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# INVESTIGATION OF THE EFFECTS OF TRACE METALS ON THE THERMAL STABILITY OF JP-7 FUELS

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Southwest Research Institute

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Air Force Systems Command  
Wright-Patterson Air Force Base, Ohio

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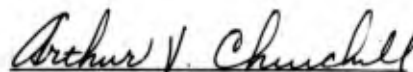
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## FOREWORD

This report was prepared by Southwest Research Institute, San Antonio, Texas, under Contract F33615-69-C-1231. The contract was initiated under Project 3048, "Fuels, Lubrication, and Fire Protection," Task 304805, "Aero Propulsion Fuels." The work was performed by contractor's personnel using Air Force facilities at Area B, Wright-Patterson AFB, Ohio. The program was administered by the Fuels Branch of the Fuels and Lubrication Division, Air Force Aero Propulsion Laboratory, Air Force Systems Command, Wright-Patterson AFB, Ohio. The Air Force project engineers during the report period were Mr. Gregory W. Gandee and Mr. Charles R. Martel (AFAPL/SFF).

This is a technical report covering work performed in one phase of the subject contract during the period from 1 December 1970 through 30 November 1971, including a summary of work performed previously. The report was submitted by the authors in December 1971. Contractor's identifying numbers are Project No. 12-2497 and Report No. RS-579.

This technical report has been reviewed and is approved.



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## ABSTRACT

Experimental studies have shown that trace amounts of fuel-soluble metal compounds can be very detrimental to JP-7, a high-quality jet fuel. Adverse effects on fuel thermal stability have been demonstrated by gas-drive fuel coker tests on JP-7 fuels containing as little as 15 to 25 parts per billion of added iron or copper, or 100 to 250 parts per billion of added zinc or lead. The true threshold concentrations were generally lower, since the added metal tended to disappear from fuel samples during storage and handling. The ambiguities in metal content hinder any clear correlation and make it impractical to recommend metal-content limits for fuel quality control.

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## SECTION I

### INTRODUCTION

It is well known that soluble metal compounds in hydrocarbon fuels can catalyze the high-temperature oxidation of the fuels and thus decrease the fuel's "thermal stability." Soluble copper compounds, which may remain in fuels after copper-sweetening processes, are especially harmful. Trace amounts of copper, iron, lead, and zinc may be picked up by fuel that comes into contact with certain materials used in fuel-handling systems. It should be expected that the most severe effects of contamination by metals will be observed in high-quality fuels that must meet severe stability requirements. It was shown in a previous study<sup>(1)\*</sup> that JP-7, a high-quality fuel consisting mainly of naphthenic hydrocarbons, can be degraded seriously by contact with steel, brass, bronze, or nitrile rubbers, all of which are present in most existing fuel-handling systems. In that study, the degradation in thermal stability was accompanied by measurable increases in dissolved metal concentrations in the parts-per-billion range: iron from bare steel, copper and zinc from brass and bronze, and zinc and lead from nitrile rubbers.

It appeared desirable to establish a correlation between dissolved metal contents and degradation of JP-7 thermal stability, independent of the possible effects of organic contaminants that may be leached from elastomers. If a clear-cut correlation could be established, it would be possible to set limits on the dissolved metal contents of fuels for quality control purposes, and also to use metal contents as a measure of contamination in investigating the compatibility of fuel-system materials.

The program described here was divided into three distinct phases. The first of these was the determination of the threshold level of each metal in JP-7 fuel, i.e., the lowest concentration at which thermal stability would be affected significantly. Some of this work has been reported previously<sup>(2,3)</sup> but is summarized here for completeness.

The second phase of the program was aimed at determining whether combinations of two or more contaminant metals have synergistic effects in degrading fuel quality. This question is of considerable practical importance, since fuel-handling systems will seldom contribute a single metal to the fuel.

The final phase of the program was a rather brief investigation to determine whether the threshold levels of metal content could be changed significantly by the use of antioxidants or metal deactivators.

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\*Superscript numbers in parentheses refer to the list of References at the end of this report.

## SECTION II

### TEST EQUIPMENT AND PROCEDURES

The effects of metals on fuel stability were measured by thermal stability tests in four gas-drive cokers. These were semiautomatic fuel cokers equipped with modified test sections conforming to current requirements of the Coordinating Research Council (CRC). In the early portion of the program, two of the cokers were equipped with stainless steel oxygen bottles as fuel reservoirs, rather than the standard CRC flanged-pipe reservoirs.

As will be noted from the flow diagram shown as Figure 1, the cokers in this program were operated *without* the in-line filter ahead of the test section that is used in the regular CRC configuration for gas-drive cokers<sup>(4)</sup>. This omission makes it possible to feed fuel directly from the reservoir to the test section without passing through any intermediate components, thus minimizing any possible cross-contamination effects from test to test. When operating without this in-line filter, the test fuel is prepared by first aerating and then prefiltering, i.e., the reverse of the usual order. The advantages of this operating scheme have been discussed previously.<sup>(2)</sup>

Midway in the test program, a sampling valve was installed in each coker immediately upstream of the test section, as shown in Figure 1. This valve was used to draw samples of influent test fuel for analysis. Such sampling became necessary when the early results indicated that the fuel composition (metal content) was changing during the fuel handling preparatory to running the actual test, so that metal analyses run at the time of fuel sample blending did not represent the amounts of metal actually "seen" by the fuel coker. Samples of the fuel drawn from the influent-line valve are a more reliable guide to the actual metal content.

All coker tests were run for 5 hours with a fuel flow rate of  $2.5 \pm 0.1$  pounds per hour. Coker warmup procedures were standardized so that the preheater and filter normally reached their respective test temperatures 15 to 20 minutes after startup. In the tests reported here, almost all warmup times fell between 13 and 23 minutes, with a few as long as 30 minutes.

Preheater tubes were rated after test in both unwiped and wiped conditions, using the standard Tuberator. The breakpoint of a given fuel is defined as the lowest preheater fuel-out temperature giving either an unwiped preheater tube rating of Code 3 or darker, or a filter pressure drop of 2.0 in. Hg or more.\*

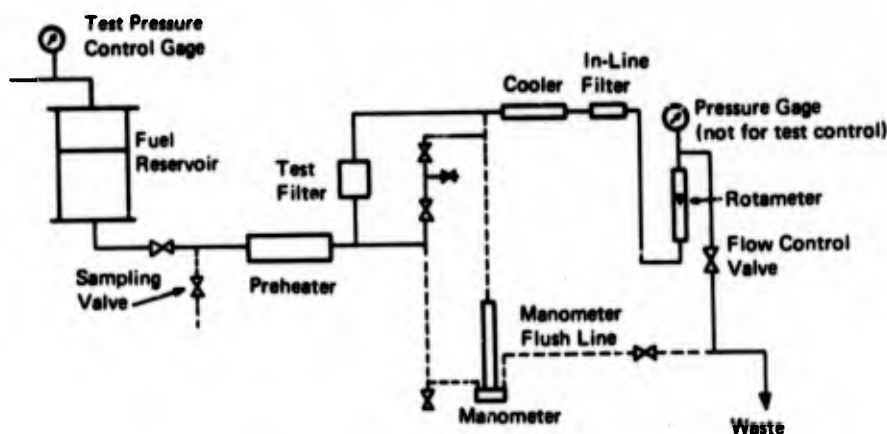


FIGURE 1. GAS-DRIVE COKER

\*The criterion of 2.0 in. Hg was adopted several years ago for the gas-drive coker in work performed by SwRI. Currently, the standard coker criterion usually cited in specifications is 3.0 in. Hg. A scaledown to the flow rate in the gas-drive coker would give 1.25 in. Hg, but the older criterion of 2.0 in. Hg has been retained here.

The basic operating procedures, starting with ASTM Method D 1660, are further defined for the CRC gas-drive cokers in Reference 4. Additional modifications are given in Reference 2 and are understood to apply here unless otherwise indicated.

For all of the work reported here, nitrogen was used as the drive gas. A drive pressure of 250 psi was used in all except a few tests in which fuel boiling necessitated an increase to 280 psi.

Preheater tubes were polished with A-1 metal polish in accordance with ASTM D 1660-69. A few tests were run with a substitute polish, which was under consideration by the ASTM at that time, and was subsequently adopted as standard.

## SECTION III

### FUEL BLENDING AND METAL ANALYSES

#### 1. GENERAL

In the preparation, sampling, and analysis of fuel blends with metal contents in the parts-per-billion range, it is extremely difficult to obtain stable, repeatable metal contents. Some of the difficulties encountered in the early stages of this program were probably caused by weaknesses in the sampling and analytical techniques; in some cases, these techniques were being developed during the course of the program. During the later stages of the program, however, it became evident that the metal contents of the fuel blends were indeed changing during the interval between preparation and testing. Hence, for much of the work reported here, it is not possible to arrive at an unambiguous statement of the true metal contents of fuel blends at the time of thermal stability testing. The blending, sampling, and analytical techniques are given here in some detail to illustrate the difficulties encountered and to aid in the interpretation of results.

#### 2. BASE FUELS

The three JP-7 base fuels used in this program were materials conforming to MIL-T-38219(USAF), 17 December 1970, except that they contained no fuel system icing inhibitor (FSII). The specification requires the presence of 0.10 to 0.15 percent FSII in the finished fuel; the FSII contents of the fuels used in this program were all essentially zero, i.e., below 0.02 percent as determined by analysis. It is known that at least one of these fuels contained the required amount of FSII when purchased, but nonvolatile fuels such as JP-7 tend to lose FSII through evaporation, especially when stored in aboveground vented tanks.

Partial inspection data on the three base fuels are shown in Table 1. Fuel 10-12-T was used in the earlier portion of the program; the past history of this fuel was reported previously<sup>(2)</sup>. The other two fuels (A and Z) were each from a different procurement of JP-7. Fuel Z was known to contain the lubricity additive specified for use in JP-7 conforming to MIL-T-38219. It was not known if any of the fuels contained any antioxidant or metal deactivator, both of which are optional items. However, there is a strong probability that they did not contain either.

During the period of the investigation, Fuel 10-12-T was held indoors in a 600-gallon aluminum tank, vented to the atmosphere. Fuel A was stored in two aboveground (outdoor), vented, 1000-gallon unlined steel tanks, while Fuel Z was stored in two similar epoxy-lined tanks. These base fuels were rechecked toward the end of the program to verify that they had not picked up any significant amounts of iron or other metals.

The use of three different JP-7 fuels in the investigation of metal-content effects was dictated primarily by availability. The use of three different fuels does broaden the base of the program somewhat, since the conclusions are not restricted to one particular fuel or one supplier.

#### 3. METALS

All metals used in the program were in the form of commercial metal naphthenates, with nominal metal contents 8 percent zinc, 24 percent lead, 8 percent copper, and 6 percent iron.

It is believed that the use of naphthenates as the "soluble metals" is a reasonable simulation of the form in which metals occur in fuels under field conditions. All fuels will contain at least traces of acidic materials, and dissolved metals are most likely to occur as metal salts of organic acids. Another possible source of dissolved metals in field service is contamination of jet fuels with leaded gasolines, in which the lead is present in the form of a tetraalkyl compound. No attempt was made in this program to investigate the behavior of this type of soluble lead.

TABLE 1. INSPECTION DATA ON BASE FUELS

Inspection test	Specs <sup>a</sup>	Fuel 10-12-T	Fuel A	Fuel Z
Distillation: IBP, °F	360 min	387	382	404
10%, °F	385 min	402	399	412
20%, °F	403 min <sup>b</sup>	406 <sup>b</sup>	407 <sup>b</sup>	414 <sup>b</sup>
50%, °F	To be reported	420	424	422
90%, °F	500 max	455	458	443
EP, °F	550 max	494	486	476
Residue, %	1.5 max	1.0	1.0	1.0
Loss, %	1.5 max	1.0	1.0	1.0
Gravity, API/60°F	44-50	45.9	46.3	45.4
Existent gum, mg/100 ml	5.0 max	3.8	0.0	0.0
Total potential residue 16-hr, mg/100 ml	10.0 max	3.8	0.0	0.0
Flash point (P-M), °F	140 min	162	150	170
Water separator, WSIM	85 min	100	100	98
Aromatics, vol percent	5 max	---	2.6	2.8
Aniline-gravity product	7380 min	---	7709	7536

a. MIL-T-38219 (USAF), 17 December 1970, Turbine Fuel, Low Volatility.  
b. Corrected for emergent stem.

#### 4. BLENDING, SAMPLING, AND ANALYSIS

In the earlier work, the 10-12-T fuel was blended with lead or zinc naphthenate to prepare concentrates containing 250 or 2000 ppm\* of metal, respectively; these were kept in cold storage in one-gallon amber glass bottles. No precipitate or any other evidence of insolubility was observed. Final test blends, generally 14 gallons, were prepared in stainless steel containers by adding the concentrate to 10-12-T fuel. Samples of concentrates and test blends were submitted for metal content determinations.

In the more recent part of the program, similar concentrates of iron, lead, zinc, and copper naphthenate were blended with Fuel A or Fuel Z, each concentrate containing 1000 ppm of a single metal. These concentrates were blended in one-gallon clear glass bottles and were stored in the dark at ambient temperature. Cold storage had been ruled out previously because of a solubility problem with the iron naphthenate. Even at ambient temperature, the 1000-ppm iron concentrate was quite unstable, and precipitate could be observed within about two weeks after blending. Frequent preparation of fresh concentrate was required. Finally, 250 ppm iron concentrates were prepared using each of the two base fuels, and no more solubility problems were encountered.

Final test blends, generally 14 gallons, were prepared in stainless steel containers by adding the appropriate concentrate to the base fuel and stirring thoroughly.

\*All metal concentrations in this report are given in wt/wt units of parts per million (ppm) or parts per billion (ppb).



Blends containing more than one metal were tested in the later part of the program. Sometimes a blend containing only one metal was tested first, then other metals were added and the new blend was retested. At other times, blends containing more than one metal were prepared initially and tested without further additions.

All metal analyses were performed at Monsanto Research Corporation under the direction of Dr. W. G. Scribner. The methods for trace amounts of copper, iron, and zinc have been summarized by Lander<sup>(5)</sup>; the method for iron has been discussed in more detail by Scribner et al.<sup>(6)</sup>; and the method for lead has been presented in a recent report by Scribner and Borchers.<sup>(7)</sup> For the present work, minor changes were made in the test methods listed in these references in order to adapt the procedures to the special problems involved.<sup>(8)</sup> We wish to acknowledge the close cooperation and valuable comments of Dr. Scribner in this work.

As reported previously<sup>(2)</sup>, test blends in the initial series containing lead in the parts-per-billion concentration range lost much of this lead at some stage in the sample handling. It was suggested by Dr. Scribner that the most likely cause of the lead loss was adsorption on the interior surfaces of the glass sample bottles. In order to eliminate the possibility of such loss, a new sampling technique was adopted for lead samples: each sample bottle was precleaned with hot nitric acid, distilled water, and reagent-grade acetone; a fuel sample of the proper size was poured into the bottle and weighed; this sample was then analyzed, using nitric acid for quantitative transfer of the lead from the sample bottle.

In all of the later tests, this sampling technique was applied to all metal naphthenate solutions, both concentrates and final test blends, in order to avoid any possible recurrence of similar problems with other metals. The only change in technique that was necessary was one that was applied to iron-containing fuel blends: hot hydrochloric acid was used instead of nitric acid to prepare the sample bottles and to remove the sample quantitatively for analysis.

Metal contents of the original naphthenates and of the concentrates, determined by Monsanto, are listed in Table 2. The metal contents found for the naphthenates were close to the nominal contents, and the metal contents found for the concentrates were close to the nominal (added) values. Apparently there were no particular problems with loss of metal from these relatively concentrated products.

Two of the base fuels used in this work were checked for metal contents, with the following results:

	Metal content, ppb			
	Pb	Zn	Fe	Cu
10-12-T	8	<5	5	<5
Fuel A	<5	<5	<5	<5

The detectable contents of lead and iron in the 10-12-T fuel were probably picked up by the fuel in previous handling. In any case, these concentrations are low enough to cause no trouble in the present program.

The metal contents of final test blends containing a single added metal are listed in Table 3; those of multimetal blends are listed in Table 4. It will be noted that there were often large discrepancies between the amounts added and the amounts found by analysis. In most instances, the amount found was less than the amount added, indicating that metal had been lost somewhere in the process of blending, storage, sampling, and analysis. As soon as these problems became evident, the sampling and analysis program was expanded to include materials other than the "initial blend." The samples are coded in Tables 3 and 4 as follows:

A	—	blend container immediately after blending
B	—	blend container after finishing all coker tests (generally 4 to 7 days after blending)
C	—	coker influent line at start of first test
D	—	coker influent line at end of first test
E	—	coker influent line at start of later test
F	—	coker influent line at end of later test.

TABLE 2. METAL CONTENTS OF NAPHTHENATES AND FUEL CONCENTRATES

Naphthenate	Nominal concentration, % metal	% metal found			Average % metal
<i>Fuel 10-12-T series</i>					
Z-1 (zinc)	8.0	8.34 <sup>a</sup>	8.39 <sup>b</sup>	8.43 <sup>c</sup>	8.39
L-1 (lead)	24.0	24.2 <sup>d</sup>	24.2 <sup>d</sup>	---	24.2
<i>Fuel A and Fuel Z series</i>					
Z-2 (zinc)	8.0	7.99 <sup>d</sup>	7.99 <sup>d</sup>	8.02 <sup>d</sup>	8.00
L-2 (lead)	24.0	23.97 <sup>d</sup>	24.09 <sup>d</sup>	---	24.03
C-2 (copper)	8.0	8.13 <sup>e</sup>	8.11 <sup>e</sup>	8.06 <sup>e</sup>	8.10
I-2 (iron)	6.0	5.84 <sup>f</sup>	5.82 <sup>f</sup>	---	5.83
Metal-fuel concentrate	Nominal concentration, ppm metal	ppm metal found			Average ppm metal
<i>Fuel 10-12-T series</i>					
S-I (zinc)	2000	2090 <sup>d</sup>	2090 <sup>d</sup>	---	2090
S-II (lead)	250	247 <sup>g</sup>	---	---	247
<i>Fuel A series</i>					
S-III (iron)	1000	1005 <sup>f</sup>	1000 <sup>f</sup>	---	1002
S-IV (copper)	1000	1005 <sup>h</sup>	1004 <sup>h</sup>	---	1004
S-V (iron)	1000	986 <sup>f</sup>	981 <sup>f</sup>	---	984
S-VI (lead)	1000	1026 <sup>g</sup>	1030 <sup>g</sup>	---	1028
S-VII (zinc)	1000	999 <sup>d</sup>	998 <sup>d</sup>	---	998
S-VIII (lead)	1000	1000 <sup>g</sup>	1007 <sup>g</sup>	---	1004
S-IX (iron)	250	247 <sup>f</sup>	---	---	247
<i>Fuel Z series</i>					
S-X (iron)	250	239 <sup>f</sup>	---	---	239
S-XI (copper)	1000	1006 <sup>h</sup>	1006 <sup>h</sup>	---	1006
S-XII (zinc)	1000	1000 <sup>d</sup>	1002 <sup>d</sup>	---	1001
S-XIII (lead)	1000	997 <sup>g</sup>	1001 <sup>g</sup>	---	999
<p>a. Organic material was destroyed with sulfuric-nitric acid. Metal was titrated at pH 10 with (ethylenedinitrilo) tetra-acetate (EDTA) using Eriochrome Black T as indicator.</p> <p>b. Two-phase titration with EDTA using Zincon as indicator and 1:1:1 isopropyl alcohol-benzene-water.</p> <p>c. Sample was dissolved in toluene and the metal ion was extracted with aqueous acid and subsequently titrated at pH 10 with EDTA.</p> <p>d. Sample was dissolved in toluene and the metal ion was extracted with aqueous acid and subsequently titrated at pH 5 with EDTA using Xylenol Orange indicator.</p> <p>e. Sample was dissolved in toluene and the metal ion was extracted into aqueous acid and subsequently titrated at pH 5.5 with EDTA using PAN indicator.</p> <p>f. Metal ion was titrated with EDTA at pH 3 using salicylic acid indicator after destruction of organic matter with sulfuric-nitric acids.</p> <p>g. Two-phase titration with EDTA in the presence of 1:1:1 isopropyl alcohol-water-fuel; Xylenol Orange indicator at pH 5.</p> <p>h. EDTA titration at pH 4.0 with 1-(2-pyridylazo)-2-naphthol indicator after destruction of organic matter with sulfuric-nitric acid.</p>					



TABLE 3. METAL CONTENTS OF SINGLE-METAL BLENDS

Base fuel	Sample no.	Metal added, ppb	Metal found, ppb <sup>a</sup>					
			A	B	C	D	E	F
<i>Lead naphthenate blends</i>								
10-12-T	M-4	530	<5	18	---	---	---	---
	M-6	530	44	---	---	---	---	---
	M-8	530	9	---	---	---	---	---
	M-10	530	98	---	---	---	---	---
	M-16	375	323	156	---	---	---	---
	M-12	250	183	---	---	---	---	---
	M-13	250	13	---	---	---	---	---
	M-15	125	61	---	---	---	---	---
	M-18	50	9	---	---	---	---	---
Fuel A	M-161	600	---	---	---	398	---	341
	M-53	500	431	253	---	---	---	---
	M-159	500	---	254	---	198	---	---
	M-57	435	372	251	---	---	---	---
	M-157	400	---	---	---	217	---	93
	M-55	300	224	---	---	---	---	---
	M-155	300	---	---	---	135	102	87
	M-86	250	238	---	---	---	---	---
	M-52	200	181	99	---	---	---	---
	M-151	200	---	---	64	70	---	---
	M-50	100	37	6	---	---	---	---
	M-46	50	14	---	---	---	---	---
	M-45	25	<5	---	---	---	---	---
Fuel Z	M-181	500	---	---	---	---	---	235
	M-184	400	---	---	---	---	---	178
<i>Zinc naphthenate blends</i>								
10-12-T	M-1	6250	5280	---	---	---	---	---
	M-2	3000	2540	---	---	---	---	---
	M-3	3000	2710	2980	---	---	---	---
	M-5	3000	2560	---	---	---	---	---
	M-7	3000	1820	---	---	---	---	---
	M-9	3000	2310	---	---	---	---	---
	M-11	1000	520	---	---	---	---	---
	M-14	1000	730	---	---	---	---	---
	M-17	500	390	---	---	---	---	---
M-19	100	b	---	---	---	---	---	
Fuel A	M-54	200	184	---	---	---	---	---
	M-109	125	---	116	---	---	---	---
	M-48	100	86	54	---	---	---	---
	M-51	100	94	65	---	---	---	---
	M-56	100	82	64	---	---	---	---

TABLE 3. METAL CONTENTS OF SINGLE-METAL BLENDS (Cont'd)

Base fuel	Sample no.	Metal added, ppb	Metal found, ppb <sup>a</sup>					
			A	B	C	D	E	F
<i>Zinc naphthenate blends (cont'd)</i>								
Fuel A	M-102	100	72	106	---	---	---	---
	M-105	100	109	108	---	---	---	---
	M-49	75	51	88	---	---	---	---
	M-47	50	25	---	---	---	---	---
	M-44	25	13	---	---	---	---	---
	M-43	5	4	---	---	---	---	---
Fuel Z	M-182	200	---	---	---	---	---	37
	M-185	150	---	---	---	---	---	75
	M-180	100	---	---	---	---	---	14
<i>Iron naphthenate blends</i>								
Fuel A	M-20	500	453	---	---	---	---	---
	M-22	500	484	424	---	---	---	---
	M-21	200	174	---	---	---	---	---
	M-23	200	183	160	---	---	---	---
	M-24	100	b	---	---	---	---	---
	M-25	100	133	---	---	---	---	---
	M-41	25	34	53	---	---	---	---
	M-42	5	30	40	---	---	---	---
Fuel Z	M-175	35	---	---	---	---	---	31
	M-172	25	30	---	---	---	---	---
<i>Copper naphthenate blends</i>								
Fuel A	M-32	500	451	---	---	---	---	---
	M-26	200	146	---	---	---	---	---
	M-27	200	b	---	---	---	---	---
	M-29	100	98	---	---	---	---	---
	M-28	50	b	---	---	---	---	---
	M-31	50	57	---	---	---	---	---
	M-30	25	32	---	---	---	---	---
	M-37	25	29	31	---	---	---	---
	M-124	25	---	23	---	---	---	---
	M-39	15	17	---	---	---	---	---
	M-40	15	22	19	---	---	---	---
	M-80	15	20	22	---	---	---	---
	M-33	5	8	---	---	---	---	---
	M-34	5	7	---	---	---	---	---
	M-36	5	6	---	---	---	---	---
	M-38	5	9	10	---	---	---	---
	M-35	0	5	---	---	---	---	---

TABLE 3. METAL CONTENTS OF SINGLE-METAL BLENDS (Cont'd)

Base fuel	Sample no.	Metal added, ppb	Metal found, ppb <sup>a</sup>					
			A	B	C	D	E	F
<i>Copper naphthenate blends (cont'd)</i>								
Fuel Z	M-177	75	---	---	---	---	---	24
	M-176	50	---	---	---	---	---	14
	M-188	50	---	---	---	---	---	b
	M-174	25	---	---	---	---	---	11
	M-173	15	---	---	---	---	---	10
<p>a. Code letter indicates time and manner of drawing sample for analysis:  A - From blend container, shortly after preparation of blend.  B - From blend container at conclusion of coker tests (4 to 7 days later).  C - From coker influent line at start of first test.  D - From coker influent line at end of first test.  E - From coker influent line at start of later test.  F - From coker influent line at end of later test.</p> <p>b. Results unavailable; sample loss or contamination.</p>								

The "later test" sampling (Codes E and F) was intended to represent the last coker test in a given series. However, in some cases, when additional coker tests were required to confirm a breakpoint, the "later test" would not be the *last* test run on the blend.

The results on lead content were examined in some detail, since it had been established that lead loss was occurring in glass sample bottles, presumably by adsorption of the lead soap on the interior surfaces of the bottle. After a sampling technique had been adopted to prevent such losses, it was observed that the lead found by analysis was still generally lower than the amount added. The lead-content data, excluding the early data on Fuel 10-12-T, have been examined by linear regression analysis, grouping the coker-influent samples as C-D and E-F.\* The number of samples, n, the correlation coefficient, r, and the regression equation for y on x (amount found versus amount added) are as follows:

Sample group	n	r	Regression line
A	14	0.988	$y = 0.866x - 5$
B	9	0.980	$y = 0.505x - 2$
C-D	16	0.914	$y = 0.761x - 79$
E-F	19	0.945	$y = 0.764x - 144$

The regression lines are shown in Figure 2 in comparison with the  $y = x$  line. It will be noted that the "as-blended" samples (line A) did not deviate too greatly; the average loss of lead was about 15 percent except at very low concentrations. The samples taken from the blend containers 4 to 7 days later (line B) showed much greater lead losses, averaging about 50 percent loss over the entire range of lead contents. The coker influent samples (C-D and E-F) also showed drastic lead losses; the relative loss was greatest at low lead concentrations. On the average, a 100-ppb lead blend would be expected to be essentially lead-free by the time it entered the first coker test, and a 200-ppb lead blend would likewise be lead-free by the time it entered the last coker test in the series.

Although the regression lines give the general trends in lead loss, they cannot be used to assign "true" lead contents to coker test blends; there is simply too much scatter in the data. Hence, in the discussion of coker test results, one must generally speak of "nominal" (added) lead contents, keeping in mind that the true lead contents may be much lower.

\*The number of "start-of-test" samples (C and E) was insufficient to form separate groups.

TABLE 4. METAL CONTENTS OF MULTIPLE-METAL BLENDS

Starting blend <sup>a</sup>			Final blend								
Sample no.	Added, ppb	Found, ppb <sup>c</sup>	Sample no.	Added, ppb <sup>b</sup>				Found, ppb <sup>c</sup>			
				Pb	Zn	Fe	Cu	Pb	Zn	Fe	Cu
M-111	Fe 25	---	M-114	---	---	25	25	---	---	26(B)	20(B)
M-106	Fe 25	---	M-108	---	---	25	15	---	---	---	13(A)
M-95	Fe 25	50(A),53(B)	M-97	---	---	25	5	---	---	54(A),65(B)	8(A),9(B)
M-104	Fe 25	---	M-107	---	---	25	5	---	---	---	7(A),7(B)
Base fuel	---	---	M-147	---	---	10	10	---	---	---	10(B)
M-98	Fe 5	22(A)	M-101	---	---	5	5	---	---	14(B)	9(A),8(B)
M-117	Cu 25	---	M-120	---	---	5	25	---	---	31(A)	18(B)
M-110	Cu 15	---	M-112	---	---	25	15	---	---	37(B)	11(B)
M-99	Cu 15	17(A)	M-103	---	---	5	15	---	---	20(B)	11(B)
M-141	Cu 10	---	M-103	---	---	5	15	---	---	28(A)	16(A),14(B)
			M-142	---	---	10	10	---	---	23(D)	29(D)
M-137	Fe 25	---	M-139	---	175	25	---	---	133(D)	77(D)	---
M-88	Fe 25	32(A)	M-89	---	75	25	---	---	64(B)	13(A),87(B)	---
M-91	Fe 25	43(A)	M-92	---	75	25	---	---	64(A),64(B)	62(A),67(B)	---
M-134	Fe 25	58(C),15(D)	M-136	---	10	25	---	---	12(D)	37(D)	---
M-87	Fe 5	18(A),31(B)	M-90	---	75	5	---	---	62(A),73(B)	21(A),41(B)	---
M-93	Fe 5	30(A),42(B)	M-94	---	75	5	---	---	80(A),82(B)	32(A),210(D)	---
M-113	Fe 5	---	M-115	---	50	5	---	---	44(B)	9(B)	---
M-122	Zn 200	194(C),201(D)	M-125	---	200	5	---	---	196(D)	21(D)	---
M-96	Zn 100	95(A)	M-100	---	100	5	---	---	84(A),78(B)	67(A),50(B)	---
M-140	Zn 70	---	M-142	---	70	5	---	---	48(B)	14(B)	---
M-127	Zn 50	53(C),50(D)	M-130	---	50	5	---	---	48(D)	40(D)	---
M-129	Zn 10	16(C),7(D)	M-131	---	10	5	---	---	5(D)	23(D)	---
Base fuel	---	---	M-162	600	---	10	---	454(D),364(F)	---	27(D)	---
Base fuel	---	---	M-160	500	---	10	---	239(D),240(F)	---	16(D)	---
M-128	Cu 25	27(C),26(D)	M-132	---	10	---	25	---	13(D)	---	25(D)
M-62	Cu 15	22(A)	M-66	---	75	---	15	---	89(B)	---	18(B)
M-83	Cu 15	17(A),20(B)	M-85	---	75	---	15	---	70(A),74(B)	---	20(A),26(B)
M-67	Cu 5	12(A)	M-71	---	100	---	5	---	87(A),79(B)	---	9(A),6(B)
M-60	Cu 5	---	M-61	---	75	---	5	---	40(B)	---	10(B)
M-123	Cu 5	8(C),8(D)	M-126	---	50	---	5	---	58(B)	---	9(B)
M-116	Zn 200	---	M-118	---	200	---	5	---	182(B)	---	6(B)
M-63	Zn 100	81(A)	M-65	---	100	---	5	---	87(B)	---	10(B)
M-74	Zn 100	83(A)	M-77	---	100	---	5	---	83(A),88(B)	---	10(A),13(B)
M-58	Zn 75	---	M-59	---	75	---	5	---	47(B)	---	12(B)
Base fuel	---	---	M-154	---	75	---	5	---	24(D)	---	7(D)
M-119	Zn 50	---	M-121	---	50	---	5	---	54(B)	---	7(B)
Base Fuel	---	---	M-153	---	50	---	5	---	13(C),14(D)	---	6(C),4(D)
M-148	Zn 15	---	M-149	---	15	---	5	---	8(B)	---	6(B)
M-133	Zn 10	14(C),10(D)	M-135	---	10	---	5	---	8(D)	---	8(D)
M-68	Cu 15	24(A)	M-72	50	---	---	15	37(A)	---	---	19(A),29(B)
M-75	Cu 5	11(A)	M-78	50	---	---	5	45(A)	---	---	7(A)
Base fuel	---	---	M-158	500	---	---	10	d	---	---	d
M-144	Zn 70	46(C),54(D)	M-146	---	75	---	---	---	36(B)	---	---
M-70	Zn 100	92(A)	M-73	50	100	---	---	52(A),50(B)	87(A),95(B)	---	---
M-81	Zn 100	92(A)	M-82	50	100	---	---	57(A),33(B)	81(A),93(B)	---	---
M-64	Zn 75	64(A)	M-69	100	75	---	---	91(A),22(B)	74(A),59(B)	---	---
M-76	Zn 75	75(A)	M-79	40	75	---	---	51(A),40(B)	75(A),67(B)	---	---
Base fuel	---	---	M-164	500	20	---	---	371(D)	22(D)	---	---
Base fuel	---	---	M-163	500	10	---	---	236(D)	8(D)	---	---
Base fuel	---	---	M-152	---	20	10	10	---	10(D)	8(D)	6(D)
Base fuel	---	---	M-156	---	20	10	10	---	10(D)	11(D)	7(D)
Base fuel	---	---	M-145	---	10	10	10	---	8(C),7(D)	20(C),5(D)	6(C),9(D)
Base fuel	---	---	M-150	---	10	10	10	---	d	d	d
Base fuel	---	---	M-138	---	5	5	5	---	8(C),13(D)	15(D)	8(D)
Base fuel	---	---	M-165	500	---	10	10	317(D),187(F)	---	16(D),10(F)	5(D),10(F)
Base fuel	---	---	M-166	400	---	10	10	231(D),133(F)	---	27(D)	9(D)
Base fuel	---	---	M-167	300	---	10	10	161(D),105(F)	---	9(D)	7(D)
Base fuel	---	---	M-168	300	10	10	---	121(F)	---	---	---

TABLE 4. METAL CONTENTS OF MULTIPLE-METAL BLENDS (Cont'd)

Starting blend <sup>a</sup>			Final blend								
Sample no.	Added, ppb	Found, ppb <sup>c</sup>	Sample no.	Added, ppb <sup>b</sup>				Found, ppb <sup>c</sup>			
				Pb	Zn	Fe	Cu	Pb	Zn	Fe	Cu
Base fuel	---	---	M-171	300	20	10	10	182(D),28(F)	4(F)	---	---
Base fuel	---	---	M-169	300	10	10	10	184(D),109(F)	12(D)	13(D)	6(D)
Base fuel	---	---	M-170	200	10	10	10	77(D),26(F)	6(D)	15(D)	7(D)
Base fuel Z	---	---	M-178	---	---	25	25	---	---	16(F)	15(F)
Base fuel Z	---	---	M-179	---	---	10	10	---	---	147(F)	7(F)
Base fuel Z	---	---	M-183	---	20	10	10	---	3(F)	22(F)	5(F)
Base fuel Z	---	---	M-186	---	10	10	10	---	4(F)	23(F)	4(F)
Base fuel Z	---	---	M-187	---	5	5	5	---	d	d	d
Base fuel Z	---	---	M-204	500	5	5	5	211(F)	10(F)	18(F)	7(F)
Base fuel Z	---	---	M-201	400	5	5	5	181(F)	---	---	---
Base fuel Z	---	---	M-189	300	5	5	5	86(F)	4(F)	45(F)	2(F)
Base fuel Z	---	---	M-191	200	5	5	5	7(F)	---	---	---
Base fuel Z	---	---	M-190	100	5	5	5	d	d	d	d

a. Base fuel A in all blends except where otherwise indicated.  
b. Amounts added include amounts in "starting blend."  
c. Code letters in parentheses indicate sample source (see Table 3 footnotes).  
d. No valid data obtained.

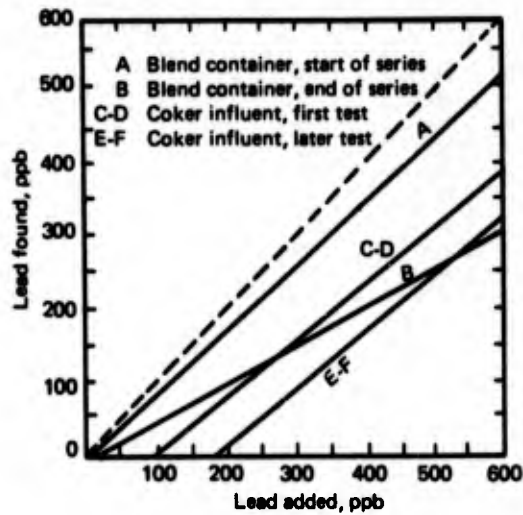


FIGURE 2. LEAD LOSS DURING COKER TEST SERIES

The mechanism of the lead loss is not known, although it is suspected that the principal contributing factor is adsorption on the surfaces of the blending container, the fuel coker reservoir, and the coker inlet lines. It is also likely that some of the original lead is adsorbed on suspended particles of contaminants and is thus removed in the prefiltration step, which is performed before each coker test. In any case, the data do illustrate quite clearly the hazards in drawing conclusions about the effects of trace metals on any laboratory test involving hardware. When parts per billion of contaminant metals are critical, they can be "lost" in the preparation of the sample for test.

The iron contents shown in Tables 3 and 4 are quite erratic. In many instances, particularly for the lower iron contents, the amount found by analysis was considerably greater than the amount added. Part of this problem was traced to an error in the procedure used to clean sample bottles, but correction of this error did not bring the results into line. It was later found that the sample bottles themselves retained enough iron, even after the most thorough cleaning, to cause a 10- to 20-ppb positive error. It was also found that the reagents used in cleaning the bottles, although ACS reagent grade, had allowable limits of iron concentration high enough to cause part of the error. In view of these errors, none of the analytical results for iron contents can be regarded as truly representative of fuel actually entering the fuel coker.

The copper contents shown in Tables 3 and 4 are generally in reasonable agreement with the amounts added. Only in one series of fuel blends (Fuel Z, Table 3) was there any consistent loss of copper.

The zinc blends also gave reasonable agreement of the amounts added and found, possibly with more instances of consistent zinc loss than were observed for copper.

Because of the different patterns of metal loss and the uncertainties introduced by stray metals in the sampling procedures, it has not been feasible in most cases to relate fuel coker results to the true metal contents of the fuels entering the coker. Obviously, this lessens the value of the data. It should be pointed out, however, that these same problems have existed in previous studies of the effects of trace metals on fuel quality, at least in any study in which the metals were dissolved in the form of salts of organic acids. The present work has merely revealed the magnitude of a problem that was largely ignored in earlier work.

As noted in the introductory portion of this report, one phase of this program was devoted to determining whether metal deactivators and antioxidants are capable of changing the threshold levels at which metal contents become important. Preparation of the test blends for this work was very similar to preparation of the metal blends. Concentrates of the antioxidant or metal deactivator were prepared using commercially available formulations of each additive. The antioxidant, 2,4-dimethyl-6-tertiary-butylphenol, was prepared as a concentrate in Fuel Z. The metal deactivator, N,N'-disalicylidene-1,2-propanediamine, was prepared as a concentrate in a mixture of equal volumes of ACS reagent grade toluene and Fuel Z, since the deactivator is only partially soluble in straight JP-7 fuel at high concentrations. Test blends, generally 14 gallons, were prepared as before in stainless steel containers. The additive concentrate, either metal deactivator or antioxidant, was added to the fuel and mixed thoroughly for approximately 30 minutes, then the metal concentrate was added to the fuel while mixing. The resulting additive/metal blends were allowed to stand overnight before testing.

The metal deactivator and the antioxidant were tested at the respective maximum concentrations allowed in JP-7, according to MIL-T-38219, 17 December 1970: metal deactivator 2.0 pounds of active ingredient per 1000 barrels of fuel, antioxidant 8.4 pounds of active ingredient per 1000 barrels of fuel. Test blends containing only the additives in metal-free fuels were prepared and tested as controls.

Metal contents of the additive/metal blends are shown in Table 5. As with the nonadditive blends, the lead contents were low and the iron contents were erratic. The copper and zinc contents were surprisingly low in the blends with antioxidant.

TABLE 5. METAL CONTENTS OF  
ADDITIVE FUEL BLENDS

Sample no.	Metal added and amount, ppb	Metal found, ppb <sup>a</sup>		
		A	D	F
<i>Fuel Z plus metal deactivator</i>				
M-202	Fe 200	95	---	---
M-200	Fe 100	55	---	---
M-196	Fe 50	74	---	---
M-192	Fe 35	21	---	---
M-199	Cu 100	97	---	---
M-194	Cu 75	80	---	---
M-208	Zn 600	---	347	419
M-210	Zn 500	---	---	519
M-205	Zn 400	388	---	---
M-203	Zn 300	---	---	339
M-197	Zn 200	---	---	167
M-195	Zn 150	---	---	122
M-207	Pb 700	---	376	333
M-211	Pb 600	---	---	390
M-198	Pb 500	---	---	192
<i>Fuel Z plus antioxidant</i>				
M-206	Fe 35	---	---	83
M-217	Cu 100	---	---	79
M-214	Cu 75	---	---	25
M-215	Zn 200	---	---	34
M-212	Zn 150	---	---	20
M-216	Pb 600	---	428	441
M-213	Pb 500	---	---	260
a. Code letters indicate sample source (see Table 3 footnotes).				



## SECTION IV

### GAS-DRIVE COKER RESULTS ON SINGLE-METAL NAPHTHENATE BLENDS

#### 1. EFFECTS OF METALS ON THERMAL STABILITY

Breakpoints for the single-metal test fuel blends are listed in Table 6. The "base fuel" samples shown in this table are samples taken from 55-gallon lined drums used for fuel transfer from the storage tanks to the blending operation. The "control fuel" samples are those taken from the stainless steel blending containers without any added metal. Many of the breakpoints are composite results based on several fuel blends.

Interpretation of these results is complicated not only by uncertainty as to what metal contents are actually "seen" by the fuel coker, but also by problems in interpreting off-color deposits, as discussed in Section IV, subsection 2. Here we will give a qualitative comparison of results on the basis of added-metal contents.

The three JP-7 fuels used in this work were close in stability as measured by breakpoint: Fuel 10-12-T, 625°F; Fuel A, 675 to 700°F; and Fuel Z, 700°F. It does not necessarily follow that each fuel will be equally susceptible to metal contamination, but it is reasonable to suppose that the effects of metals will at least be on the same order of magnitude for the three fuels. It is believed that loss of metals, particularly lead, is the major source of discrepancies in the data, and that differences among the three fuels play a relatively minor part.

Based on the thermal stability breakpoints, the threshold concentration of a metal is defined as the lowest concentration sufficient to cause a significant change in thermal stability. Such a change is considered significant when the breakpoint of the metal-containing blend is lower than the "minimum failure temperature" of the metal-free fuel. For example, Fuel Z had a breakpoint of 700°F, but gave occasional failures at 675°F; for this fuel, a metal is not considered to have a significant effect on thermal stability unless it drops the breakpoint at least 75°F.

Thus defined, the threshold concentrations in ppb of *added* metal are as follows:

	<u>10-12-T</u>	<u>Fuel A</u>	<u>Fuel Z</u>
Pb	125	435	500
Zn	100	100	150
Fe		25	25
Cu		15-25	75

The agreement among the fuels is reasonable for zinc and iron. The added copper content of 75 ppb in Fuel Z is probably not at all representative of the actual copper content of the fuel passing through the coker, in view of the large losses of copper from Fuel Z (see Table 3). In this light, the true threshold concentration of copper appears to be on the order of 15 to 25 ppb. Similarly, the threshold concentration of zinc is best represented by the 100-ppb value. The "best" threshold concentration of lead is difficult to assign, not only because of the large lead losses during handling, but also because of certain operating difficulties with the fuel cokers at the time the 10-12-T/lead data were obtained. A review of the coker and analytical data indicates that the threshold concentration of lead is within the range of 100 to 250 ppb.

Thus, it appears that as little as 15 ppb copper, 25 ppb iron, 100 ppb zinc, or 100 to 250 ppb lead can cause significant degradation of JP-7 thermal stability. The relatively high levels of lead are surprising, in view of the usual activity of this material as an oxidation catalyst. The very low level of iron that can cause degradation of thermal stability should cause considerable concern. Although bare-steel tanks and piping are normally prohibited in systems handling JP-7 fuel, it is extremely difficult in a practical system to exclude all ferrous-metal components, and very little would be required for the fuel to pick up traces of iron when any significant amounts of moisture are present. The absence of any significant pickup of iron by Fuel A during its storage in an unlined steel tank must be regarded as somewhat fortuitous.



TABLE 6. EFFECT OF SINGLE METALS ON FUEL  
BREAKPOINT IN GAS-DRIVE COKER

Metal added, ppb	Breakpoint, °F	Remarks
<i>Fuel 10-12-T</i>		
None <sup>a</sup>	625 (tube)	
Pb 50	575 (tube)	
125	500 (tube)	
250	500 (tube)	Results erratic at 450°F
375	300 (filter)	No tube failures up to 350°F
530	300 (filter)	Occasional tube failures above 375°F
Zn 100	350 (filter)	Occasional tube failures at 350°F
500	350 (filter)	Tube breakpoint 375°F
1000	375 (tube)	Filter breakpoint also 375°F
3000	350 (tube)	Erratic results at 325°F
6250	350 (tube)	Only two tests run
<i>Fuel A</i>		
None <sup>a</sup>	675-700 (tube)	Occasional passes in breakpoint range
None <sup>b</sup>	675-700+ (tube)	One set of tests passed at 700°F
Pb 25	>650	
50	>650	
100	>650	
150	>600	
200	>650	Only two tests run
250	>625	Slight filter plugging in all tests
300	>650	Slight filter plugging in most tests
400	>650	Slight filter plugging in most tests
435	625 (filter)	Filter plugging in all tests
500	600 (filter)	Marginal pass at 575°F
600	575 (filter)	Filter plugging in all tests
Zn 5	>650	
25	>650	
50	>650	
75	650 (tube)	Occasional passes at 650°F
100	550 (tube)	Some passes up to 650°F; 11 tests run
200	550 (tube)	
Fe 5	>650	
25	550 (tube)	
100	550 (tube)	Occasional failures down to 500°F
200	500 (tube)	One test passed at 500°F
500	400 (tube)	Occasional filter failures at 350°F

TABLE 6. EFFECT OF SINGLE METALS ON FUEL BREAKPOINT IN GAS-DRIVE COKER (Cont'd)

Metal added, ppb	Breakpoint, °F	Remarks
Cu 5	650-675 (tube)	Occasional failures down to 550°F Erratic results at 550°F One failure at 525°F Occasional failures below 525°F
15	575 (tube)	
25	550 (tube)	
50	525 (tube)	
100	550 (tube)	
200	525 (tube)	
500	450 (tube)	Some tube and filter failures below 525°F Also severe filter plugging
<i>Fuel Z</i>		
None <sup>a</sup>	700 (tube)	Occasional failures at 675°F
None <sup>b</sup>	>700	
Pb 400	>650	Occasional filter plugging below 625°F
500	625 (tube)	
Zn 100	>650	
150	600 (tube)	
200	600 (tube)	
Fe 25	550 (tube)	Occasional passes up to 650°F
35	525 (tube)	
Cu 15	>625	Tube deposits marginal (small area)
25	>650	
50	>650	
75	625 (tube)	
<p>a. Base fuel for test series. b. Control fuel from blend container before adding metal.</p>		

The preceding conclusions and comments are based on tests in which the metals were present as salts of organic acids; this form should be fairly typical of the contaminant metals encountered in service. During the course of the program, some concern arose as to whether the acid moiety of the metal-salt molecule or the mineral spirits used as a diluent in the commercial naphthenates could have any effect on fuel thermal stability. The effect of the acid moiety cannot be evaluated directly, but some indication of the possible effects can be gained by examining the effects of free naphthenic acids. No such experimental work was performed in the present program. In a study of fuel contamination carried out in 1961, Grandey and Wehner<sup>(9)</sup> found that a good-quality JP-6 fuel could tolerate up to 6 ppm crude naphthenic acids. This is several orders of magnitude higher than any of the nominal naphthenic acid contents of critical-concentration blends in the present program. Further, the commercial naphthenates used in the present program were probably made from refined naphthenic acids. Hence, even though the JP-7 used here was a much higher quality fuel than JP-6 fuels in general, it appears improbable that the naphthenic acid portion of the naphthenate molecule had any effect on the thermal stability test results. This is not to say that the *form* of the metal (e.g., soap versus metal alkyl) has no influence; this question was not investigated here.

Possible effects of the mineral spirits used as a diluent-solvent in commercial naphthenates were evaluated by obtaining a sample of the mineral spirits used by the manufacturer of the particular naphthenates used in this

program. This solvent was then blended with Fuel Z at a concentration equivalent to that in a 6250-ppb zinc blend, i.e., at the maximum concentration of mineral spirits encountered in any of the test fuel blends. In comparative coker tests, the fuel itself gave a breakpoint at 700°F, and the fuel plus mineral spirits gave a breakpoint of 700°F or higher. Thus, the mineral spirits had no detectable effect on thermal stability.

It appears that the thermal stability changes caused by metal naphthenates are attributable directly to the metals and not to other components of the naphthenates.

## 2. PROBLEMS IN RATING COLORED DEPOSITS

As would be expected in tests on metal-contaminated fuels, preheater deposits appeared in a variety of colors other than those represented in the ASTM-CRC color standards. Problems in rating such deposits have been discussed in some detail previously<sup>(3)</sup> and will be summarized here.

The standardized test procedure, ASTM D 1660, deals with the question of iridescent, multicolored, "peacock" deposits; these are considered to be thin deposits that should not be construed as failures. They are reported as "P" in rating the tube sections, but are ignored in arriving at the final "maximum" rating reported for the test. There are no guidelines in the ASTM method for dealing with deposits that are green, blue, gray, white, orange, purple, or any color other than the normal tan-brown or peacock. All of these colors may be encountered when testing practical fuels.

In the present program, deposits having colors other than the normal tan-brown were arbitrarily ignored in arriving at the pass-fail ratings on which breakpoints are based. Although this is not a satisfactory solution, there is no satisfactory alternative.

Among the iron blends, 500-ppb concentrations often gave heavy peacocking, somewhat on the greenish side, sometimes wipable. Such stains were generally associated with normal brownish deposits in the color code range of 3 to 4, hence caused no problem in assigning pass-fail ratings.

In all three test fuels, zinc and lead often gave a wipable bluish-white "haze" at the hot end of the tube, generally appearing at lead concentrations above 400 ppb or zinc concentrations of 100 ppb or higher. Again, these deposits were generally associated with normal failure-type deposits, so caused no special problems in pass-fail ratings.

Blends with added copper contents of 25 ppb or more generally showed wipable blue deposits. These were present in almost all tests on Fuel A blends, and also in some of the tests on Fuel Z blends. The appearance of these deposits has been described in detail in a previous report.<sup>(3)</sup> It was noted that all such deposits occurred upstream from the hottest position of the tube. Using the temperature relations given in Reference 10, it was determined that the blue deposits formed at a tube surface temperature of about 475 to 500°F, regardless of the metal concentration of the blend or the test temperature. There was absolutely no correlation between the blue deposits and the presence or absence of normal tan-brown deposits; i.e., the blue deposits appeared in both "passing" and "failing" tests. Obviously, if the blue deposits were considered to indicate instability, the fuel breakpoints would have been much lower than those reported, sometimes by as much as 150°F. The frequency of occurrence of blue stains is listed in Table 7; the breakpoints shown are those established without taking the blue stains into account.

It was noted that the blue color observed in the Tuberator changed to a definite brown when viewed under ordinary "cool white" fluorescent light in the laboratory, often corresponding rather closely to a No. 3 or a No. 4 color code. This observation casts considerable doubt on the validity of the color standard color ratings, or in fact, of any rating based on color or light reflectance.

It will be noted from Table 7 that very low concentrations of copper, on the order of 15 ppb added metal, are evidently sufficient to catalyze the reactions that form "normal" deposits in Fuel A. When more copper is added, it simply reacts and forms blue deposits on the tube at temperatures below those needed to form the "normal" deposits. Additional amounts of copper did not cause any drastic decrease in breakpoint until the 500-ppb level was reached.

**TABLE 7. OCCURRENCE OF BLUE STAINS IN  
COKER TESTS ON FUEL A PLUS COPPER**

Copper added, ppb	Total number of coker tests	Coker tests with blue stain	Test fuel breakpoint, °F
500	6	6	450
200	12	12	500-525
100	5	5	550
50	12	11	525
25	12	8	550
15	12	0	575
5	24	1	650-675

The problem of the significance of blue deposits from copper-containing fuels was discussed by Smith<sup>(11)</sup>, who found that 50 µg/liter (approximately 70 ppb by weight) of added copper caused significant drops in the heat transfer coefficient that were not predicted by conventional fuel coker ratings. It was concluded that the current D. Eng. R.D. 2494 specification limit of 150 ppb of copper is too tolerant.

In our work, added copper contents as low as 15 ppb did cause changes in thermal stability that could be detected by conventional observation of preheater deposit color. Larger amounts of added copper, in the 25- to 200-ppb range, gave more and more blue deposits but little change in breakpoint if

measured conventionally. Fuels with 25 to 200 ppb copper gave conventional breakpoints of 500 to 550°F, but would have been rated some 100°F lower if the blue deposits had been accounted as failures.

The JP-7 fuel used in our work was much more stable than the kerosines used in the British work, which had conventional coker breakpoints of 375 to 400°F. It would be expected that the more stable JP-7 would be more sensitive to trace amounts of copper than would the kerosines. If the blue deposits caused by the copper are present in sufficient amounts to interfere with heat transfer, it seems that copper will bring any reasonably stable fuel down to some common level of stability, on the order of 400°F or lower.

## SECTION V

### GAS-DRIVE COKER RESULTS ON MULTIPLE-METAL BLENDS

The second phase of this program was concerned with the effects of combinations of two or more contaminant metals on the thermal stability of JP-7 fuel. Such combinations of metals represent a closer approach to practical fuel-contamination situations than do single-metal blends.

The first part of this work was concerned with fuels containing only two contaminant metals. For most of the test, the fuel was first contaminated with a single metal and the fuel breakpoint was determined on the gas-drive coker. Then the second metal was added and the breakpoint was redetermined. In this way, changes in breakpoint were determined which could hopefully be attributed to the effects of one or both of the metals in the test blend. The end result of such testing would be an indication of any synergistic effects of the metals.

The metal concentrations used in this work were at or near the threshold concentrations determined for the individual metals. Test results for the bimetal blends are summarized in Table 8. The same color-rating problems

**TABLE 8. EFFECT OF TWO-METAL COMBINATIONS ON FUEL  
BREAKPOINT IN GAS-DRIVE COKER**

Metal added, ppb				Metal added first	Breakpoint, °F (tube or filter)			Sample no. <sup>a</sup>	
Pb	Zn	Cu	Fe		First metal	Both metals	Decrease	First metal	Both metals
50	75	---	---	Zn	650 T	650 T	0	M-76	M-79
100	75	---	---	Zn	625 T	<550 T	≥75	M-64	M-69
50	100	---	---	Zn	550 T	550 T	0	M-70	M-73
50	100	---	---	Zn	575 T	575 T	0	M-81	M-82
500	10	---	---	---	---	600 F	---	---	M-163
500	20	---	---	---	---	550 F	---	---	M-164
50	---	5	---	Cu	>675	>700	0	M-75	M-77
50	---	15	---	Cu	575 T	575 T	0	M-68	M-72
500	---	10	---	---	---	575 F	---	---	M-158
500	---	---	10	---	---	>650 <sup>b</sup>	---	---	M-160
600	---	---	10	---	---	600 F	---	---	M-162
---	10	5	---	Zn	>657	650-675 T	≥25	M-133	M-135
---	15	5	---	Zn	>650	>650	0	M-148	M-149
---	50	5	---	Zn	625 T	<550 T	≥75	M-119	M-121
---	50	5	---	Cu	>675	550 T	>125	M-123	M-126
---	50	5	---	---	---	>650 <sup>c</sup>	---	---	M-153
---	75	5	---	Zn	>675	650 <sup>c</sup> T	>25	M-58	M-59
---	75	5	---	Cu	650-675 T	650 <sup>c</sup> T	0	M-60	M-61
---	75	5	---	---	---	>650 <sup>c</sup>	---	---	M-154
---	100	5	---	Zn	625 T	525 T	100	M-63	M-65
---	100	5	---	Cu	>675	525-550 T	>125	M-67	M-71
---	100	5	---	Zn	575 T	525 T	50	M-74	M-77
---	200	5	---	Zn	550 T	550 T	50	M-116	M-118
---	75	15	---	Cu	575-625 T	550 T	25-75	M-62	M-66
---	75	15	---	Cu	600 T	<550 T	≥50	M-83	M-85
---	10	25	---	Cu	625 T	<550 T	≥75	M-128	M-132

TABLE 8. EFFECT OF TWO-METAL COMBINATIONS ON FUEL BREAKPOINT IN GAS-DRIVE COKER (Cont'd)

Metal added, ppb				Metal added first	Breakpoint, °F (tube or filter)			Sample no. <sup>a</sup>	
Pb	Zn	Cu	Fe		First Metal	Both metals	Decrease	First metal	Both metals
---	10	---	5	Zn	>675	650 T	>25	M-129	M-131
---	50	---	5	Fe	650 T	625 <sup>d</sup> T	25	M-113	M-115
---	50	---	5	Zn	625 T	500 T	125	M-127	M-130
---	70	---	5	Zn	650 T	575 T	75	M-140	M-143
---	75	---	5	Fe	>650	<550 T	>100	M-87	M-90
---	75	---	5	Fe	675 T	<550 T	≥125	M-93	M-94
---	100	---	5	Zn	550-575 T	525 T	25-50	M-96	M-100
---	200	---	5	Zn	550 T	500-525 T	25-50	M-122	M-125
---	10	---	25	Fe	525-575 T	>500	0	M-134	M-136
---	75	---	25	Fe	525 T	500 T	25	M-88	M-89
---	75	---	25	Fe	550 T	475 T	75	M-91	M-92
---	175	---	25	Fe	550 T	500 T	50	M-137	M-139
---	---	5	5	Fe	>650	>675	0	M-98	M-101
---	---	10	10	Cu	675 T	575 T	100 <sup>e</sup>	M-141	M-142
---	---	10	10	---	---	>625	---	---	M-147
---	---	15	5	Cu	600 T	600 T	0	M-99	M-103
---	---	5	25	Fe	525-550 T	>500	0	M-95	M-97
---	---	5	25	Fe	550 T	>525	0	M-104	M-107
---	---	25	5	Cu	600 T	>575	0	M-117	M-120
---	---	15	25	Fe	550 T	>525	0	M-106	M-108
---	---	15	25	Cu	>625	575 T	>50	M-110	M-112
---	---	10	10	---	---	650 T	---	---	M-179 <sup>f</sup>
---	---	25	25	---	---	550 T	---	---	M-178 <sup>f</sup>
---	70 <sup>g</sup>	---	---	70	600 T	>575	0	M-144	M-146
---	5 <sup>g</sup>	---	---						

- a. Base fuel A unless otherwise indicated.  
b. Some filter plugging at 575°F.  
c. Low zinc contents; see Table 4.  
d. One filter failure at 625°F.  
e. Copper content excessive for two-metal blend (29 ppb).  
f. Base fuel Z used for these blends.  
g. Successive addition of zinc to base fuel.

encountered for the single-metal blends were compounded for the bimetal blends. Even more serious were the problems involving the true concentration of the dissolved metals. Even minor differences in individual metal concentrations tended to make each blend a unique test solution in itself with its own definite thermal stability characteristics—a product that could never be duplicated exactly. Hence, the only conclusions that can be drawn from Table 8 are based on general trends rather than on specific test results.

The most obvious trend is the change in breakpoint brought on by the presence of zinc in combination with any of the other three metals. For most of the zinc-free fuel blends, there were no alarming changes in fuel breakpoint that cannot be attributed directly to the individual effect of one or the other contaminant metals. For the zinc blends, however, test solutions with zinc far below the threshold concentration of 100 ppb, plus a very small amount (5 ppb) of copper or iron, display very poor thermal stability characteristics. The same situation exists with zinc-lead combinations, except that the threshold concentration of lead is much higher.



For test blends containing iron and copper, it must be remembered that the threshold concentrations for each of these metals is very low, 15 ppb for copper and 25 ppb for iron. Therefore, any poor thermal stability for any copper-iron blend except those containing very low concentrations of each metal may be attributed to the effects of either one or the other metal. For blends containing zinc plus either copper or iron, however, it must be remembered that the zinc threshold concentration is fairly high (100 ppb). It is possible to have a solution containing zinc and either copper or iron with the concentration of each metal far below the respective threshold concentrations, and yet the *total metal concentration* exceeds the threshold concentration for either copper or iron. Thus, it is not possible to distinguish whether the joint effect is synergistic or merely additive.

Whatever the mechanism for the zinc reactivity, test results indicate that the threshold concentration for iron or copper in JP-7 is very low when zinc is also present. The following threshold concentrations (ppb) of added metal in two-metal combinations are compared with the single-metal values, based on analysis of the over all coker results and metal content data:

	<u>Pb</u>	<u>Zn</u>	<u>Fe</u>	<u>Cu</u>
Two metals:			10	10
	<500		10	
		10	10	
	<500			10
		10		10
	<500		10	
One metal:	<500	100	25	15

The lead concentrations are all listed as "below 500 ppb," in view of the consistent loss of lead from the test blends.

The results of fuel coker tests on Fuel A and Fuel Z blends containing three and four contaminant metals are listed in Table 9. Although there are discrepancies between the results on the two fuels, the trend is the same—when three or four metals contaminate JP-7 fuel, the amount of each that can be tolerated is very low. This can be illustrated by the following threshold concentrations in ppb of added metal:

	<u>Pb</u>	<u>Zn</u>	<u>Fe</u>	<u>Cu</u>
Three metals:		10	10	10
	<400		10	10
	<400	10	10	
	<400	10		10
Four metals:	<300	10	10	10

Here again, the concentrations are nominal (added) concentrations, and the true lead concentrations are generally far below the nominal values.

The threshold concentrations that have been presented here are maximum values in the sense that high-quality JP-7 fuel certainly cannot tolerate any greater concentrations without significant loss of thermal stability. It is not possible in a program of this type to determine the true threshold concentrations, owing to limitations imposed by loss of metals in sample handling and also by the lower limits of metal concentrations that can be determined accurately by analysis.

TABLE 9. EFFECT OF MULTIMETAL COMBINATIONS ON FUEL BREAK-POINT IN GAS-DRIVE COKER

Metal added, ppb				Breakpoint, °F
Fe	Cu	Zn	Pb	
<i>Fuel A</i>				
5	5	5	---	675 (tube)
10	10	10	---	600-625 (tube) <sup>a</sup>
10	10	20	---	600 (tube)
10	10	---	300	650 (tube)
10	10	---	400	600 (filter)
10	10	---	500	600 (filter)
10	---	10	300	>650
10	10	10	200	>700
10	10	10	300	575 (filter)
10	10	20	300	550 (tube)
<i>Fuel Z</i>				
5	5	5	---	600 (tube)
10	10	10	---	575 (tube)
10	10	20	---	600 (tube)
5	5	5	100	>650
5	5	5	200	>650
5	5	5	300	600 (tube)
5	5	5	400	>650
5	5	5	500	650 (tube)
<p>a. Composite result for two blends; one test failed at 525°F.</p>				



## SECTION VI

### EFFECT OF ADDITIVES ON THRESHOLD METAL CONCENTRATIONS

#### 1. GENERAL

A series of tests was run to determine whether the threshold metal concentrations established previously would be affected by the presence of a metal deactivator or an antioxidant, either or both of which may be used in JP-7 and other jet fuels at the option of the manufacturer.

A certain ambiguity should be noted, in that it was impossible to establish from the available records whether or not the base fuel (in this case Fuel Z) did or did not contain these additives. Presumably it did not, since no positive evidence could be found for the addition of such materials.

#### 2. METAL DEACTIVATOR

The only metal deactivator approved for use in JP-7 fuel is N,N'-disalicylidene-1,2-propanediamine. A commercially available formulation of this material was tested in Fuel Z at the maximum allowable concentration of 2.0 pounds of active ingredient per 1000 barrels of fuel. Blending procedures and the results of metal-content analyses were presented previously (see Table 5).

Since the metal deactivator was diluted with toluene to prepare concentrates in the blending operation, it was necessary to determine whether the toluene itself could affect the thermal stability of JP-7 fuel. A special blend of fuel with toluene (without metal deactivator) was prepared, using the same proportion of toluene present in the finished blends containing metal deactivator. Thermal stability tests on this special blend indicated that the toluene had no detectable effect on the fuel's breakpoint.

Gas-drive fuel coker test results on blends of Fuel Z, metal deactivator, and metal naphthenates are summarized in Table 10. The metal deactivator did produce an increase in threshold concentrations, as can be seen from the following comparison:

	Threshold concentration, ppb			
	<u>Pb</u>	<u>Zn</u>	<u>Fe</u>	<u>Cu</u>
<u>Based on metal added</u>				
For all fuels ("best values")	250	100	25	15
For Fuel Z	500	150	25	75
For Fuel Z + metal deactivator	600	600	200	100
<u>Based on metal found</u>				
For Fuel Z	235	75	?	24
For Fuel Z + metal deactivator	390	419	?	?

The comparisons based on "metal found" are incomplete since the comparison was restricted to "F" samples, i.e., those taken from the coker influent during one of the later tests. Despite the gaps in the data, the trend is quite evident—the metal deactivator did increase the threshold concentrations at which metals begin to affect thermal stability.

As noted in Table 10, there were numerous instances of blue or bluish-white deposits in the coker tests on blends containing a metal deactivator. As previously, these deposits were ignored in arriving at the breakpoint ratings and the threshold concentrations. If such deposits had been taken into account, breakpoints and threshold concentrations would have been lower, and the use of a metal deactivator would show little advantage.

**TABLE 10. GAS-DRIVE COKER BREAKPOINTS FOR  
FUEL BLENDS CONTAINING METAL DEACTI-  
VATOR AND METAL NAPHTHENATES**

Metal added, ppb	Breakpoint, °F	Remarks
None (control fuel) <sup>a</sup>	>675	
35 Fe	>650	
50 Fe	>650	
100 Fe	>650	
200 Fe	≤600 (tube)	
75 Cu	>650	One failure at 600°F; blue on tube for all tests
100 Cu	≤650 (tube)	Blue on tube for all tests
500 Pb	>650	Bluish-white on tube for all tests
600 Pb	≤650 (tube)	Bluish-white on tube for all tests
700 Pb	650 (tube)	Bluish-white on tube for all tests
150 Zn	>650	
200 Zn	>650	Bluish-white on tube for 1 test
300 Zn	>650	
400 Zn	>650	
500 Zn	>650	
600 Zn	≤600 (tube)	

**a. Fuel Z plus 2 lb/1000 bbl N,N'-dialicylidene-1,2-propane-  
diamine.**

### 3. ANTIOXIDANT

Similar tests were conducted on an antioxidant, 2,4-dimethyl-6-tertiary-butylphenol, approved for use in JP-7 fuels at a maximum concentration of 8.4 pounds per 1000 barrels of fuel. Gas-drive fuel coker test results on these blends are summarized in Table 11. Because of the limited number of blends tested, it is not possible to draw any positive conclusions as to the effect of antioxidant on metal threshold concentrations. If one compares the nominal (added) concentrations, the antioxidant did appear to raise the threshold concentrations for copper, lead, and zinc, but no such trend appears if the comparison is based on amounts of metal found.

TABLE 11. GAS-DRIVE COKER BREAKPOINTS FOR FUEL BLENDS CONTAINING ANTIOXIDANT AND METAL NAPHTHENATES

Metal added, ppb	Breakpoint, °F	Remarks
None (control fuel) <sup>a</sup>	>700	
35 Fe	≤600 (tube)	
75 Cu	>650	
100 Cu	>600, ≤650 (tube)	Blue-green on tube for one test
500 Pb	>650	Blue on tube
600 Pb	650 (tube)	Blue on tube
150 Zn	>650	
200 Zn	>600, ≤650 (tube)	

a. Fuel Z plus 8.4 lb/1000 bbl 2,4-dimethyl-6-tert-butylphenol.

## SECTION VII

### OTHER SPECIFICATION TESTS

Selected JP-7 specification tests were run on various blends of Fuel A with metal naphthenates to determine whether any characteristics other than thermal stability would be changed by the presence of these contaminants. It was found that only the water separator results (WSIM) were affected, and such effects were restricted to blends with high contents of iron naphthenate. The ranges of added-metal content that were checked were as follows:

Lead	25 to 50 ppb (no effect)
Zinc	5 to 50 ppb (no effect)
Copper	5 to 25 ppb (no effect)
Iron	5 to 25 ppb (no effect)
Iron	200 to 500 ppb (WSIM lowered about 30 units)

It is probable that any metal salt of an organic acid will have some effect on the fuel's WSIM if present in sufficient quantities. Such effects cannot be attributed to the metal *per se*, but rather to the entire metal-salt molecule, which acts as a surfactant. If the metal is present as a naphthenate or similar salt, the concentration necessary to affect the fuel WSIM adversely will probably be well above the concentration at which thermal stability effects become apparent in JP-7 fuel.

## SECTION VIII

### CONCLUSIONS

This program has demonstrated that the thermal stability of JP-7 fuel can be affected adversely by trace amounts of lead, zinc, iron, or copper dissolved in the form of naphthenic acid salts. Added-metal contents as low as 15 ppb copper, 25 ppb iron, 100 ppb zinc, or 100 to 250 ppb lead can lead to serious degradation of thermal stability in a high-quality JP-7 fuel. Studies of different metals in combination did not give any clear-cut evidence of synergistic action but did indicate the possibility that fuels containing traces of zinc may be especially susceptible to the effects of other metals. The use of N,N'-disalicylidene-1,2-propanediamine, a metal deactivator approved for use in JP-7 fuels, appears to raise the tolerable levels of metal contamination.

Correlations and conclusions based on added-metal contents must be tentative because of the fugitive nature of these metals when present in such low concentrations. In this program, loss of metal during the various fuel blending and handling operations was the rule rather than the exception, and additional complications were introduced by the pickup of extraneous iron in many samples. With the manner of fuel sample handling that must be used in running fuel coker tests, it is literally impossible to provide a sample that will maintain a steady composition from test to test. No doubt this conclusion is equally true for other (nonmetallic) soluble contaminants, but it has seldom been shown so graphically as by the shifting metal contents reported here.

Because of the unstable contents of metals, the threshold values for added-metal content that are reported here must be regarded as maximum values; the true threshold concentrations are generally lower. Similar reservations should apply to conclusions from any test program in which added-metal contents are reported without the most rigorous checking of actual metal contents of fuel entering the test equipment.

The difficulties with shifting metal contents that were encountered here point out the impracticality of setting low limits on metal contents for fuel specification purposes, unless sampling, sample transfer, and analytical procedures are specified in a manner to ensure that the results are indeed characteristic of the fuel batch at a given point in its history.

## REFERENCES

1. Johnston, R. K., and Monita, C. M. (Southwest Research Institute), "Jet Fuel Stability and Effect of Fuel System Materials," AF Aero Propulsion Lab, Technical Report AFAPL-TR-68-20, February 1968.
2. Johnston, R. K.; Monita, C. M.; Reed, D. V.; and Schenk, L. W. (Southwest Research Institute), "Research on Hydrocarbon Fuels and Related Application," AF Aero Propulsion Lab, Technical Report AFAPL-TR-70-5, April 1970.
3. Johnston, R. K.; Monita, C. M.; Linder, R. E., et al (Southwest Research Institute), "Research on Hydrocarbon Fuels and Related Applications," AF Aero Propulsion Lab, Technical Report AFAPL-TR-70-5, Part II, May 1971.
4. Coordinating Research Council, "Evaluation and Precision of the Gas-Drive Modified Standard Fuel Coker," CRC Report No. 428, December 1969.
5. Lander, H. R., Jr., "Stability of High-Temperature Hydrocarbon Jet Fuels During Storage," AF Aero Propulsion Lab, Technical Report APL-TDR-64-107, November 1964.
6. Scribner, W. G., et al (Monsanto Research Corporation), "Determination of Parts per Billion Iron in Hydrocarbon Jet Fuels," AF Aero Propulsion Lab, Technical Report AFAPL-TR-66-44, April 1966.
7. Scribner, W. G., and Borchers, M. J. (Monsanto Research Corporation), "Effect of Additives on the Determination of Parts per Billion Lead in JP-4, JP-5, JP-7, and JP-8," AF Aero Propulsion Lab, Technical Report AFAPL-TR-69-86, October 1969.
8. Scribner, W. G., "Revised Procedures for the Determination of ppb Iron, ppb Copper, and ppb Zinc in Fuels," letter of July 29, 1968, Monsanto Research Corporation.
9. Grandey, M. F., and Wehner, E. H., "Thermal Stability of Clean and Contaminated JP-6 Fuels," SAE, National Aeronautic and Space Engineers and Manufacturers Meeting, Los Angeles, California, October 9-13, 1961, pp 5, 6.
10. Coordinating Research Council, "An Investigation of the Performance of Jet Engine Fuels for Supersonic Transport Aircraft," (Small-Scale Fuel Coker Studies), CRC Report No. LD-151, June 1, 1965.
11. Smith, J. D., "Thermal Stability of Fuels. The Effect of Copper on Deposit Formation and Heat Transfer in a Tubular Heat Exchanger," Shell Research Ltd, Thornton Research Center, March 1970.