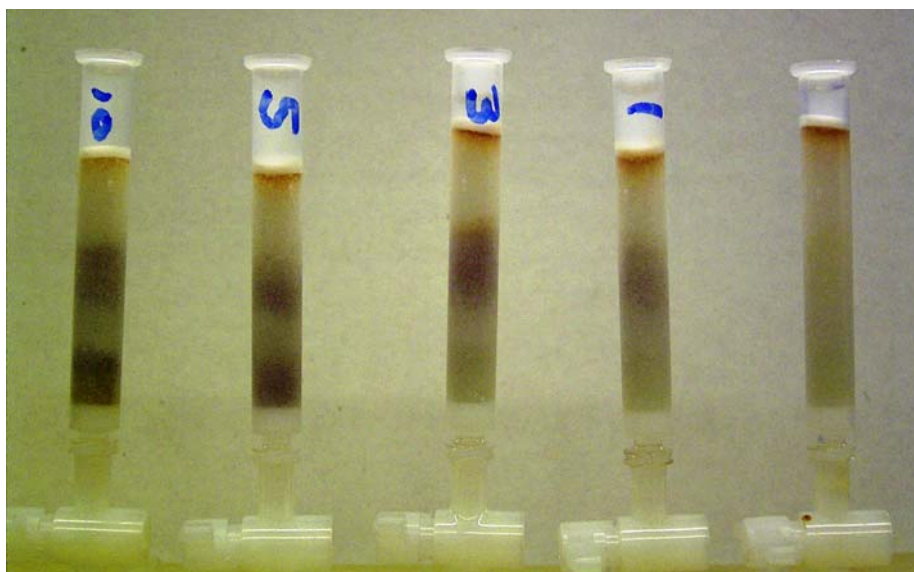


Figure 8: Copper-MDA 0.07 – 0.15 mm grade silica colour formation in test columns after 100 mls of fuel has passed through each column. The concentration of MDA in each 100 ml aliquot was from left to right 10, 5, 3, 1, 0 ppm

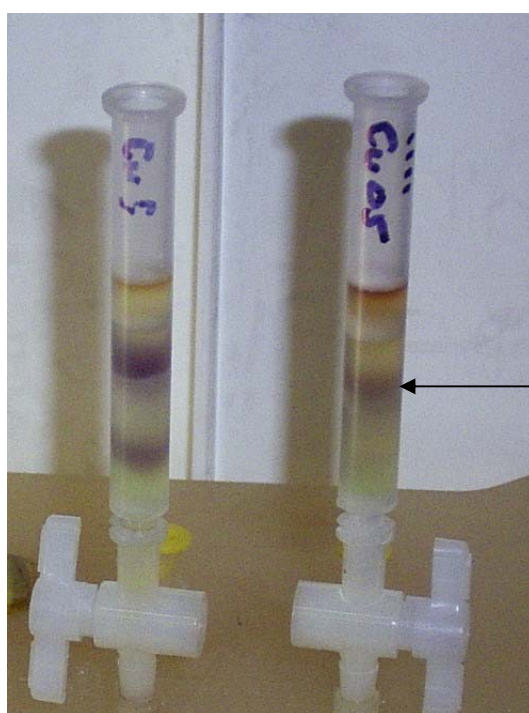


Figure 9: Copper – MDA 200 – 425 mesh 60A silica left = 5 ppm MDA x 100 ml fuel, right = 0.5 ppm MDA x 400 ml fuel

Both copper and nickel MDA salts were prepared and their molar absorptivities determined at the wavelengths that gave maximum absorbance. The molar absorptivities indicate how intense the colour will be in the visual wavelengths, Table 2.

Table 2: *Metal Chelate Molar Absorptivity for Copper and Nickel ligands*

Ligand	Molar Absorptivity, ϵ , in CH_2Cl_2 ($\text{L mol}^{-1} \text{cm}^{-1}$)	Molar Absorptivity, ϵ , in CH_2Cl_2 ($\text{L mol}^{-1} \text{cm}^{-1}$)	Molar Absorptivity, ϵ , in CH_2Cl_2 ($\text{L mol}^{-1} \text{cm}^{-1}$)	Visual colour in 1 cm cuvette
Copper-MDA	$\lambda_{365} = 10980$	$\lambda_{564} = 384$		Indigo-violet
Nickel-MDA	$\lambda_{315} = 9326$	$\lambda_{403} = 7850$	$\lambda_{540} = 145$	Red in concentrations > 3000 ppm, Yellow in dilute solutions

2.2.4 MDA metal complex elution

It was observed that at high concentrations of MDA in the test fuel the copper-MDA complex would tend to elute from the band of metal doped silica gel, Figure 10. This effect was less prominent when lower concentrations of MDA were used. The elution properties of the copper and nickel MDA complexes was examined in a range of solvents as shown in Table 3. It was observed that both the nickel and copper MDA complexes eluted with methanol but had very little elution with all other solvents tested.

Table 3: *Retention characteristics of metal-MDA compounds*

Solvent	Nickel-MDA, Rf	Copper-MDA, Rf	MDA, Rf
Methanol	0.84	0.79	0.64
Heptane	0	0	0.18
Toluene	0.01	0.01	0.30
(20:80) toluene: heptane	0.01	0.01	0.16
Jet A1	0.01	0.01	0.17

Rf = Chromatographic response factor = distance compound elution / solvent front

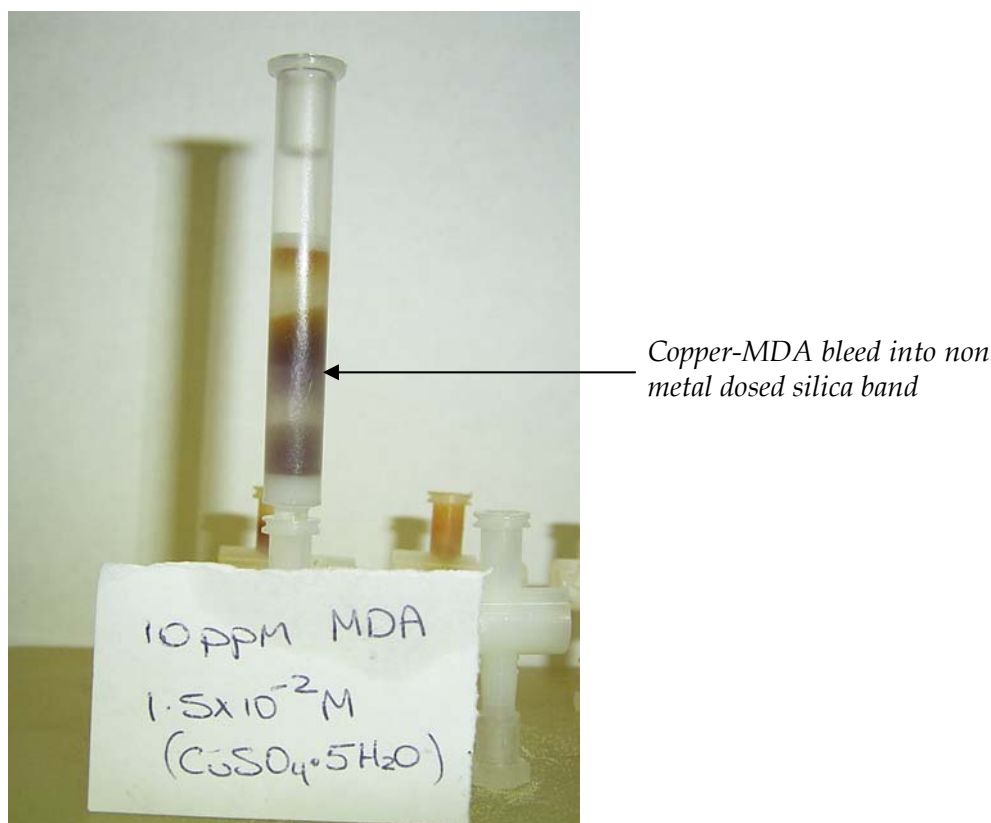


Figure 10: Copper-MDA test column showing 'bleed' of copper-MDA compounds through tube

3. Discussion

One shortcoming of the DSTO test is that the method relies on the MDA being present in solution and that it has not been consumed by reacting with metal species in the fuel in storage or adsorbed to the fuel system and storage facilities. As noted care must be taken in the laboratory when undertaking quantitative determination of MDA in fuel to ensure MDA does not transfer to glassware and pipette surfaces.

Fuels that have been stored for an extended duration that contain the MDA additive may have a decreased concentration of the additive in solution. This effect has not been examined. This is not expected to be an issue for fuels containing the thermal stability additive due to current fuel management procedures requiring it to either be used or diluted in storage.

The nickel-MDA test tube was not used in the final version of the test tube due to potential interference with yellow coloured bands observed on the silica tubes. The yellow colour formed even when the fuel contained no MDA, Figure 11. The yellow band occurred for all fuel types examined. Chemical analysis of the yellow band found a range of polar phenolic species. Many phenolic compounds will form yellow quinones and cycloketones when they oxidise. This is evident when a common phenolic antioxidant such as 2,6-di-tert-butyl-4-methyl phenol oxidises. Degradation products of phenolic antioxidants form yellow coloured

compounds. One such compound found in a yellowed sample was 2,5-cyclohexadiene-1,4-dione 2,6 bis(1,1 dimethylethyl). This compound imparts a strong yellow colour to the fuel. The silica will have a strong affinity for these polar species and will concentrate them on the column forming a yellow band as they are eluted through the column with the fuel.

It was observed that the silica gel may become translucent on contact with the fuel. This did not always occur but was observed to increase with fuel contact time. The silica gel becomes translucent as all air pockets in the loosely packed silica gel bed have been filled with fuel and the bed becomes homogeneous. The silica gel can be reverted to its original white appearance by draining all fuel from the tube with pressure assistance[10].

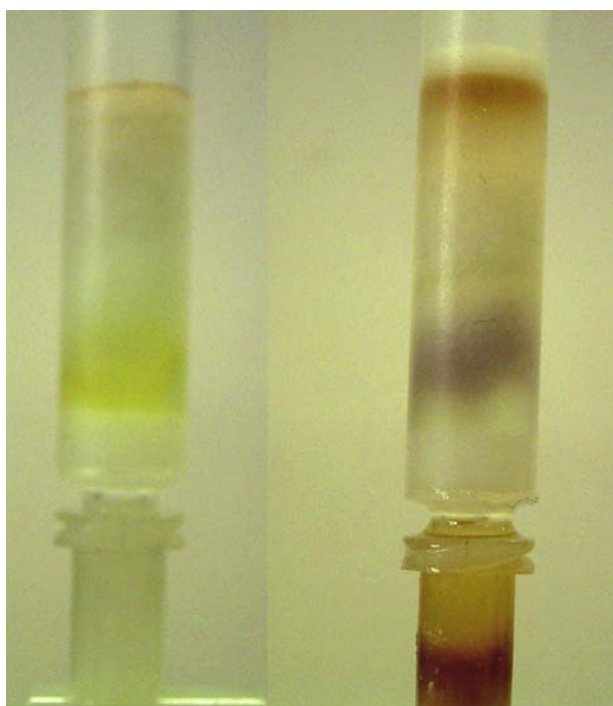


Figure 11: Comparison of test column zero MDA fuel vs. 5 ppm MDA in fuel. Note the strong yellow-green coloured band in the zero ppm MDA column on the left.

The particle size of the silica gel stationary support was found to strongly affect the intensity of the copper-MDA salt. When 100 – 200 mesh grade gel was used the colour formation was more diffuse as compared with the 200 – 425 mesh sized gel. The tubes in this set up have two layers of silica gel with the top layer having no copper salt. Note the yellow colour in the zero ppm MDA tube on the far left.

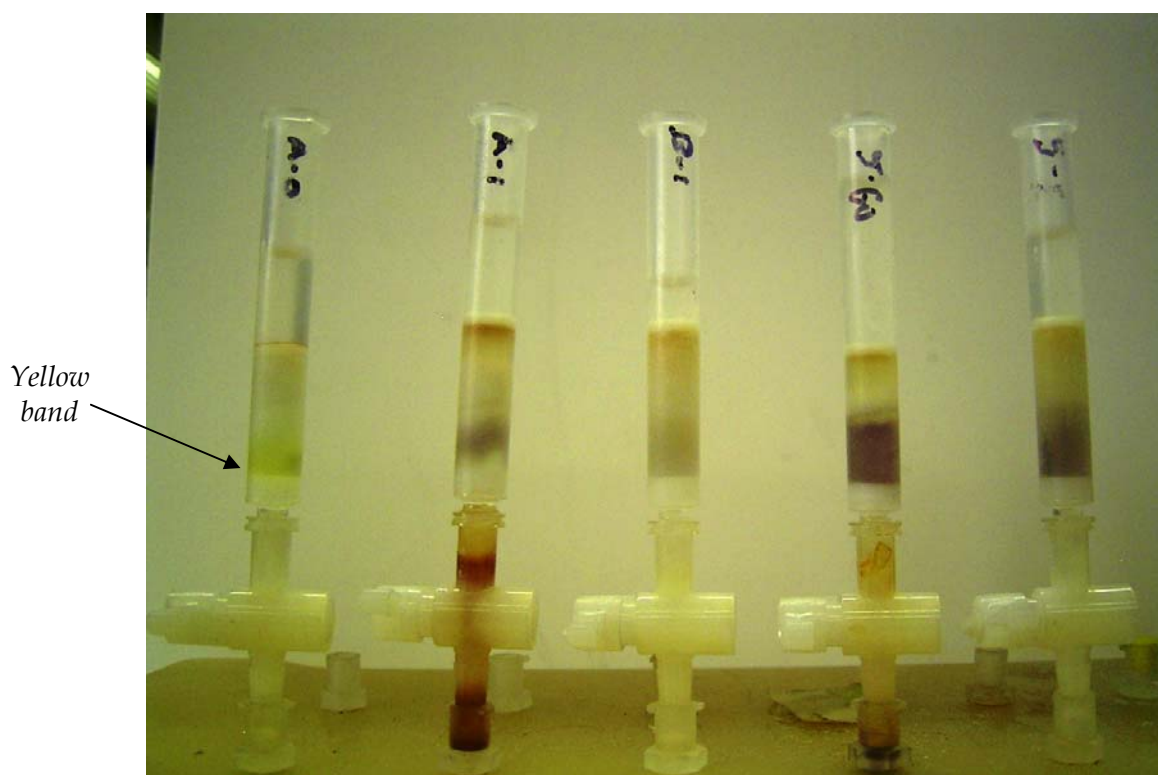


Figure 12: Comparison of MDA chelate colour intensity as a function of silica gel particle size. From left to right. 100 ml of fuel in all cases.

Photo test column ID	MDA, ppm	Silica
A-0	0	200 - 425 mesh 60A
A-1	1	200 - 425 60A
B-1	1	100 - 200 mesh
5-60	5	200- 425 mesh 60A
5-1	5	100 - 200 mesh

All ADF RAAF base laboratories are equipped to undertake gravimetric analysis of particulate material in fuel using ASTM D5452 "Particulate Contamination in Aviation Fuels by Laboratory Filtration". This method is often called the Millipore bomb test by RAAF fuel laboratory staff. This equipment has an adapter that will fit the DSTO developed test tubes. Thus the DSTO MDA test method would require no extra equipment and minimal training for use at RAAF bases.

4. Conclusions

A technique has been developed that is suitable to qualitatively assess the presence of metal deactivator additive or the S-1749 thermal stability additive in jet fuel. The technique is suitable for use at ADF RAAF bases or locations where a standard Millipore bomb filtration test is conducted. The method is suitable as a field technique utilising only a disposable syringe and the disposable test tube. The technique is capable of detecting the presence of MDA at concentrations down to 0.5 ppm in fuel.

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Appendix A: Tube Production

A.1. Method for Production of Indicating Gel and Field Test Tubes

1. The indicating gel used in the final version of the field technique is chromatography grade 200 – 425 mesh 60Å silica gel
2. The metal salts which have been successfully dosed onto the silica gel are
 - a. Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)
 - b. Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)
3. The silica gel and metal salt is added to a beaker by dry mass and stirred in 50 ml methanol.
4. The weight ratio is 0.04 g metal salt to 18 g silica gel.
5. The mixture is stirred for 10 minutes then the methanol is filtered off and the metal doped silica gel is dried at 120°C for 2 hours before use.
6. The bulk prepared gel is stored in a desiccator.
7. To enable 100 ml aliquots of fuel to be tested a large volume empty syringe may be attached to the top of the test tube using an Alltech SPE syringe adaptor.

A.1.1 Sample tube

The sample tubes used were Alltech Extract Clean SPE 1.5 ml Reservoirs. The tubes are not completely transparent but were found suitable for development of the method and colours produced by as little as 0.5 pp, MDA were discernable.

The tubes are filled with alternating layers of dosed and non-dosed silica gel. With a containing frit at the top and bottom of the gel beds. An inline syringe filter may also be added to assist in eliminating any colour formation at the top of the silica bed when fuel is passed through the test tube.

Appendix B: Copper vs. Nickel Salt Colour Formation

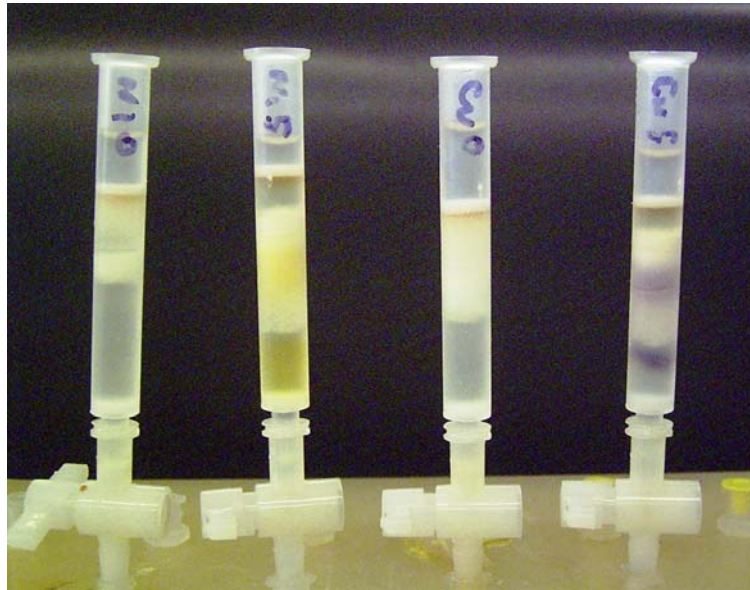


Figure 13: Tubes from left to right 0 ppm MDA Nickel, 5 ppm MDA Nickel, 0 ppm MDA copper, 5 ppm MDA Copper. Note the degree of silica becoming translucent in all of the tubes.



Figure 14: Comparisons of starting colours of tubes prior to test fuel. Tube layout identical to Figure 13.

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19. ABSTRACT Jet fuel may contain a range of additives to improve its thermal and storage stability. One additive is a Metal Deactivator Additive (MDA) which reacts with metal in the fuel to form a stable metal chelate. This metal-MDA chelate is no longer chemically able to catalyse degradation reactions in the fuel. A thermal stability additive used within NATO, designation S-1749, also contains MDA as an integral component. A method, suitable for use in the field or in RAAF fuel testing laboratories, was required to assist fuel management procedures by allowing qualitative assessment of the presence of the additive in fuel. A colourimetric technique was developed using copper dosed silica gel which forms a strong coloured reaction product when exposed to MDA. The test method was found capable of detecting MDA in fuel at concentrations down to 0.5 ppm. The method was suitable as a field technique as it requires only the test tube and a disposable syringe.					