Liquid chromatographic determination of copper speciation in jet fuel resulting from dissolved copper

Daniel B. Taylor and Robert E. Synovec*

Department of Chemistry, BG-10, University of Washington, Seattle, WA 98195 (USA)

ABSTRACT

A method involving a dual normal-phase/ion-exchange mechanism, preconcentration and separation of copper cyclohexanebutyrate, copper tetramethylheptanedionate and N,N'-disalicylidene-1,2-propylenediaminocopper on the polymeric stationary phase poly(vinyl alcohol) using a ternary gradient of 2-propanol, acetonitrile and 10 mM KCF$_3$SO$_3$ in methanol was developed. Copper compounds with formation constants of 10^{20} or greater in water were retained via a normal-phase mechanism, whereas copper compounds with formation constants of 10^{15} or less were retained via an ion-exchange mechanism. The method was used to characterize and to determine copper compounds with a limit of detection of 10 μg/l. The developed method was used to monitor the five classes of copper complexes formed when jet fuel samples with and without DuPont Metal Deactivator (DMD), the active ingredient of which is N,N'-disalicylidene-1,2-propylenediamine, were placed in contact with a metallic copper surface.

INTRODUCTION

Scientists in a number of fields including marine chemistry [1–4], biochemistry [5], environmental chemistry [6], food chemistry [7] and medicinal chemistry [8] are interested in the development of methods capable of yielding information about the speciation of metals in solution. It is believed that methods capable of yielding information about metal speciation, where the speciation of a metal is defined by the ligands associated with the metal ion, will be useful in the study of properties such as catalytic activity, transport mechanisms, bioavailability and mobility of metals in systems [9–12]. Methods that determine the speciation of metals in solution will ultimately lead to a better understanding of the chemistries that involve those metals than is possible by methods that simply determine the bulk concentrations of those metals. The coupling of high-performance liquid

chromatography (HPLC) with element-specific detection is one technique that has been used to gain information about the speciation of metals dissolved in aqueous [1,2,4] and non-aqueous systems [13,14].

The speciation of metals in petroleum is not generally determined; only the metal bulk concentrations are traditionally determined [15–17]. Metal complexes have been shown to poison catalysts [15] and act as catalysts in the autoxidation of finished petroleum products [18–23]. The ability to determine the speciation of a metal in solution will permit the investigation of not only metal ions, but also of the specific metal ligand complexes responsible for the degradation of fuel and gasoline. Specifically, a method is needed that can determine the concentrations of the copper compounds present in hydrocarbon matrices. Such a method would allow the determination of the identity of the specific copper ligand complex that decreases the thermal stability of finished petroleum products.

While striving to develop a method for determining the speciation of copper in jet fuel, it

_____
* Corresponding author.

became evident that the chromatographic techniques periodically reported for determining the speciation of metals in aqueous systems could not be used [1,2,5,7]. Jet fuel is much less polar than water and is immiscible with the mobile phases traditionally used with reversed-phase separations. Because copper compounds are more polar than the petroleum matrix in which they are dissolved, one can reason that it should be possible to separate the copper compounds using normal-phase chromatography. A stationary phase that retains the copper compounds without inducing the dissociation of the ligands from the copper ion is needed if one is to gain information about copper speciation. The ideal stationary phase for the normal-phase separation of the copper complexes in jet fuel would be polar enough to retain the copper complexes, but the polar groups would have a very low affinity for copper ions. Every polar stationary phase has a threshold that is a function of its propensity to release H^+ ions and to complex with copper ions. Strongly bound copper complexes, those with formation constants, K_f, sufficiently greater than the threshold of the stationary phase, will be retained via a normal-phase mechanism and the copper complexes will be eluted intact by polar solvents. Copper complexes with formation constants below the threshold of the stationary phase will dissociate into copper ions and ligand ions as they interact with the stationary phase. The copper ions will be retained via an ion-exchange mechanism. The copper can then only be eluted by adding an ion-pairing agent or additional cations to the eluent.

The search for a suitable stationary phase revealed that copper could not be eluted from alumina, a stationary phase used in normal-phase liquid chromatography [24], unless acid was added to the mobile phase [14]. The addition of acid to the mobile phase caused all the copper species to co-elute. The alumina retained all the copper compounds injected via an ion-exchange mechanism [14,25], indicating that alumina had a threshold greater than the formation constants of all the copper compounds tested. The formation constant for the most stable copper compound injected, copper Du-Pont Metal Deactivator (CuDMD), was 10^{21} in

water [26]. This is not to say that 10^{21} described the formation constant of CuDMD in 2-propanol or hexane, the solvents used, but that the relative relationship between the formation constants of different copper compounds should remain nearly constant when the compounds are in a solvent system other than water.

Although alumina was not satisfactory for preserving copper speciation, it does provide a useful reference point against which polar polymeric stationary phases can be evaluated. Polymeric stationary phases offer advantages in the realm of preserving metal speciation because they are more covalent than alumina. The feasibility of preserving metal speciation on a polymeric stationary phase was investigated by Mackey [2,27], who found that even poly(styrene–divinylbenzene) (PS–DVB), a stationary phase thought to possess negligible ion-exchange properties, retained metal cations. The metal cations could only be eluted by mobile phases modified with acids or ion-pairing agents.

In a previous report, an investigation with the polymeric stationary phase polyvinylpyrrolidone (PVP) for the separation of copper species was described [14]. A column was packed with PVP particles, a fairly novel stationary phase, that enabled two classes of copper compounds in a petroleum matrix to be separated. Unfortunately, the particles were not engineered for HPLC and were very sensitive to the amount of water in the eluent. The efficiency of the column packed with PVP was not as high as the efficiencies provided by most commercially available HPLC columns.

Recent investigations with the stationary phase poly(vinyl alcohol) (PVA) [28] have indicated significant improvements relative to the previously reported method using PVP [14]. The PVA stationary phase has been specifically "engineered" for chromatography, which has led to a higher efficiency column. PVA columns have been utilized in the micelle exclusion separation of heavy metals [29] and in the determination of the speciation of arsenic compounds in marine life [4], but no one has reported the suitability of PVA for the separation of copper compounds. The alcohol groups of the PVA polymer should make the stationary phase polar enough to retain the copper complexes when the mobile phase is

non-polar. The non-polar components in jet fuel should act as a non-polar mobile phase that is unretained by PVA when a jet fuel sample is injected. Given the observation by Mackey [2,27] that PS–DVB exhibited ion-exchange properties, one should carefully consider the likelihood that PVA will exhibit ion-exchange behavior. Further, alumina acts as a cation exchanger at pH 7.6 [30]. The cation-exchange behavior of PVA has not been evaluated. It is less likely that PVA will act as an ion exchanger and cause the copper complexes in the fuel to dissociate, as reversible proton exchange on PVA is not favored. PVA should be more suitable than alumina or PS–DVB for the separation of copper complexes in jet fuel.

A liquid chromatographic method, consisting of the preconcentration and separation of a group of standard copper compounds, was developed utilizing PVA as a stationary phase. Solutions of copper compounds with a range of formation constants were analyzed by the method to determine the speciation/ionization threshold of PVA for copper. The threshold determined the minimum formation constant value required to keep the native ligands associated with copper ion when copper compounds were exposed to PVA. The developed method was then used to determine the concentrations of the copper species formed when jet fuel samples, with and without DMD added, were exposed to copper metal. Grabel and Nowack [22] determined the bulk concentration of copper solvated by jet fuel exposed to metallic copper, but made no attempt to determine the copper complexes formed in the jet fuel. No one has addressed the issue of how a copper atom is transformed from the metallic state to a copper(II) complex in jet fuel. Assignments of the ligands associated with the solvated copper were made based on the retention times of the copper compounds used as standards.

EXPERIMENTAL

Reagents

N,N'-disalicylidene-1,2-propylenediamine, the active ingredient in DMD, potassium trifluoromethanesulphonate (KCF_3SO_3), copper cyclohexanebutyrate and copper dimethyldithiocar-

bamate were purchased from Pfaltz and Bauer (Waterbury, CT, USA), technical-grade copper naphthenate from Chem Service (West Chester, PA, USA), copper(II) tetramethylheptanedionate and analytical-reagent grade copper acetate from Aldrich (Milwaukee, WI, USA), copper powder from J.T. Baker (Phillipsburg, NJ, USA) and ACS reagent grade electrolytic copper foil from E.M. Science (Gibbstown, NJ, USA). No attempt was made to clean or modify the surface of either the copper foil or the copper powder. Copper organometallic standard (1000 $\mu g/g$) was purchased from SPEX Industries (Edison, NJ, USA). Because the copper naphthenate and cyclohexanebutyrate were of unknown purity, solutions of all three carboxylates were made and the copper content was determined by flame atomic absorption spectrometry (FAAS). Baker analyzed HPLC reagent grade 2-propanol, acetonitrile and hexane were purchased from J.T. Baker. The jet fuel analyzed was provided by the Fuels Research Branch at Wright-Patterson Air Force Base (Dayton, OH, USA).

Column

The column was a 100 mm × 7.5 mm I.D. Asahipak GS-510M column packed with 9-μm PVA particles made by Asahi Chemical Industry and purchased from Keystone Scientific (Bellefonte, PA, USA).

Apparatus

The HPLC system was a Dionex BioLC system with a variable-wavelength absorbance detector. The system provides a metal-free eluent flow path which ensured no sample contamination by the chromatographic system and a low baseline. The HPLC system was coupled to the FAA spectrometer by connecting the variable-wavelength absorbance detector outlet tubing to the FAA nebulizer with an 18-gauge blunt-tipped needle and 20-gauge Teflon tubing. A Perkin-Elmer (Norwalk, CT, USA) Model 403 FAA spectrometer with a manual controller, a spoiler nebulizer and a 10.5-cm three-slot burner was used as an element-specific detector. The operating conditions for FAAS are given in Table I.

TABLE I

FLAME ATOMIC ABSORPTION SPECTROMETRIC OPERATING CONDITIONS

Lamp current	15 mA
Slit	1 mm, 0.7 nm
Wavelength	326.4 nm
Flame	Air–acetylene
Air–acetylene flow-rate ratio	1.5/1.0
Nebulizer type	Spoiler
Burner type	10.5 cm, three-slot

Mobile phase program

The trace in Fig. 1a shows the mobile phase program delivered by the solvent programmer which was used to separate the copper complexes. The solvent programmer delivered 2-propanol for the first 10 min of the run with a 50-μl or 1.00-ml sample injection at 0.5 min. A linear gradient from 100% 2-propanol to 100% acetonitrile was delivered by the solvent programmer between 10 and 15 min. The solvent programmer delivered a linear gradient from 100% acetonitrile to 100% 10 mM KCF$_3$SO$_3$ in methanol
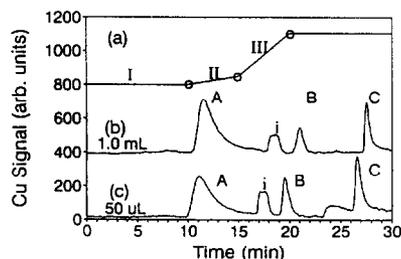

Fig. 1. (a) Solvent program: (I) 0 to 10 min, 2-propanol; (II) 10 to 15 min, gradient from 100% 2-propanol to 100% acetonitrile; (III) 15 to 20 min, gradient from 100% acetonitrile to 100% 10 mM KCF$_3$SO$_3$ in methanol; a mobile phase of 10 mM KCF$_3$SO$_3$ in methanol was delivered for the duration of the separation on PVA. After the separation was complete the mobile phase is switched directly to 2-propanol. The flow-rate was 1.0 ml/min. (b) Separation of a 1.00-ml injection volume containing (A) 200 ppb of Cu complexed with DMD. (B) 100 ppb of Cu complexed by dimethyldithiocarbamate and (C) 170 ppb of Cu complexed with cyclohexanebutyrate. (c) Separation of a 50-μl injection containing (A) 3750 ppb of Cu complexed with DMD, (B) 1840 ppb of Cu complexed with dimethyldithiocarbamate and (C) 3100 ppb Cu complexed with cyclohexanebutyrate. Peak i in both chromatograms is due to an impurity in the DMD. Detection was accomplished by FAAS; see Table I for details.

from 15 to 20 min and then held the solvent composition at 100% 10 mM KCF$_3$SO$_3$ in methanol for the duration of the separation.

Data acquisition, control and quantitative analysis

The data acquisition and system control were done using an IBM (Boca Raton, FL, USA) AT computer with an IBM DACA board. The data acquisition and system control software was written in-house using Microsoft Quick Basic (Microsoft, Bellevue, WA, USA). Copper in jet fuel samples was determined using peak areas for known concentrations of CuDMD and copper cyclohexanebutyrate. For peaks eluting before 24 min CuDMD was used as the standard, and for those after 24 min copper cyclohexanebutyrate was used.

RESULTS AND DISCUSSION

A separation of standard copper compounds was developed using the PVA column and a solvent program. The standard copper compounds included CuDMD, copper dimethyldithiocarbamate and copper cyclohexanebutyrate. A separation of the standard copper compounds and the solvent program used to affect that separation are shown in Fig. 1. The mobile phase program used to separate the copper compounds was developed by injecting solutions of the individual copper compounds on to the column under isocratic conditions with the different mobile phases to determine which mobile phase most effectively eluted the individual copper compounds. Fig. 1b and c show the separation of mixtures of the standard copper compounds. The solvent programmer delivered 2-propanol for the first 10 min of the run. Initially, we shall consider the separation using a 50-μl injection volume (Fig. 1c). The 2-propanol eluted the peak labeled A, CuDMD, at 11 min. 2-Propanol was a suitable initial solvent because it eluted non-polar compounds such as CuDMD. 2-Propanol was miscible with non-polar solvents such as hexane and jet fuel and also polar solvents such as acetonitrile and methanol. When jet fuel samples were injected, the 2-propanol eluted all the non-polar components in the fuel.

The peak at 17.5 min is due to an impurity in the DMD. The peak labeled B in Fig. 1c, eluting at 20 min, was copper dimethyldithiocarbamate. The copper dimethyldithiocarbamate was eluted by the linear gradient from 100% 2-propanol to 100% acetonitrile delivered by the solvent programmer between 10 and 15 min. The 5-min difference in the elution time of 20 min and the linear gradient ending at 15 min was due to the combination of the dead volumes of the column and tubing connecting the solvent programmer, pump, injection valve, UV absorbance detector, FAAS detector, the gradient system delivery response rate and the pump flow-rate. The last peak in Fig. 1c, labeled C, was copper cyclohexanebutyrate, which was eluted by the linear gradient from 100% acetonitrile to 100% 10 mM potassium trifluoromethanesulphonate in methanol delivered by the solvent program between 15 and 20 min. The programmer delivered 100% 10 mM KCF_3SO_3 in methanol for the duration of the separation to be certain that any compounds retained by an ion-exchange mechanism on the PVA were eluted.

As the mobile phase program was being developed, the copper compounds were found to elute earlier as the mobile phase became more polar, suggesting that the copper compounds were indeed retained by a normal-phase mechanism. This was important because one does not want the non-polar components in the jet fuel to disrupt the separation of the polar copper compounds when a jet fuel sample was injected. The polarity of a copper compound is defined by the portion of the ligand that binds the copper ion. The region of the ligand that binds to the copper has a permanent dipole and is capable of hydrogen-bonding. Thus, the portion of the ligand that binds to the copper determines how strongly the copper compound is retained by the stationary phase. The separation in Fig. 1c of the three copper compounds used as standards is an indication the speciation of the copper compounds was being preserved. If the copper compounds had dissociated, all the copper compounds would have eluted at the same time. To determine whether the separation could be used to differentiate between copper compounds with similar binding groups, solutions of copper acetate and

copper naphthenate were injected as well as a dilution of a SPEX organometallic copper standard containing a copper sulphonate and a solution of copper(II) tetramethylheptanedionate. All these copper compounds were strongly retained by the PVA stationary phase and required the addition of KCF_3SO_3, an ion-pairing reagent, to the mobile phase to elute the copper. The copper from solutions of all these compounds eluted at the same time as the copper cyclohexanebutyrate (27 min). The absorbance of the eluent at 300 nm was monitored for all the separations. The copper peak eluting at 27 min did not absorb at 300 nm while the solutions of the individual copper compounds did absorb at 300 nm, which led us to the conclusion that the more strongly retained copper compounds, the copper carboxylates, copper sulphonate and copper(II) tetramethylheptanedionate, were indeed dissociating as they were absorbed on the PVA and the copper was eluting as $Cu(CF_3SO_3)_2$.

One of the consequences of having a polar copper ligand bond is that as the bond becomes more ionic in character, the species become capable of existing as separate ions. This is evidenced by the small formation constant of copper cyclohexanebutyrate listed in Table II. The formation constants of the five copper compounds eluting at 27 min are less than or equal to 10^{15}. PVA appears to have a threshold for displacing ligands from copper compounds with K_f values in water between 10^{15} and 10^{20}. The ion-exchange retention of copper compounds by polymeric stationary phases is in agreement with the results reported by Mackey [2,27], who found that even PS–DVB stationary phases exhibit ion-exchange characteristics.

The limit of detection for the method was 160 ppb of copper as CuDMD when the volume injected was 50 μl. A detection limit of 20 ppb or less was needed if the technique was to be useful in the determination of the concentrations of the copper species that could cause fuel instability. One way to lower the detection limit was to use on-column preconcentration. With a normal-phase retention mechanism, on-column preconcentration involved injecting a large volume of non-polar sample, which acted as a non-polar mobile phase, causing the copper com-

TABLE II

FORMATION CONSTANTS IN WATER AND LIMITS OF DETECTION (LOD) FOR COPPER COMPOUNDS

Species	Log K_f [26]	Concentration LOD (μg/l Cu)		Mass LOD (ng CU)
		50 μl	1.0 ml	
CuDMD	21	162	10	10
Cu dimethyldithiocarbamate	29	198	16	16
Cu cyclohexanebutyrate	3	168	10	10
Cu tetramethylheptanedionate	15	$-^a$	$-^a$	$-^a$

^{a} Not measured.

pounds to be strongly retained by the stationary phase and focused on to a much smaller volume on the column. The copper compounds were then eluted by a polar mobile phase as narrowed peaks, and the limit of detection was improved by the ratio of the injection volumes as long as the peak widths did not substantially increase. The chromatograms in Fig. 1b and c show that the peak width was not substantially increased, but remained at approximately 1.5 ml for all the species except CuDMD, when the injection volume was increased by a factor of 20 from 50 μl to 1.00 ml. Table II shows the 3σ limits of detection for the technique were lowered by a factor of 16 from 160 to 10 ppb of copper as CuDMD with a 1.00-ml injection loop using on-column preconcentration [31]. The time shift between the two chromatograms in Fig. 1b and c was produced by the difference in injection volumes. An additional *ca.* 1 min was required for the solvent program to travel through the injection loop when the volume was increased from 50 μl to 1.00 ml.

Once the separation had been developed, the detection limit had been lowered to a suitable level using on-column preconcentration and the reproducibility of the separation had been demonstrated, the method was used to characterize the copper dissolved by a jet fuel sample exposed to copper metal. The observation that copper metal is solvated by jet fuel has been reported by Grabel and Nowack [22], who monitored the bulk concentration of copper solvated by jet fuel. The method described above was used both to monitor the concentrations of the

copper species formed and to gain information about their speciation as a function of the number of days the jet fuel had been exposed to metallic copper. Fig. 2a shows a summary of the
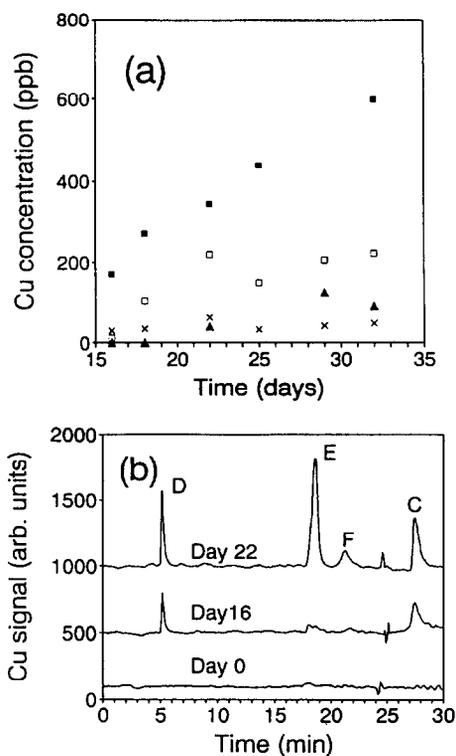

Fig. 2. (a) Concentrations of the copper complexes formed in 30 ml of JP8-S15 as a function of the number of days the fuel has been exposed to 0.2 g of copper powder. × = peak D in (b); □ = peak E in (b); ▲ = peak F in (b), ■ = peak C in (b). (b) Representative chromatograms of the same samples as in (a) for the number of days given. The disturbance between 24 and 25 min is explained in the text.

concentrations of the copper species in the jet fuel sample as a function of the time the fuel sample had been in contact with copper powder. The emergence of several classes of copper compounds in Fig. 2a indicates that more than one copper species is formed in the fuel. The presence of more than one peak also indicates the presence of several ligands native to the fuel capable of complexing the copper. The increasing concentrations of the classes of copper in Fig. 2a is an indication that the copper powder is being dissolved by the jet fuel.

Fig. 2b shows three representative chromatograms of a jet fuel sample that had been standing over copper powder for the number of days indicated. The chromatogram of the jet fuel before it had been exposed to metallic copper, day 0, does not show an appreciable amount of copper. This was confirmed when the fuel was analyzed by FAAS directly. After the jet fuel had been exposed to the metallic copper for 16 days, Fig. 2a shows the fuel had solvated 200 ppb copper as two different species. An amount of 170 ppb of copper was solvated as the complex eluting as the peak labeled C. Based on our copper standards we can speculate that this species had a binding group similar to a carboxylate or at least the K_f of the copper complex formed was less than 10^{15}. An amount of 28 ppb of copper was solvated as the peak labeled D eluting at 5 min. The early elution time of peak D is an indication that the copper compound is less polar than any of the standards. Peak E was just above the detection limit of the method on day 16. Fig. 2b indictes that after the fuel had been exposed to copper for 22 days, significant concentrations of all four of the copper species reported in Fig. 2a had been solvated by the fuel. The lack of a peak at 11 min, as in peak A in Fig. 1b, indicates that the jet fuel sample had not been treated with DMD. Based on the retention time of the copper dithiocarbamate standard, peak B in Fig. 1b, one can speculate that peak F in Fig. 2a is due to a copper complex with ligands with chemical functionalities similar to a dithiocarbamate, resulting in the formation of a copper complex with a polarity similar to that of copper dithiocarbamate. The very narrow disturbance at 24 min in the three chromato-

grams was an artifact of the solvent program. Between 24 and 25 min was the region when the potassium trifluoromethanesulphonate and methanol first reached the detector and were aspirated by the nebulizer. The flame characteristics changed owing to the transition from acetonitrile to methanol and the combustion of the potassium yielded an intensely orange flame. The binding functionalities of the ligands of the classes of copper compounds labeled D and E in Fig. 2 are unknown. The ligands attached to copper having these retention times would have to be determined by mass spectrometry or some other technique capable of yielding information about the ligands.

The data shown in Fig. 2 demonstrated the feasibility of using the developed method to differentiate between the copper complexes in jet fuel and monitor their concentrations. The method was then used to characterize the copper complexes formed when a jet fuel sample treated with DMD was exposed to copper foil. The active ingredient in DMD was added to an aliquot of the same fuel used in the study in Fig. 2 near the maximum concentration allowed by the US Air Force [32]. The fuel with added DMD was then placed in a polyethylene bottle with a strip of copper foil. Aliquots of the fuel were withdrawn and analyzed to monitor the solvation of copper by the fuel. Fig. 3 summarizes the results of the study of the fuel treated with DMD and exposed to copper foil. Fig. 3a shows chromatograms from injections of the aliquots of fuel treated with DMD and exposed to copper foil. The most prominent feature of the chromatograms in Fig. 3a is the peak labeled A, the peak due to the CuDMD complex. The peak due to the CuDMD complex increased with the time the fuel was exposed to copper until all the DMD was consumed, as shown in Fig. 3b. A comparison of the shape of peak i in Fig. 3a with the peak labeled i in Fig. 1b and c suggests the peak is due to an impurity in the DMD. The increase in the ratio of the height of the impurity peak to the height of the CuDMD peak in the chromatogram for day 17 compared with that for day 10 suggests the DMD has either a higher binding constant than the impurity, but not excessively higher, or a difference in the rate of
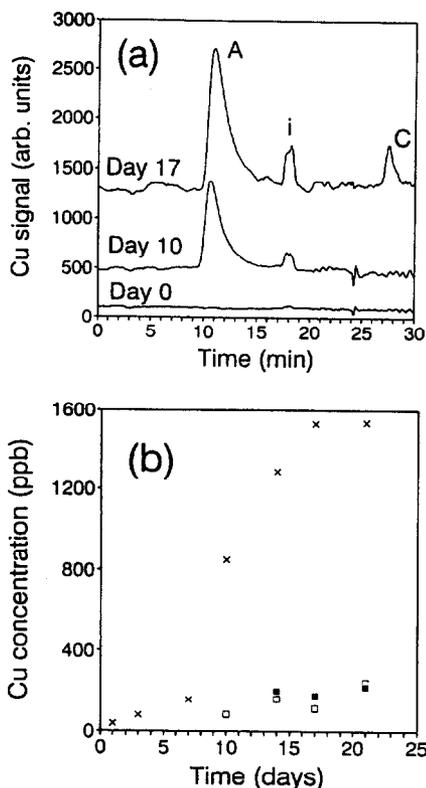
Fig. 3. (a) Representative chromatograms of 16 ml of JP8-S15 with 6.3 mg/l of DMD exposed to 0.3 g of copper foil for the number of days given. Peak A is CuDMD, peak i is a copper complex formed by copper and an impurity in DMD and peak C is due to copper with weakly bound ligands. (b) Concentrations of the copper species formed in the jet fuel as a function of the number of days the fuel was exposed to copper foil. × = peak A in (a); □ = peak i in (a); ■ = peak C in (a).

copper complex formation between DMD and the impurity. The binding constant of the CuDMD complex is given in Table II.

Fig. 3b indicates that peak C in Fig. 3a was only present once the DMD in the fuel sample had been consumed. Peak C was not present until the DMD had been consumed, indicating that DMD has a higher binding constant than the ligands native to the fuel; therefore, all the copper solvated by the jet fuel was complexed by the DMD ligand as long as there was uncomplexed DMD. Once all the DMD had been consumed, the additional copper solvated by the fuel was complexed by native ligands in the fuel. Based on the retention times of the standards

used to develop the separation, one can speculate that peak C in Fig. 3a is due to a carboxylate or other potential native ligand in the fuel, forming a copper complex with a K_f value less than 10^{15}.

It is interesting to consider Figs. 2 and 3 and to compare the copper species formed when a jet fuel sample without DMD was exposed to copper with the copper species formed when the same fuel was treated with DMD and exposed to copper. The fuel not treated with DMD solvated four different classes of copper compounds, while most of the copper solvated by the fuel treated with DMD was complexed by the DMD or the impurity in the DMD. A comparison between the species formed and the concentrations of solvated copper in the two studies should not be attributed solely to the presence of DMD, because the physical forms of the copper used in the two studies were different. In the study summarized in Fig. 2 the jet fuel was standing over copper powder and in the study in Fig. 3 the jet fuel was standing over copper foil.

In order to gain a better understanding of how the physical form of the copper affected the concentration of copper solvated by the fuel and the copper species formed in the jet fuel, 140 ml of jet fuel were treated with 3.1 mg/l of DMD and placed over copper in two physical forms. Half of the treated jet fuel was placed over copper powder and the other half over an equivalent mass of copper foil. The DMD-treated fuel over copper foil solvated 700 ppb of copper as CuDMD in 12 days, which was sufficient copper to consume all the DMD added to the fuel, whereas the fuel over copper powder solvated only 160 ppb of copper as DMD in 17 days. The same species, CuDMD and the Cu peak due to the impurity in the DMD, were formed in both aliquots of jet fuel. This observation is contrary to what would be expected on the basis of the surface areas of the two physical forms of copper. One explanation for the difference in the concentrations of copper solvated by the fuels is the copper must be oxidized by the oxygen dissolved in the jet fuel to be solvated by the fuel. Only the copper atoms that jet fuel containing dissolved oxygen can circulate past are likely to be oxidized. The rigid structure of

the copper foil allowed the jet fuel to circulate past much of the copper, whereas the copper powder formed a pile in the bottom of the container and the jet fuel only circulated past the copper on the outer layer of the pile.

CONCLUSIONS

A method capable of distinguishing between several classes of copper compounds in jet fuel has been developed. The method offers significant improvements in chromatographic resolution over the previously reported method [14]. The increased chromatographic resolution facilitated the determination and characterization of five classes of copper compounds formed when jet fuel is exposed to metallic copper. The method is capable of determining copper at the concentrations that have reportedly caused fuel stability problems [18,19,22,23]. The method provides a valuable tool in the effort to determine the copper species responsible for catalyzing autoxidation in petroleum products and degrading fuel stability. The method could also be used to measure the effectiveness of potential metal deactivators by determining how well the active ingredients complex the metal ions.

ACKNOWLEDGEMENTS

REFERENCES

1 D.J. Mackey and H.W. Higgins, *J. Chromatogr.*, 436 (1988) 243.
2 D.J. Mackey, *J. Chromatogr.*, 236 (1982) 81.
3 A. Mazzucotelli, R. Frache, A. Viarengo and G. Martino, *Talanta*, 35 (1988) 693.
4 M. Morita and Y. Shibata, *Anal. Sci.*, 3 (1987) 575.
5 D. Behne, *Analyst*, 117 (1992) 555.
6 Y.K. Chau and P.T.S. Wong, *Fresenius' J. Anal. Chem.*, 339 (1991) 640.
7 G. Weber, *Anal. Chim. Acta*, 200 (1987) 79.
8 J.W. O'Laughlin, *J. Liq. Chromatogr.*, 7 (1984) 127.
9 Y.K. Chau, *Analyst*, 117 (1992) 571.
10 C.J. Cappon, *LC · GC*, 6 (1987) 584.
11 B.P. Karcher and I.S. Krull, *Trace Metal Analysis and Speciation (Journal of Chromatography Library*, Vol. 47), Elsevier, Amsterdam, 1991, p. 123.
12 E.M. Perdue, *Aquatic Humic Substances; Influence on Fate and Treatment of Pollutants*, American Chemical Society, Washington, DC, 1989, p. 281.
13 M.R. Danna, *Dissertation*, Michigan State University, East Lansing, MI, 1985.
14 D.B. Taylor and R.E. Synovec, *Talanta*, 40 (1993) 495.
15 A.J. Smith and C. Collins *At. Spectrosc.*, 8 (1987) 96.
16 J.H. Karchmer and E.L. Gunn, *Anal. Chem.*, 24 (1952) 1733.
17 J.L. Fabec, *Anal. Chem.*, 57 (1985) 208R.
18 C.J. Pederson, *Oil Soluble Complexing Agents as Metal Deactivators*, DuPont, Wilmington, DE, 1955.
19 *DMD and DMD-2 Petroleum Additives*, DuPont, Wilmington, DE, 1987.
20 R.H. Clark, in H.N. Giles (Editor), *Proceedings of the 3rd International Conference on Stability and Handling of Liquid Fuels*, 1988, p. 283.
21 Coordinating Research Council (Editor), *Literature Survey on the Thermal Oxidation Stability of Jet Fuel*, Vol. 509, CRC Inc., Atlanta, GA, 1979, p. 1, 53.
22 L. Grabel and C. Nowack, *CRC Jet Fuel Thermal Oxidation Stability Symposium, Los Angeles, CA*, CRC Inc., Atlanta, GA, 1977.
23 R.E. Morris and N.H. Turner, *Fuel Sci. Technol. Int.*, 8 (1990) 327.
24 G.L. Schmitt and D.J. Pietrzyk, *Anal. Chem.*, 57 (1985) 2247.
25 J. Michal, *Inorganic Chromatographic Analysis*, Van Nostrand Reinhold, New York, 1973, p. 75.
26 A.E. Martell and R.M. Smith, *Critical Stability Constants*, Vol. 3, Plenum Press, New York, 1977.
27 D.J. Mackey, *J. Chromatogr.*, 242 (1982) 275.
28 E.V. Hort, in *Kirk-Othmer, Encyclopedia of Chemical Technology*, Vol. 23, Wiley-Interscience, New York, 1978, p. 848.
29 T. Okada, *Anal. Chem.*, 60 (1988) 2116.
30 M. Tanaka, T. Ashizawa and M. Shikata, *Kagaku no kenkyo*, 5, *Inorg. Anal. Chem.*, (1949) 35.
31 B.F. Johnson, J. Bramlage and J.G. Dorsey, *Anal. Chim. Acta*, 255 (1991) 127.
32 *Military Specification Turbine Fuel, Aviation, Grades JP-4, JP-5 and JP-5/JP-8 ST*, MIL-T-5624N, 1989, ASD/ENES, Wright-Patterson Air Force Base, Dayton, OH.