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INVESTIGATION OF CHLORINE CONTAMINATION
IN AIR FORCE MIL-H-5606 HYDRAULIC FLUID
IN AIRCRAFT HYDRAULIC SYSTEMS

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Fluids, Lubricants and Elastomers Branch
Nonmetallic Materials Division

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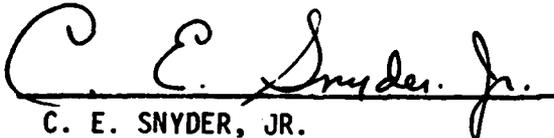
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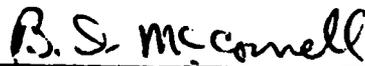
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FOR THE COMMANDER



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20. Abstract (continued)

✓ Fluorescence spectroscopy as primary and gas liquid chromatography and micro-coulometry as acceptable alternates were established as test methods to monitor the chlorine content of MIL-H-5606 aircraft hydraulic fluid.

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FOREWORD

This report was prepared in the Fluids, Lubricants and Elastomers Branch (AFWAL/MLBT), Materials Laboratory, Nonmetallic Materials Division, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio 45433. The investigation was performed under Project 2421, "Aerospace Fluids, Lubricants and Fluid Containment," Task 242102, "Lubricating Materials and Tribology," Work Unit 24210213.

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SUMMARY

A field problem in the C-141 aircraft, associated with hydraulic selector valve malfunctions in landing gear and door systems was attributed to corrosion of the valve spool and sleeve. This corrosion was caused by the presence of chlorine in the operational hydraulic fluid which attacked the highly polished close tolerance surfaces in some valves. The primary source of chlorine contamination was determined to be from residual chlorine containing solvents remaining in system components after normal cleaning, flushing and/or vapor degreasing operations. The initial action to reduce the incidence of chlorine contamination was to revise the Technical Order covering C-141 hydraulic system maintenance procedures to replace the chlorinated solvents with P-D-680, Type II hydrocarbon solvent. An additional maintenance procedure at periodic depot maintenance (PDM) was instituted at Warner-Robins Air Force Base to monitor and control the C-141 hydraulic fluid chlorine contamination to a maximum allowable concentration of 200 ppm. Concurrent with this, AFWAL/MLBT and the ALC laboratories coordinated to develop an AF standardized procedure for determining low levels of chlorine in new and used hydraulic fluids - up to 200 ppm (the operational system fluid requirement). Three analytical methods were adopted in the following order of usage, i.e., X-ray fluorescence, gas chromatography and microcoulometry.

SECTION I
INTRODUCTION

In February, 1975 the Deputy Inspector General for Inspection and Safety, USAF, reported to AFLC/MM, AFSC/SD and AFWAL/MLBT that recent information and laboratory data had indicated that the use of halogen type (chlorine/fluorine) cleaning compounds in aircraft hydraulic system components had resulted in contaminated hydraulic fluid, which, in turn, had caused corrosion of hydraulic system components. They reported that this had resulted in failure of hydraulic components, such as landing gear struts, servo valves, actuators, pumps, etc. Chlorine-contaminated hydraulic fluid was believed to cause general deterioration of actuator spool surfaces, thus resulting in erratic operation of the system components and in some cases, subsequent failure. Their review of selected aircraft mishaps indicated a high incidence of failed hydraulic components due to stress corrosion. Stress corrosion was apparently initiated by the chlorine contaminated hydraulic fluid. Chlorine contamination of aircraft hydraulic systems was viewed as a source of accident potential. A joint study by AFLC/AFSC resources was recommended with the following objectives:

- a. Determine the magnitude of halogen (chloride/fluoride) contamination in hydraulic systems and fluids (MIL-H-5606 and MIL-H-6083).
- b. Determine the detrimental effects on system operation.
- c. Investigate what is being accomplished to control chemical contamination of hydraulic fluid.
 - (1) determine if there is a need to revise MIL-H-5606/6083 contamination control.
 - (2) Determine the adequacy of moisture control.
- d. Identify procedures used in overhaul and cleaning hydraulic component and systems in which halogenated contaminants are introduced.
- e. Determine the recommended practices for cleaning, drying and flushing hydraulic assemblies.

f. Determine if a reliable method exists for checking halogen levels in hydraulic fluids.

g. Determine whether or not there are nonhalogenated solvents that can be used safely in cleaning operations.

An initial meeting in April, 1975 attended by concerned Air Force personnel was held at AFLC Headquarters to review the above points raised by the Inspector General. It was concluded that there was insufficient organized information within the Air Force to reach a final judgement of the magnitude of the use of halogen-containing fluids in operational aircraft systems. To remedy this information gap, surveys were to be initiated to 1) determine the extent of halogenated solvent use in cleaning hydraulic systems at the ALC's, 2) analyze used MIL-H-5606 fluid samples for chlorine content at the ALC and 3) survey correlative data of accident/incident on all aircraft hydraulic components and landing gear strut failures that were identified as cause/contributing in the mishaps. SA-ALC were to determine their capabilities to test for halogen-type solvents (chlorine and fluorine) in MIL-H-5606. Specifications MIL-H-5606 and MIL-H-6083 were to be surveyed to determine if revisions were necessary to control chemical and moisture contamination levels. By February, 1976 subsequent reviews of these surveys indicated that halogenated solvents were used liberally throughout ALC's in flushing and cleaning hydraulic systems and components but that the chlorine content of used MIL-H-5606 fluid analyzed at various ALC's was generally low, in the neighborhood of 0 to 57 ppm. The surveys showed no data to correlate hydraulic fluid chlorine content to component or systems failure resulting in loss of aircraft. No action was deemed necessary in the area of specification revisions to control chlorine contamination at that time.

In July, 1975 a problem surfaced at McGuire AFB relative to selector valve malfunctions in landing gear and door systems of the C-141 aircraft. It was speculated that this problem was due to the viscosity index improver of the fluid coming out of solution. An interim laboratory procedure was issued at OC-ALC that covered the removal of the polymer from the valve but it was never officially implemented. In July, 1976 MAC Headquarters requested that the problem be given additional attention because

valve failures of this type were once again prevalent in the C-141 fleet. As a result of the combined efforts of ASD/ENFEM, AFWAL/MLBT and SA-ALC/SFQLA personnel, surface analysis of a stuck selector valve and instrumental analysis of hydraulic fluid samples from incident aircraft were accomplished. As will be discussed later in this report, these analyses showed that chlorine contamination was present in the hydraulic fluid samples and the valve spool and sleeve were corroded as a result of the attack of some form of reactive chlorine on the metal surfaces. This was the first documented case of the use of chlorinated solvents in the maintenance of hydraulic systems causing operational malfunctions in Air Force aircraft systems.

SECTION II

DISCUSSION

1. ORIGIN AND DEGREE OF CONTAMINATION

As a result of the 1975/1976 surveys, it was determined that the primary source of aircraft hydraulic fluid contamination was considered to occur during repair of system components when they were cleaned with chlorinated solvents by immersion and/or vapor degreasing. Several other potential sources as listed below were identified.

- a. Hydraulic fluid servicing carts
- b. Hydraulic fluid test benches
- c. New fluid
- d. Flight line maintenance procedures

The investigation into the degree of contamination included analysis of hydraulic fluid from test stands, servicing carts and suspected contaminated samples. Hydraulic fluid samples from crashed aircraft and aircraft undergoing overhaul were also analyzed. The Air Logistic Center's (ALC's) laboratories and AFWAL/MLBT analyzed nearly 1000 hydraulic fluid samples from aircraft, ground support equipment and new hydraulic fluid samples from four fluid suppliers. The aircraft samples consisted of the analysis of hydraulic fluid from actuators, main landing gears and struts and nose and power control units from C-141's, B-52's, F-105's, F-111's, F-4's, T-38's, C-5A's, KC-135's and F-106's.

a. A total of 250 aircraft fluid samples were analyzed. The results in parts per million (ppm) chlorine and percentages of the total samples appear below:

1. 300 ppm and above = 1 samples or less than 1 percent
2. 200-300 ppm = 5 samples or 2 percent
3. 100-199 ppm = 38 samples or 15 percent
4. 0-100 ppm = 206 samples or 82 percent

b. A total of 703 ground support equipment hydraulic fluid samples were analyzed. Results in parts per million chlorine and percentages of total samples appear below:

1. 39950-43460 ppm = 2 samples or less than 1 percent
2. 2000-9600 ppm = 97 samples or 14 percent
3. 1000-1999 ppm = 55 samples or 8 percent
4. 500-999 ppm = 131 samples or 19 percent
5. 200-499 ppm = 82 samples or 12 percent
6. 100-199 ppm = 78 samples or 11 percent
7. 0-99 ppm = 258 samples or 36 percent

Slightly less than 54 percent were above 200 ppm.

c. A total of 25 new hydraulic fluid samples from four fluid suppliers were analyzed for chlorine with the following results:

1. 200+ ppm = 2 samples or 8 percent
2. 101-199 ppm = 3 samples or 12 percent
3. 51-100 ppm = 7 samples or 28 percent
4. 11-50 ppm = 6 samples or 24 percent
5. 0-10 ppm = 7 samples or 28 percent

Eight percent of the new fluid samples contained chlorine above the 200 ppm level.

(At the time these analyses were conducted, the potential analytical error in the chlorine analysis data due to the lack of X-ray method standardization was not realized. Although this does cause a lack of confidence in the accuracy of the reported data in this section, the trends of chlorine contamination levels reported were considered to be representative of those contained in the samples.)

The laboratories analyzed 272 hydraulic fluid samples from ground support equipment, aircraft and new hydraulic fluid for water content. The results are as follows:

- a. 2001+ ppm = 4 samples or 2 percent
- b. 1001-2000 ppm = 8 samples or 3 percent
- c. 401-1000 ppm = 22 samples or 8 percent
- d. 100-400 ppm = 139 samples or 51 percent
- e. 0-99 ppm = 99 samples or 36 percent

The above analysis indicated that sufficient amounts of water are present in hydraulic fluids used in ground support equipment and aircraft to combine with chlorinated solvents to form acids which can cause corrosion.

2. DETERMINATION OF DETRIMENTAL EFFECTS OF CHLORINE CONTAMINATION

In early July, 1976 Aeronautical Systems Division (ASD) and AFWAL/ Materials Laboratory were notified of sticking solenoid operated, 4-way selector valves in Military Airlift Command (MAC) C-141 aircraft (The spool would stick in the sleeve of a lapped spool-sleeve assembly). The stuck valve in the landing gear subsystem prevented the gear from extending and emergency procedures were required to lower the gear. Failed valves and hydraulic fluid samples from the aircraft in which the problem had occurred were submitted to WPAFB for analysis. ASD and AFWAL/MLBT personnel disassembled the "stuck" valve and performed optical and scanning Auger Spectroscopic analysis of the spool and the interior surface of the sleeve assembly (Reference 1).

Steel valve surfaces, wetted by hydraulic fluid had an olive drab coloration. After removal of the fluid, the residue on the spool and sleeve surface had a reddish-brown appearance (Figure 1). A noncorroded spool is included in the figure for comparison. The problem was diagnosed as chlorine contamination of MIL-H-5606 hydraulic fluid, which was confirmed by X-ray fluorescence and gas chromatographic analysis on fluid samples taken from problem aircraft. Analysis of the fluid sample revealed that the chlorine contamination level ranged from 225 to 405 ppm in the systems.

Pitting corrosion was visually evident on the spool under moderate magnification (Figure 2). Surface analysis of spool and sectioned sleeve assembly by Auger Spectroscopy showed elemental chlorine, oxygen, iron and carbon (Figure 3). Separate analysis of the fluid samples by gas chromatography indicated the presence of 1,1,2-trichlorotrifluoroethane solvent which was the only chlorinated solvent observed.

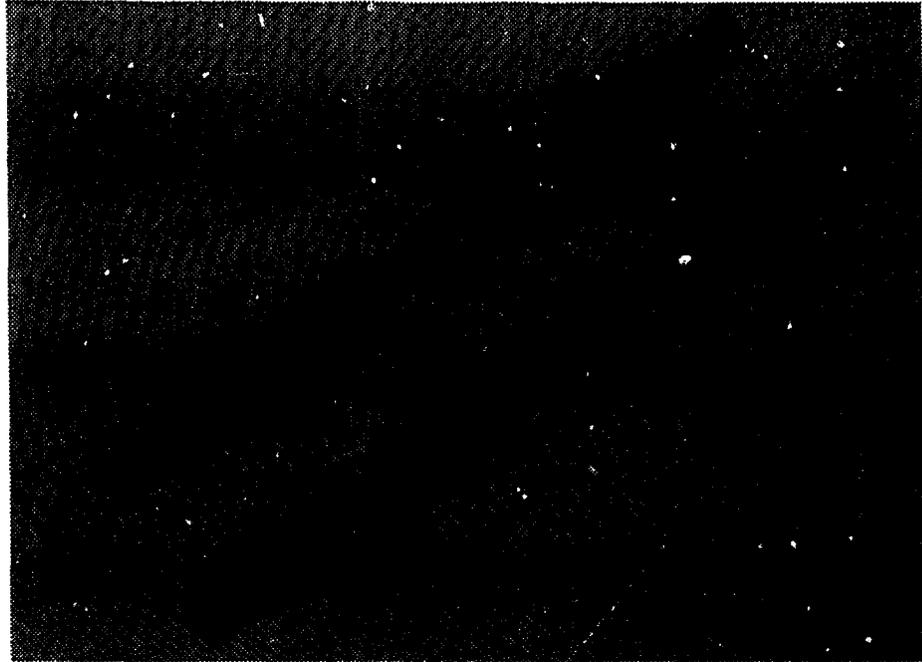


Figure 1. Spools from Selector Valve Assembly

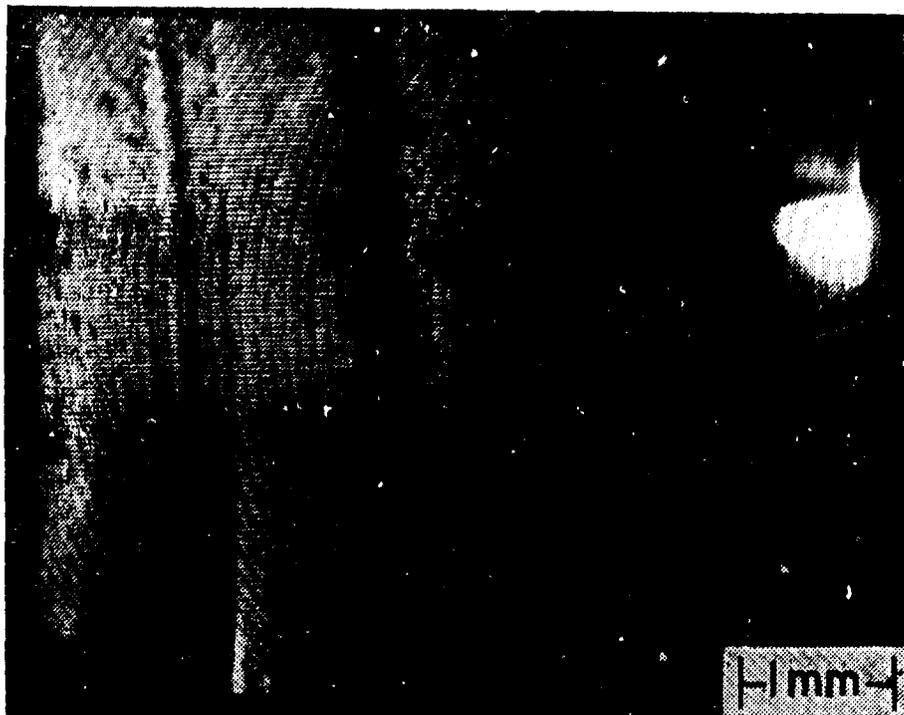


Figure 2. Spool Housing

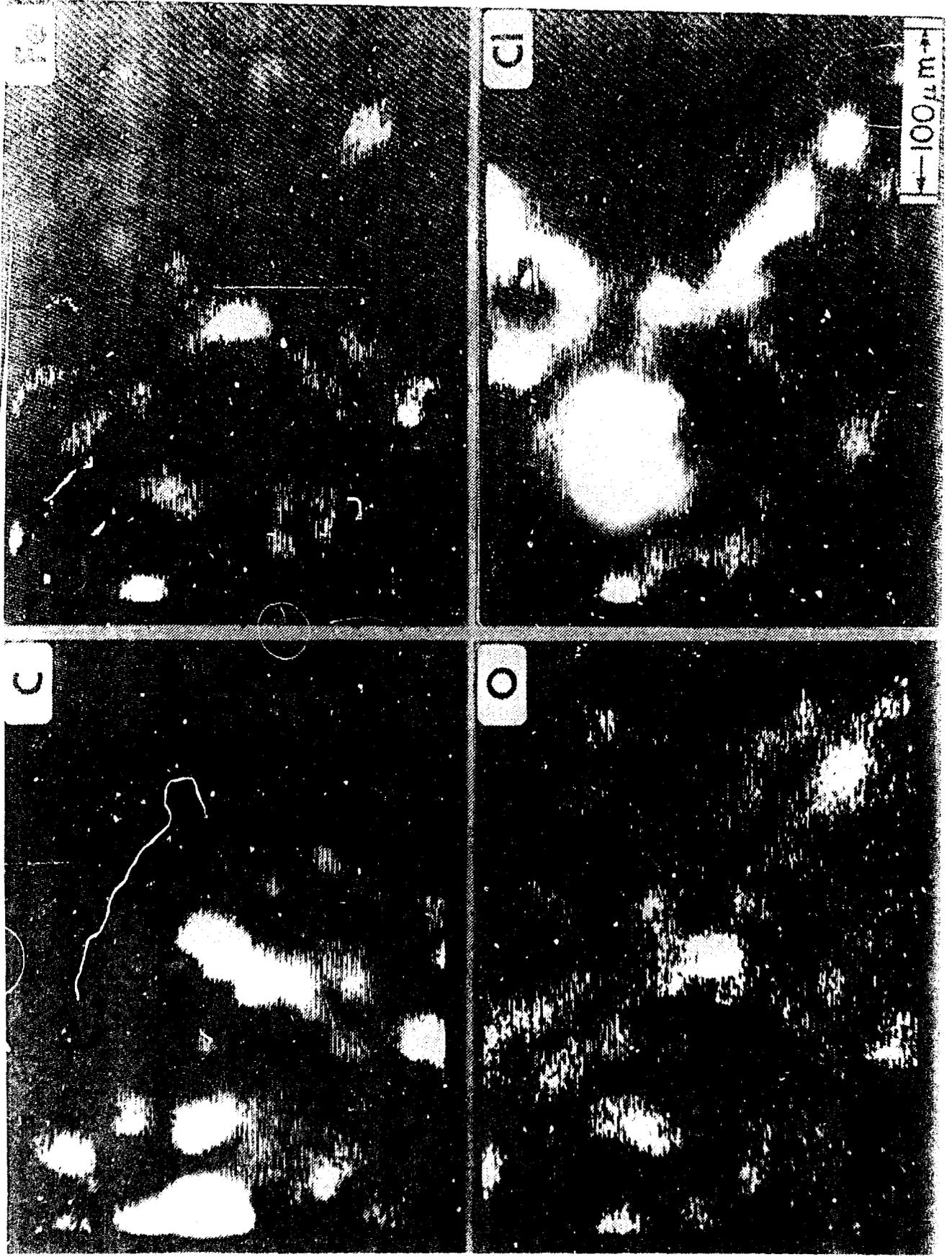


Figure 3. Spool Housing 250x Magnification, Scanning Auger Microscope

There is more than one supplier of C-141 selector valves. The spool and sleeve material is nitrided nitralloy in one valve design and 52100 in another valve design. These are both low chrome steels (less than 2 percent) and have poor resistance to corrosion. Low chrome steels are permitted to be in contact with hydraulic fluid in Type I (-65 to 160°F) systems per MIL-H-8775 hydraulic component specification, but are not permitted, however, in Type II (-65 to 275°F) hydraulic systems. It has been shown (See Appendix A) that when the landing gear door valve solenoid is energized, a temperature rise of approximately 85°F occurs. With the input of this additional heat, the fluid and valve temperature would achieve temperatures above a Type I hydraulic system. Assuming hydraulic fluid temperature of 130°F which would be typical for a Type I system immediately after shut down or landing, the temperature rise of 85°F caused by this solenoid energization would result in a fluid temperature of 215°F, clearly above the Type I limit. This is relevant because this valve is continuously energized when the landing gear is down and electrical power is required for any reason. These conditions are prevalent for a significant amount of time because electrical power is required for the majority of maintenance actions.

The C-141 has a vented reservoir which could permit moisture to enter, an ingredient considered necessary for chlorine induced corrosion (Reference 2). In the system with 405 ppm chlorine there was 153 ppm of water. MIL-H-5606 fluid specification permits 100 ppm of water in delivered fluid. There was no established limit in the Air Force as to the maximum allowable chlorine contamination in the hydraulic systems.

3. CHLORINE CONTAMINATION CONTROL METHODS

Since chlorine contamination was found to be the cause of the stuck C-141 selector valve, it was decided that action must be taken to reduce/eliminate the chlorine from the aircraft hydraulic systems. As stated previously, the primary source of the chlorine contamination was chlorinated solvents introduced during repair of system components when they were cleaned by immersion and/or vapor degreasing in these solvents. Therefore, a recommendation was made to OC-ALC, the office of primary

responsibility (OPR) for the C-141 hydraulic system, to revise the technical orders for repair of hydraulic components to prohibit the use of chlorinated solvents in overhaul and repair of hydraulic components. It was further recommended that P-D-680, Type II hydrocarbon solvent, be substituted in these applications. These recommendations were incorporated into technical order revisions.

As an interim measure, additional methods were recommended to reduce the chlorine contamination levels in C-141 aircraft hydraulic systems. First a program, as described in TO IC-141A-2-1MS-1, "Maintenance Support Information Manual", was instituted at Warner Robins AFB to sample and determine chlorine contamination levels of C-141 hydraulic systems during periodic depot maintenance (PDM). Hydraulic systems found to contain in excess of 200 ppm chlorine were drained, flushed and filled with new MIL-H-5606 hydraulic fluid. The estimated time per aircraft for performing this program was 150 manhours and the estimated cost was \$4100 per aircraft.

In an attempt to perform this same function at a lower cost, a project was funded at OO-ALC by the Air Force Productivity, Reliability, Availability and Maintainability Office (PRAM). The purpose of this program was to determine the feasibility of using a portable ground based hydraulic fluid purification unit. This unit, when attached to the aircraft, would remove chlorine, moisture and particulate matter from the aircraft hydraulic systems.

The effectiveness of the control methods for reducing the chlorine content of hydraulic systems in C-141 aircraft is demonstrated in Figure 4, which shows the percentage of C-141 PDM aircraft with at least one hydraulic system containing over 200 ppm chlorine. The methods used to accomplish these results were the revision of technical orders and the flushing program at Warner Robins. As can be seen, the chlorine contamination was drastically reduced in the June-August, 1977 time frame.

The ability to connect the portable fluid purification equipment to C-141 aircraft hydraulic systems and to achieve the desired results has not yet been successfully demonstrated. The effort here was only a preliminary attempt to evaluate this type of equipment for this application.

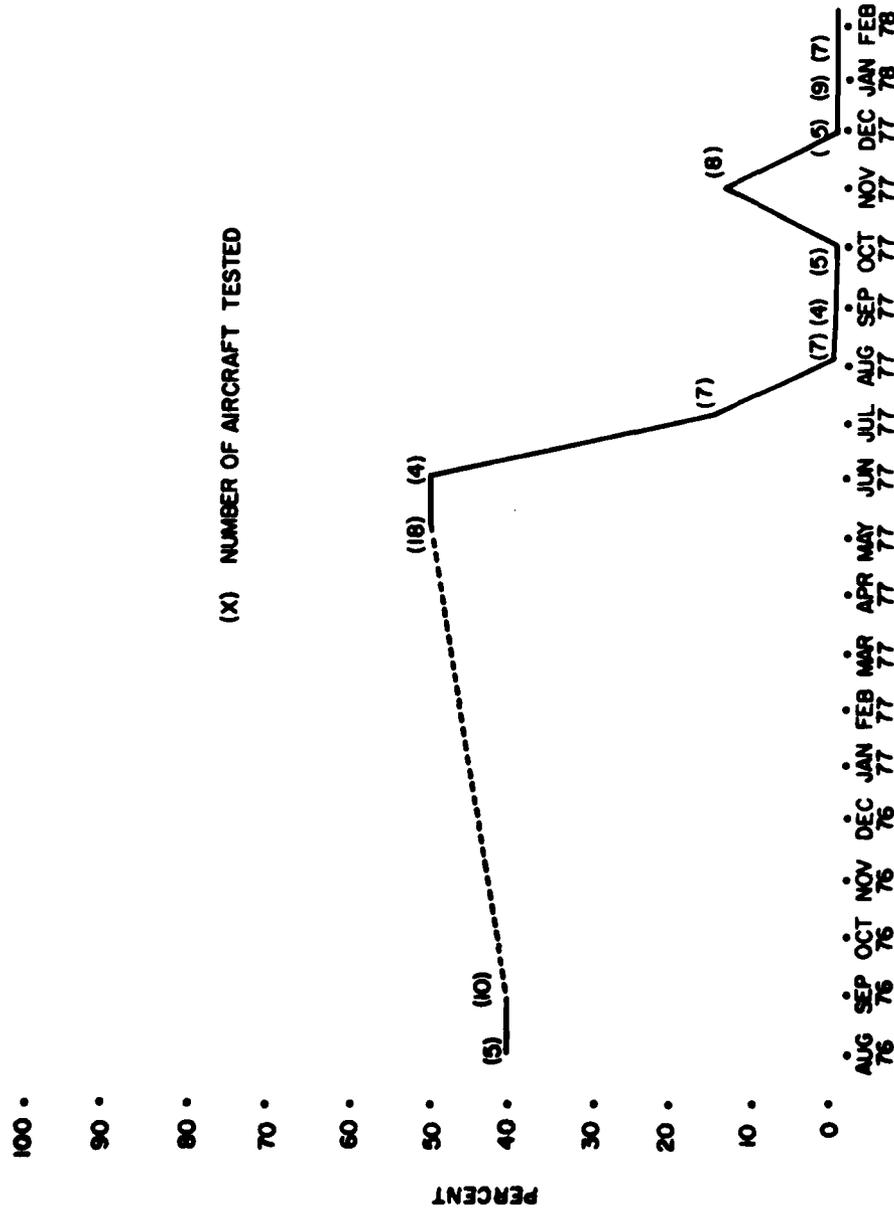


Figure 4. Percentage of C-141 PDM Aircraft with at Least One Hydraulic System Containing Over 200 ppm Chlorine

Failure to satisfactorily decontaminate fluid in this demonstration does not mean such a procedure could not be made to work satisfactorily.

4. DEVELOPMENT OF CHLORINE CONTAMINATION ANALYSIS METHODS

In order to determine the extent of hydraulic fluid contamination by chlorine in the C-141 fleet and to determine the effectiveness of the control methods at reducing the contamination levels, reliable test methods must be available for determining the amount of chlorine in the hydraulic fluid samples. Analytical methods for determining the amount of chlorine were described in an Aerospace Information Report on phosphate esters by hydraulic fluid producers (Reference 3). It was realized that the problems caused by chlorine contamination in phosphate ester based hydraulic fluids used by the commercial aviation industry were significantly different than those caused by chlorine contamination in hydrocarbon based hydraulic fluids used in military aircraft. However, it was felt that the analytical methods could be used for both types of fluids.

The analytical methods selected were:

- a. X-ray fluorescence spectroscopy
- b. Gas chromatography
- c. Microcoulometry

It was preferred to develop an optimized method using the X-ray fluorescence procedure due to the availability of equipment in the ALC laboratories. In order to determine the capabilities of the laboratories to perform these analyses a set of hydraulic fluid samples containing known amounts of chlorinated solvents was distributed to the participating laboratories. The analytical data obtained using X-ray fluorescence and gas chromatographic methods are shown in Table 1. The data indicates that very poor agreement was obtained using X-ray fluorescence by the various laboratories and in most cases poor repeatability was obtained analyzing a duplicate sample in the same laboratory. Somewhat better data were obtained using gas chromatographic methods.

TABLE 1
 FIRST INTERLABORATORY CORRELATION SAMPLES CHLORINE DETERMINATION
 (ppm CHLORINE BY WEIGHT)

METHOD/LABORATORY	CALCULATED VALUE AS PREPARED									
	47	101	161	301	207	568	1063	0		
X-RAY/LAB A	76	153	204	317	228	510	842	0		
	89	--	200	--	--	--	--			
X-RAY/LAB B	19	57	75	135	100	315	585	12		
	--	--	--	--	--	275	--	4		
X-RAY/LAB C	34	80	150	252	166	516	895	10		
	--	--	--	--	189	--	--			
X-RAY/LAB D	7	115	175	325	--	588	1035	23		
	--	--	--	--	220	--	1140			
X-RAY/LAB E	(leaked)	65	155	300	--	580	1050	0-5		
	--	--	--	--	205	--	1145			
X-RAY/LAB F	259	218	276	315	285	629	1022	244		
	--	--	--	327	--	516	--			
X-RAY/LAB G	98	109	--	779	462	619	1011	73		
	366	170	512	--	--	--	--			
GAS	65	102	--	344	233	507	1028	10		
CHROMATOGRAPHY	32	98	162	--	--	--	--			

To improve agreement in the data obtained using the X-ray fluorescence method, a review of some of the samples and instrumental parameters was conducted. The investigated parameters and the corresponding effects were as follows:

a. Volatility of solvents - gas chromatography (GC) studies revealed a problem with the high volatility of calibration solvents and the solvents being determined in the fluid samples.

1) Lower volatility solvents were investigated and used for the preparation of calibration standards.

2) Care must be exercised in handling the contaminated hydraulic fluid samples to minimize the evaporation of the volatile solvents.

b. Contamination of Mylar film used in X-ray cells - chlorine contamination of the film surface was detected when an individual rubbed the film with his hands. With proper handling of the Mylar film the effect could be avoided.

c. Analysis (count) time - count time was not found to be a critical factor.

d. Phosphorous additive interference - the phosphorous required a different set of instrument parameters than presently used for the chlorine analysis and should not pose a problem.

e. Nominal power and current setting to maximize the counts - each laboratory would have to maximize their settings to insure good sensitivity and performance.

f. Atmosphere (vacuum and helium) effects - the helium atmosphere should be used if possible.

g. Particulate contamination - A high degree of particulate contamination could affect the chlorine counts. An extremely contaminated sample (one which could not be seen through) must be filtered or centrifuged prior to analysis.

A second set of correlation samples was distributed to the participating laboratories. These samples were prepared using various concentrations of three different halogenated solvents: 1,1,2-trichlorotrifluoroethane,

trichloroethylene and 1,1,2-trichloroethane. The X-ray fluorescence analysis data are reported in Table 2. Although the data are significantly improved over those obtained during the first correlation test program, the values obtained still lacked the desired degree of repeatability. Interlaboratory agreement, especially around the 200 ppm level, was unacceptable considering the maintenance costs incurred by obtaining incorrect data. The GC and microcoulometric analyses of these samples are also shown in Table 2. Although it appears that the GC method would require some additional attention to obtain good analytical values for 1,1,1-trichloroethane, excellent accuracy was demonstrated as shown in Table 3 with 1,1,2-trichlorotrifluoroethane which was the only chlorinated solvent actually found in C-141 hydraulic fluid samples.

A third set of correlation samples was distributed to the participating laboratories for chlorine analysis. The source of chlorine contamination in these samples was limited to 1,1,2-trichlorotrifluoroethane. A standard sample containing a carefully measured level of 200 ppm chlorine in the form of chlorobenzene was included with this set of correlation samples for a check of the analytical equipment and the calibration curve. It was felt that this would provide a significant increase in confidence of the data around the critical 200 ppm range. In addition, a proposed standard X-ray fluorescence chlorine analysis procedure was sent with the samples to be used for the analyses. Significantly improved data were obtained on these samples with generally good accuracy over the entire concentration range covered with these samples of 0 to 225 ppm as shown in Table 4. The values reported for the zero level contamination were considered very important because a recommended maximum allowable limit of chlorine contamination was requested for new fluid. Modifications to the proposed standard X-ray method suggested by the participating laboratories were incorporated into the final version which is being issued as an Air Force standard procedure. The analysis data in the third set of samples using GC and microcoulometric methods are shown in Table 4. Both direct injection and head space procedures were used for the GC analysis. The data showed good accuracy using either procedure. The microcoulometric procedure was found to show good accuracy on the samples. These procedures appear in the proposed MIL-STD in Appendix B.

TABLE 2
 SECOND INTERLABORATORY CORRELATION SAMPLES CHLORINE DETERMINATION
 (ppm CHLORINE BY WEIGHT)

METHOD/LABORATORY	CALCULATED VALUE AS PREPARED									
	25	175	190	200	210	276	450			
X-RAY/LAB A	43	145	142	195	125	250	293			
	0	--	136	--	--	--				
X-RAY/LAB B	15	150	190	235	179	180	415			
	--	148	--	--	200	--				
X-RAY/LAB C	16	166	161	190	203	239	397			
	--	--	166	--	--	--	380			
X-RAY/LAB D	34	93	410	154	161	257	370			
	--	--	--	184	--	--	376			
X-RAY/LAB E	25	145	155	160	170	210	365			
	25	--	--	160	--	--				
X-RAY/LAB F	45	--	160	195	--	265	395			
MICROCOULOMETRY	--	169	135	--	171	--	384			
GAS CHROMATOGRAPHY	16	182	138	180	213	285	388			

TABLE 3
 SECOND INTERLABORATORY CORRELATION SAMPLES GAS CHROMATOGRAPHY
 SPECIFIC SOLVENT CHLORINE DETERMINATION

PARTS PER MILLION CHLORINE BY WEIGHT														
$C_2Cl_3H_3$				C_2Cl_3H				$C_2Cl_3F_3$				TOTAL		
WT. CALC.	CONTRACTOR	AFWAL MLBT	WT. CALC.	CONTRACTOR	AFWAL MLBT	WT. CALC.	CONTRACTOR	AFWAL MLBT	WT. CALC.	CONTRACTOR	AFWAL MLBT	WT. CALC.	CONTRACTOR	AFWAL MLBT
0	0	0	25	46	16	0	0	0	25	46	0	25	46	16
0	1	0	0	4	0	175	173	182	175	178	182	175	178	182
126	59	79	32	0	29	32	36	30	190	95	30	190	95	138
40	22	32	40	45	38	120	104	110	200	171	110	200	171	180
35	15	27	140	52	152	35	55	34	210	122	34	210	122	213
92	50	90	92	109	103	92	96	92	276	255	92	276	255	285
257	113	190	64	62	70	129	115	128	450	290	128	450	290	388

TABLE 4
THIRD INTERLABORATORY CORRELATION SAMPLES CHLORINE DETERMINATION
(ppm CHLORINE BY WEIGHT)

METHOD/LABORATORY	CALCULATED VALUE AS PREPARED				
	0	49	172	202	225
X-RAY/LAB A	0	25	194	190	207
X-RAY/LAB B	0	52	174	213	208
X-RAY/LAB C	0	26	168	198	190
X-RAY/LAB D	18	35	105	180	225
X-RAY/LAB E	0	110	184	212	230
X-RAY/LAB F	0	50	168	181	205
MICROCOULOMETRY GAS	0	68	197	224	226
CHROMATOGRAPHY/ LAB A GAS	0	50	175	220	235
CHROMATOGRAPHY/ LAB B	>1	56	179	200	231

AFWAL-TR-82-4027

An optimized X-ray fluorescence procedure has been developed and documented for the determination of chlorine contamination in MIL-H-5606 hydraulic fluid. Alternative methods utilizing GC and microcoulometry have been developed which demonstrated a high degree of accuracy.

SECTION III
RESULTS/CONCLUSIONS

Under certain conditions, hydraulic fluids contaminated with chlorinated cleaning solvents can cause corrosion in hydraulic system components.

The reduction of chlorine contamination in C-141 aircraft hydraulic systems was achieved by substitution of P-D-680 petroleum distillate solvent for chlorinated cleaning solvents in applicable hydraulic system maintenance technical orders. The drastic reduction of chlorinated solvent contamination in C-141 aircraft was accelerated by the adoption of a hydraulic system sampling and flushing procedure during PDM.

A maximum chlorine contamination limit of 50 ppm was established for new MIL-H-5606 hydraulic fluid. A maximum chlorine contamination limit of 200 ppm was established for hydraulic fluid in Air Force aircraft.

Three laboratory test methods were established to determine the amount of chlorine in hydraulic fluid samples. X-ray fluorescence spectroscopy was selected as the primary method with gas liquid chromatography and microcoulometry as acceptable alternatives.

APPENDIX A

APPENDIX A

A C-141 Main Landing Gear Door Selector Valve, Lockheed Part No. 3H90044, Ronson Hydraulics Units, Inc., Part No. 5C5617, Serial No. 1270, was obtained from Air Force supply. This valve is a solenoid-operated, 3/8 inch tube size, 4-way, 3 position unit. The valve was laboratory tested by the Mechanical Branch of the Flight Systems Engineering Directorate (ASD/ENFEM). Solenoid heat rise was found by connecting a regulated 28 volt power supply to the valve connector pins A and B. See Figure A-1. A thermocouple was taped to the corresponding solenoid, and temperatures were recorded every 10 minutes from a Leeds and Northrop temperature indicator. The valve ports were capped and the valve contained residual fluid. In one hour and ten minutes the measured solenoid temperature went from 80°F to 167°F, (a rise of 87°F)(Figure A-2). The heat rise may be relevant since the solenoid remains energized when the C-141 aircraft is on the ground and electrical power is on.

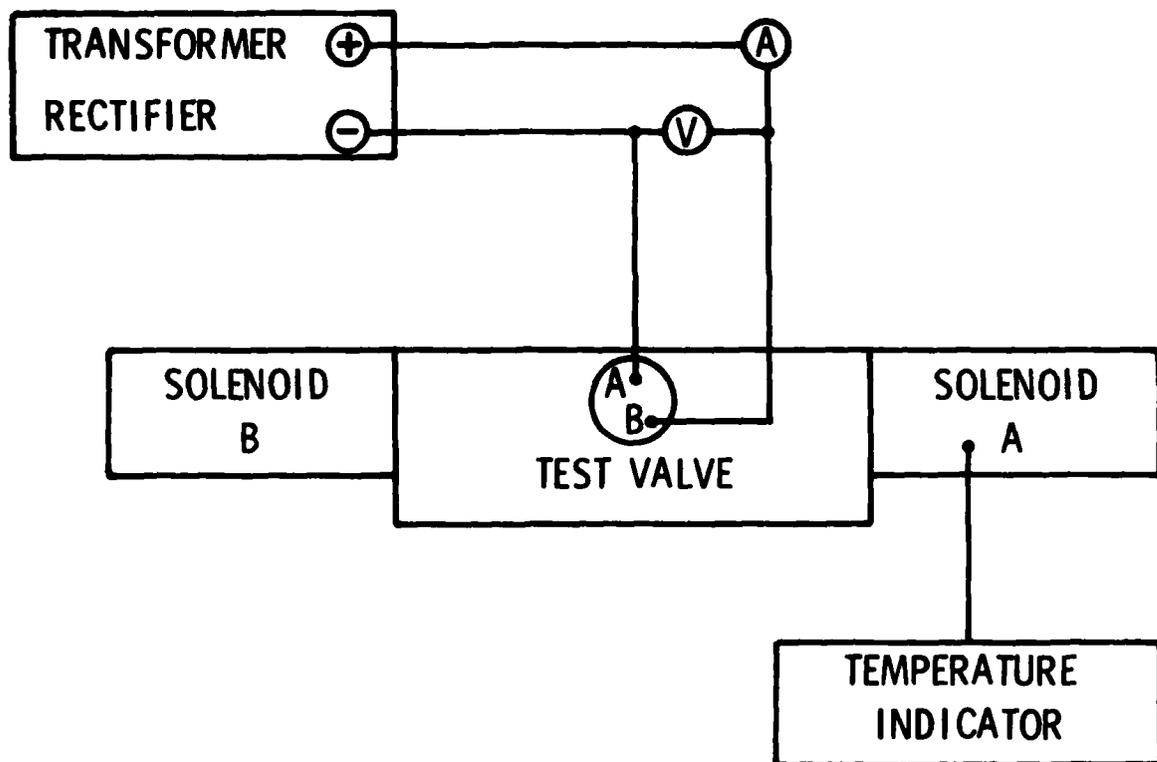


Figure A-1. Laboratory Test Schematic of Landing Gear Door Selector Valve

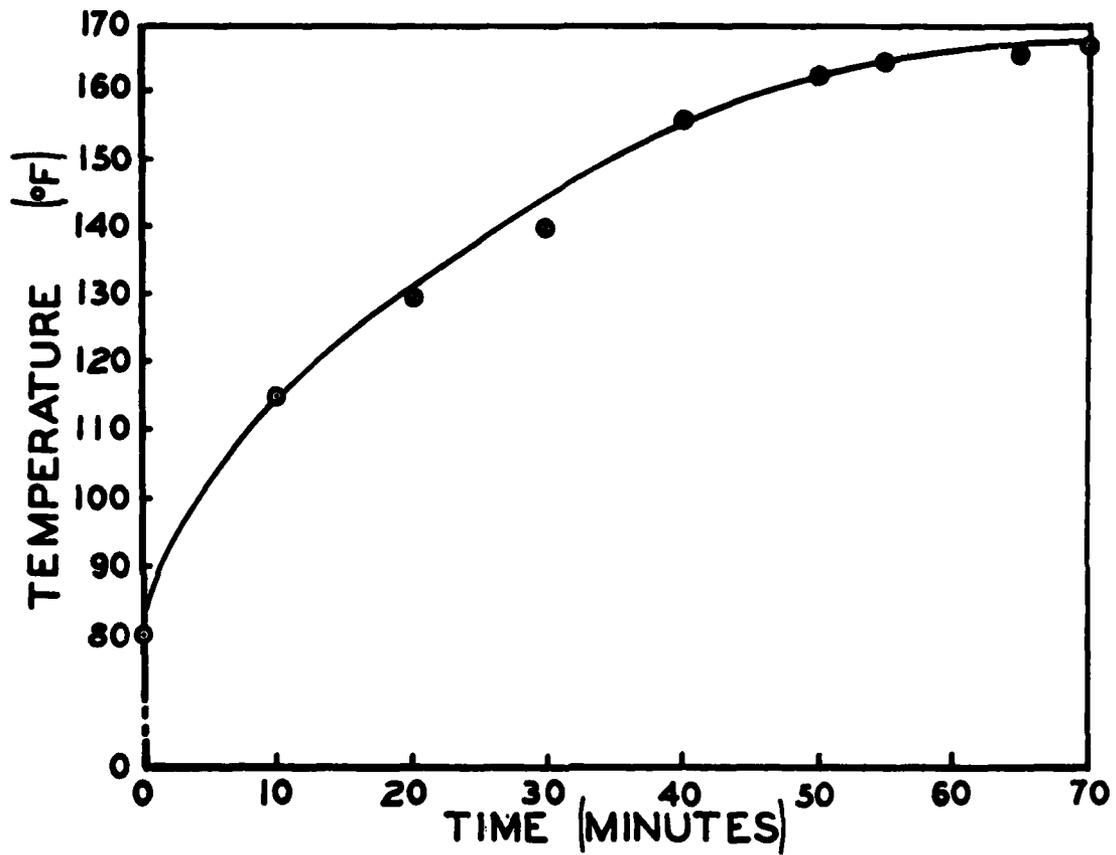


Figure A-2. C-141 Solenoid Activated Valve Temperature Experiment

APPENDIX B

MILITARY STANDARD PROCEDURE FOR DETERMINING CHLORINE CONCENTRATIONS
IN PETROLEUM BASE HYDRAULIC FLUID BY X-RAY SPECTROSCOPY
MICROCOULOMETRY AND GAS CHROMATOGRAPHY

1. SCOPE

1.1 Principal Statement. This Military Standard describes three procedures for determining the chlorine concentration in a petroleum base hydraulic fluid in the range of 0 to 500 ppm chlorine. The applicable concentration range may vary to some extent with the instrumentation used and the nature of the sample.

2. REFERENCED DOCUMENTS

MIL-H-5606

3. DEFINITIONS

Concentration - The quantity of a given substance contained in a unit quantity of sample.

Dilution, Weight - Lowering the concentration of a given material (solute) contained within another substance (solvent) by the addition of more of the latter substance (solvent). The addition is made on a weight to weight ratio.

Parameters - Instrument settings which alter absorption spectra and, as a result, affect precision and accuracy. Optimum parameters are selected to provide the best results for the specific material being analyzed.

PET - Abbreviation of pentaerythritol.

ppm - Abbreviation for parts per million, the equivalent of one milligram per liter.

Wavelength - The distance measured along the line of propagation, between two points which are in phase on adjacent waves. It is represented by the symbol λ . The unit used to express wavelength is the micrometer (μm).

Wavelength, Analytical - The wavelength selected for absorbance measurement from which contaminant or material concentration is to be determined.

Å - Symbol for angstrom, a unit used in measuring the of light waves. It is equal to one hundred-millionth of a centimeter.

4. TEST METHODS

4.1 X-Ray Chloride Calibration Standards Method Plotting Intensity vs Concentration

4.1.1 Summary of method - A sample is placed in the x-ray beam and the intensity of the chlorine $\kappa\alpha$ line at 4.727Å is measured. The intensity value is then compared to previously prepared calibration curves to obtain the concentration of chlorine in weight percent.

CAUTION

Exposure to excessive quantities of X radiation is injurious to health. The operator must avoid exposing any part of his person, not only to primary x-rays but also to secondary or scattered radiation that might be present.

4.1.2 GENERAL REQUIREMENTS

4.1.2.1 Instrument Parameters. Instrument parameters shall be set in accordance with procedures established by the instrument manufacturer.

4.1.2.2 Maintenance. After a maintenance operation has been performed on the instrument, its calibration shall be checked. This can be accomplished by preparing a standard of known concentration and comparing its concentration from analysis to the prepared calibration curve.

4.1.2.3 Interferences. Elements that will change the mass absorption coefficient of the sample more than +5 percent from the calibration standards will introduce errors in the determination of chlorine due to the changes in the absorption of chlorine $\kappa\alpha$ radiation. Absorption effects of this type can largely be overcome by diluting the sample to such an extent that the absorbing elements no longer exhibit a significant absorption effect on the emitted chlorine radiation.

4.1.3 DETAILED REQUIREMENTS

4.1.3.1 X-Ray Florescent Spectrometer capable of measuring the radiation mentioned in 4.1.1.

- a. Pulse-height analyzer or other means of energy discrimination.
- b. Optical path - helium or vacuum.
- c. Detector - proportional or scintillation.
- d. Analyzing crystal - germanium suggested. Pentaerythritol may be used but may cause chromium radiation interference.
- e. X-ray tube - chromium target suggested.

4.1.4 Materials and Supplies

- a. p - Dichlorobenzene. Reagent grade.
- b. Hydraulic fluid, MIL-H-5606, free of chlorine containing materials.
- c. Petroleum ether. Reagent grade.
- d. Beaker, 1000 ml capacity.
- e. Stirring rod, glass or stirring apparatus.
- f. Balance, at least 1200 gram capacity.
- g. Sample cells.
- h. Bottles, standard samples.

4.1.5 CALIBRATION OF X-RAY SPECTROMETER

4.1.5.1 Preparation of Standard Solutions

- a. Prepare calibration standards using the following steps:
 - (1) Preparation of 1000 ppm stock chlorine solutions.
 - (a) Introduce approximately 10 grams of hydraulic fluid into a 1000 ml beaker.
 - (b) To the above, add 2.0732 ± 0.0001 grams of p-dichlorobenzene and mix well.
 - (c) Add sufficient hydraulic fluid to make a total solution weight of 1000 ± 0.1 grams. Stir solution thoroughly.

(2) Preparation of standard chlorine solutions.

- (a) Using the above stock solution, prepare by weight dilution a series of standard solutions containing 100, 250, 500 and 750 ppm chlorine.
- (b) Introduce these standard solutions into sampling cells for use in development of calibration curves.

(3) Establish calibration curve data by carefully measuring the intensity of the emitted chlorine radiation from each of the standard solutions. Plot the data using intensity values versus chlorine concentration (ppm) as the coordinates. Calibration curves must be established for each x-ray cell that is to be used.

4.1.5.2 Development of Calibration Curves

- a. Select and label a series of x-ray cells to use for the analysis.
- b. Adjust the x-ray parameters under chlorine conditions using a sodium chloride crystal to achieve the maximum output.

NOTE

Background intensity values for the x-ray cells are negligible and are normalized by preparing a calibration curve for each cell.

4.1.6 Procedure

- a. Place the sample in an appropriate cell using techniques consistent with good practice for the particular instrument being used.
- b. Adjust the x-ray to the appropriate parameters for measuring the chlorine $\kappa\alpha$ intensity.
- c. Place the sample in the x-ray beam and allow the x-ray optical atmosphere to come to equilibrium.
- d. Determine the intensity of the chlorine $\kappa\alpha$ radiation at 4.727\AA by making measurements at the precise angular settings for this wavelength. Two 60 second exposures should yield a count sufficient for the analysis.

NOTE

The exposure time may vary depending on instrument parameters and settings.

NOTE

Since the chlorine is present as a volatile halogenated solvent, the sample should be refrigerated prior to the analysis.

- e. Average the readings and refer to the specific cell calibration curve to obtain the chlorine concentration.

NOTE

If the counting rate is higher than that of the highest point on the calibration curve, dilute the sample with hydraulic fluid until the chlorine concentration falls within the limits of the calibration curve and repeat the above procedural steps.

- f. After the analysis has been completed, wash the sampling cell a minimum of two times using petroleum ether. Allow the cell to air dry, then store for later use.

4.1.7 CALCULATIONS

- a. Calculate the correction "C" for instrument sensitivity change as shown:

$$C = \frac{I}{D}$$

Where:

- I - counting rate at the time the calibration curve was prepared.
 - D - counting rate for the daily calibration test to ascertain a change in the instrument.
- b. Apply correction factor "C" to each calibration curve as required.

NOTE

Calibration data may be stored on computer tape and updated with the proper program. This will permit the analyst to create a new graph quickly.

- c. With an average X-ray read-out for a sample convert the value to ppm using the new graph.

4.1.8 PRECISION

- a. The following criteria should be used for determining the reliability of the results.
- (1) Repeatability - Duplicate results by the same operator should be suspect if the values differ by greater than 20 ppm in the range of 0 to 500.
 - (2) Reproducibility - The results submitted by two laboratories should be suspected if the two results differ by greater than 50 ppm in the range of 0 to 500 ppm.

4.2 MICROCOULOMETRIC METHOD FOR CHLORINE DETERMINATION

4.2.1 SCOPE

This method is for the determination of chlorine in hydraulic fluid in the concentration range from 0 to 500 ppm. It is also applicable to liquids which completely vaporize from a syringe needle at 700°C.

NOTE

To insure reliable results, all possible sources of chlorine contamination during the analysis must be eliminated.

4.2.2 SUMMARY OF METHOD

The liquid sample is injected into a combustion tube maintained at about 800°C having a flowing stream of gas containing 80% oxygen and 20% inert gas such as argon, helium or nitrogen. Oxidation pyrolysis converts the chlorine to chloride and oxychlorides which then flow into a titration cell where they react with the silver ions present. The silver ions thus consumed are coulometrically replaced. The total current required to replace the silver ions is a measure of the chlorine present in the injected sample. These micro-equivalents of silver ions are equal to the number of micro-equivalents of titratable sample ions entering the titration cell.

4.2.3 GENERAL REQUIREMENTS

4.2.3.1 Instrument Parameters Instrument parameters shall be set in accordance with procedures established by the instrument manufacturer.

4.2.3.2 Maintenance After a maintenance operation has been performed on the apparatus its calibration shall be checked. This can be accomplished by preparing a standard of known concentration and comparing its concentration from analysis to the prepared calibration curve.

4.2.4 DETAILED REQUIREMENTS

- 4.2.4.1 Halide system similar to Dormann MCTS-20 consisting of the following:
- a. Pyrolysis Furnace having at least two separate and independently controlled temperature zones. A third temperature zone is optional.
 - b. Pyrolysis Tube, fabricated from quartz.
 - c. Titration Cell containing a sensor reference pair of electrodes and a generator anode - cathode pair of electrodes.
 - d. Microcoulometer having variable attenuation, gain control and capable of measuring the potential of the sensing reference electrode pair and comparing this potential with a bias potential, amplifying the potential difference, and applying the amplified difference to the working auxiliary electrode pair so as to generate a titrant. The microcoulometer output voltage signal shall be proportional to the generating current.
 - e. Recorder - Having a sensitivity of at least 0.1 MV/in with chart speeds of 1/2 to 1 in/min.
 - f. Syringe, Sampling - a 10 microlitre (μl) syringe capable of accurately delivering 1 to 10 μl of sample into the pyrolysis furnace on two 3" x 24 gauge and two 6" x 24 gauge replacement needles are required. The 3" needles are used to inject into the tube inlet while the 6" needles are used to inject directly into the titration cell.

NOTE

When chlorine concentrations of 2 ppm or below are suspected, sample volumes of 30-40 are recommended. This would require a 50 μl syringe.

4.2.5 MATERIALS AND SUPPLIES

- a. p-Dichlorobenzene, reagent grade
- b. Petroleum ether, reagent grade
- c. Nitric acid, reagent grade
- d. Oxygen gas, 99.99% purity
- e. Argon gas, 99.99% purity
- f. Hydraulic fluid, MIL-H-5606, free of chlorine containing materials
- g. Balance with at least a 1200 gram capacity
- h. Beaker, 1000 ml capacity
- i. Stirring rod or stirring apparatus

- j. Water, distilled or deionized
- k. Acetic acid, 70% V/V
- l. Silver cyanide, reagent grade
- m. Potassium cyanide, reagent grade
- n. Potassium carbonate, reagent grade
- o. Containers for standard solutions
- p. Gas regulator, two stage, Matheson Model 3104 or equal

4.2.6 PREPARATION, CALIBRATION AND STANDARDIZATION OF THE APPARATUS

4.2.6.1 Preparation of Standard Solutions

- a. Prepare calibration standards using the following steps:

(1) Preparation of 1000 ppm stock chlorine solution.

(a) Introduce about 10 grams of hydraulic fluid into a 1000 ml beaker.

(b) To this, add 2.0732 ± 0.0001 grams of p-Dichlorobenzene and mix well.

(c) Add sufficient hydraulic fluid to make a total solution weight of 1000 ± 0.1 grams. Stir solution thoroughly.

(2) Preparation of standard chlorine solution.

Using the above stock solution, prepare by weight dilution a series of standard solutions containing 50, 100, 200, 250 and 500 ppm chlorine.

4.2.6.2 Preparation of the Apparatus

- a. Assemble the apparatus
- b. Turn the heater on
- c. Adjust the flow of the gases, the pyrolysis furnace temperature, titration cell and the microcoulometer to the following operating parameters.

Reactant gas flow (oxygen)	160 cc/min
Carrier gas (Ar, He)	40 cc/min
Furnace temperatures	
Inlet temperature	700° + 25°C
Center temperature	800° ± 25°C
Outlet temperature	800° ± 25°C
Exit tube	Packed with 1/2" quartz wool
Bias voltage	221 MV
Gain	2200 (approx)

- d. With the Bias Read and Base Line Display switches activated, the digital display should read close to the bias voltage (millivolts).
- e. Activate the single cell operating switch. The titration cell is then flushed continually with 70% acetic acid until the bias voltage approaches zero on the digital display. Minor adjustments may be necessary to zero the bias voltage.
- f. To operate the microcoulometer, activate the Ng/INTEG switch. The digital display indicates nanograms of chlorine.
- g. To convert nanograms of chlorine to ppm of chlorine, divide the nanograms of chlorine by the number of microliters injected times the specific gravity of the fluid.

$$\text{chlorine (ppm)} = \frac{\text{Ng chlorine}}{\text{Microliters samples (0.87)}}$$

NOTE

Concentration is best determined by obtaining the digital readout and using the chart prepared as outlined in the next paragraph to find the concentration.

4.2.6.3 Development of Calibration Curves

- a. Using the standard solution prepared as directed in para 4.2.4.a.(a), introduce each of the samples into the apparatus according to procedural instructions in para 4.2.7.
- b. Take the digital reading for each concentration, then plot the data on a graph using the coordinates readout versus prepared concentration (ppm chlorine).

NOTE

Standard samples should be run periodically to monitor the system's recovery and reproducibility.

4.2.7 PROCEDURE

- a. Flush the syringe several times with the sample.
- b. Introduce about 8 microliters (μl) of sample into the $10\mu\text{l}$ syringe being careful to eliminate the air bubbles by retracting the plunger. Adjust the plunger until $5\mu\text{l}$ of sample remains in the syringe.
- c. Push the syringe needle through the rubber septum and inject the sample into the platinum boat, required for hydraulic fluid. When injecting the sample, the needle should be touching the inside wall of the platinum boat so that all suspended droplets will be removed from the end of the needle.
- d. Activate the instrument and slowly slide the boat into the furnace. The boat should be stopped just inside the furnace for approximately one minute and again approximately half way for approximately one minute to permit the chlorine compounds to volatilize in a regular manner.

NOTE

Too rapid volatilization of compounds will produce erroneous results.

- e. Take the reading.

NOTE

Where most precise results are desired, duplicate and sometimes triplicate samples should be run.

- f. To find the concentration of the sample, use the prepared calibration charts. Concentration will be in ppm chlorine.

4.3 GAS CHROMATOGRAPHIC METHOD FOR CHLORINE DETERMINATION

4.3.1 SCOPE

- a. This method covers the determination of chlorinated solvent in a petroleum base hydraulic fluid down to one part per million chlorine.

4.3.2 SUMMARY OF METHOD

- a. A sample is diluted with the internal standard stock solution and the concentration of chlorinated solvent is measured in part per million (ppm). This value is obtained by first establishing calibration standards which were evaluated using an internal standard method.

4.3.3.1 CHROMATOGRAPH - Any gas chromatograph, commercially available or custom designed, may be used provided the system has sufficient sensitivity to detect trace amounts of chlorine when operated at given conditions (parameters).

- a. Oven temperature 100°C - isothermal
- b. Injector temperature 200°C
- c. Detector temperature 300°C
- d. Detector; electron capture
- e. Attenuation; X32
- f. Sample size 0.2 µl

4.3.3.2 Column; six feet of 1/8 in. O.D. stainless steel tubing packed with 3% SP2100 on 80/100 mesh supelcoport.

4.3.3.3 Recorder - A recording potentiometer with a full scale deflection of 10 MV or less shall be used. The full scale response of the recorder should not exceed 25 and a maximum rate of noise of + 0.3% of full scale. Chart speed should be 0.5 in/minute.

4.3.4 MATERIALS AND SUPPLIES

- a. Balance
- b. Bottles, standard samples amber
- c. Vial, 5 ml
- d. 1,1,2-trichlorotrifluoroethane - reagent grade
- e. Tetrachloroethylene - spectro grade
- f. Hydraulic fluid, MIL-H-5606, free of chlorine containing materials

4.3.5 PREPARATION, CALIBRATION AND STANDARDIZATION OF THE EQUIPMENT

- (1) Preparation of 500 ppm stock 1,1,2-trichlorotrifluoroethane and tetrachloroethylene.

- (a) Accurately weigh* approximately 20 grams of hydraulic fluid into a two ounce amber bottle.
- (b) To this, add 0.01 grams of 1,1,2-trichlorotrifluoroethane. Cap tightly and mix well. Calculate concentration of solvent in ppm. Note Standards Sheet for sample calculation.

Where: S = weight of the solvent

T = weight of the solvent plus the oil

C = ppm of solvent in the hydraulic fluid

- (c) Repeat steps (a) and (b) for tetrachloroethylene.

NOTE

Samples should be kept tightly capped to prevent loss of solvent due to volatility.

- (2) Preparation of the Internal Standard Stock Solution from the 500 ppm Stock Solution of Tetrachloroethylene.

- (a) Accurately weigh approximately 20 grams of clean hydraulic fluid into a two ounce amber bottle.

* All weight throughout this procedure should be made to + 0.0001g.

STANDARDS

SAMPLE NUMBER	XX01
SAMPLE	Type of Fluid
TARE W/CAP	55.0000
TARE + OIL	75.0000
TARE + OIL + SOLVENT	75.0100
WT. OIL	20.0000
WT. SOLVENT	0.0100
TOTAL WT. OIL + SOLVENT	20.0100
<u>SOLVENT</u>	
TOTAL	.0004997
<u>SOLVENT</u> x 1,000,000 ppm of SOLVENT	499.7 ppm of SOLVENT
TOTAL	

- (b) To this carefully add approximately 0.1 grams of 500 ppm stock solution prepared in 1(c). Cap tightly and mix well. This mixture will provide a solution with approximately 2.5 ppm of tetrachloroethylene. Calculate the exact concentration of tetrachloroethylene using the following equation:

Calculation: $C = \frac{S}{T} \times C_o$

Where S = weight of the tetrachloroethylene stock solution

T = total weight of tetrachloroethylene stock solution and oil

C_o = concentration of the stock solution used in ppm. This is calculated when preparing stock solutions of each solvent used.

C = concentration of the solvent in ppm

(3) Preparation of the Standards

- (a) Using the above internal standard as prepared step (2) as the base hydraulic fluid, accurately prepare by weight dilution a series of standard solutions containing approximately 5, 15 and 30 ppm of 1,1,2-trichlorotrifluoroethane. This process results in a series of solution containing approximately 5, 15 and 30 ppm of 1,1,2-trichlorotrifluoroethane and 2.5 ppm tetrachloroethylene. These samples are then chromatographed. Note Figure B-1 for example of gas chromatographic separation.

One of the chromatographic analyses is used to calculate the relative response factor (1,1,2-trifluorotrifluoroethane to tetrachloroethylene) and the other two are used to verify that the relative response factor is linear over this concentration range. If this is not found to agree within 5%, new standards are prepared and the process repeated.

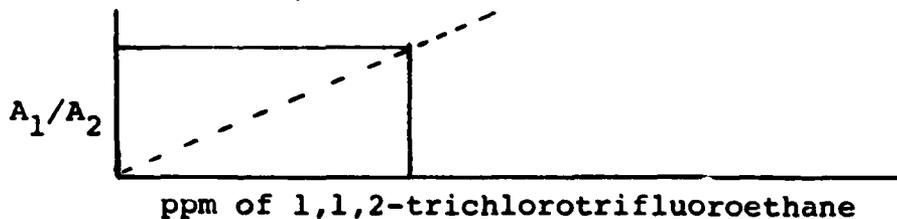
If a data system is not available to calculate the relative response factor, the following equation can be used:

$$C_1 = \frac{F_1 A_1}{F_2 A_2} \times R \times F$$

where $R = \frac{\text{"standard amount"}}{\text{"sample amount"}}$

C_1 - concentration of component i
 F_1 - relative response factor for component I
 F_2 - relative response factor for internal standard
 A_1 - area of component i
 A_2 - area of internal standard
 R - true ratio of standard to sample, obtained by dividing "STD-AMT" by "SAMP-AMT"
 F - parameter "FACTOR", normally 1

The concentration of 1,1,2-trichlorotrifluoroethane multiplied by 0.568 equals the concentration in ppm of chlorine as 1,1,2-trichlorotrifluoroethane in the hydraulic fluid sample. A calibration curve plotting A_1/A_2 where A_1 equals the area of 1,1,2-trichlorotrifluoroethane and A_2 equals the area to the internal standards versus the known concentration of 1,1,2-trichlorotrifluoroethane in the standards can be used to manually obtain the concentration of chlorine as 1,1,2-trichlorotrifluoroethane from the unknown samples. (e.g., note graph below)



4.3.6 HYDRAULIC FLUID ANALYSIS PROCEDURE

- a. Introduce approximately 2.0 grams of the internal standard stock solution in Section 5 step (2) to a small 5 ml vial.
- b. To this fluid add, 0.02 grams of the contaminated sample to be analyzed, tightly cap and mix well. Calculate dilution factor.

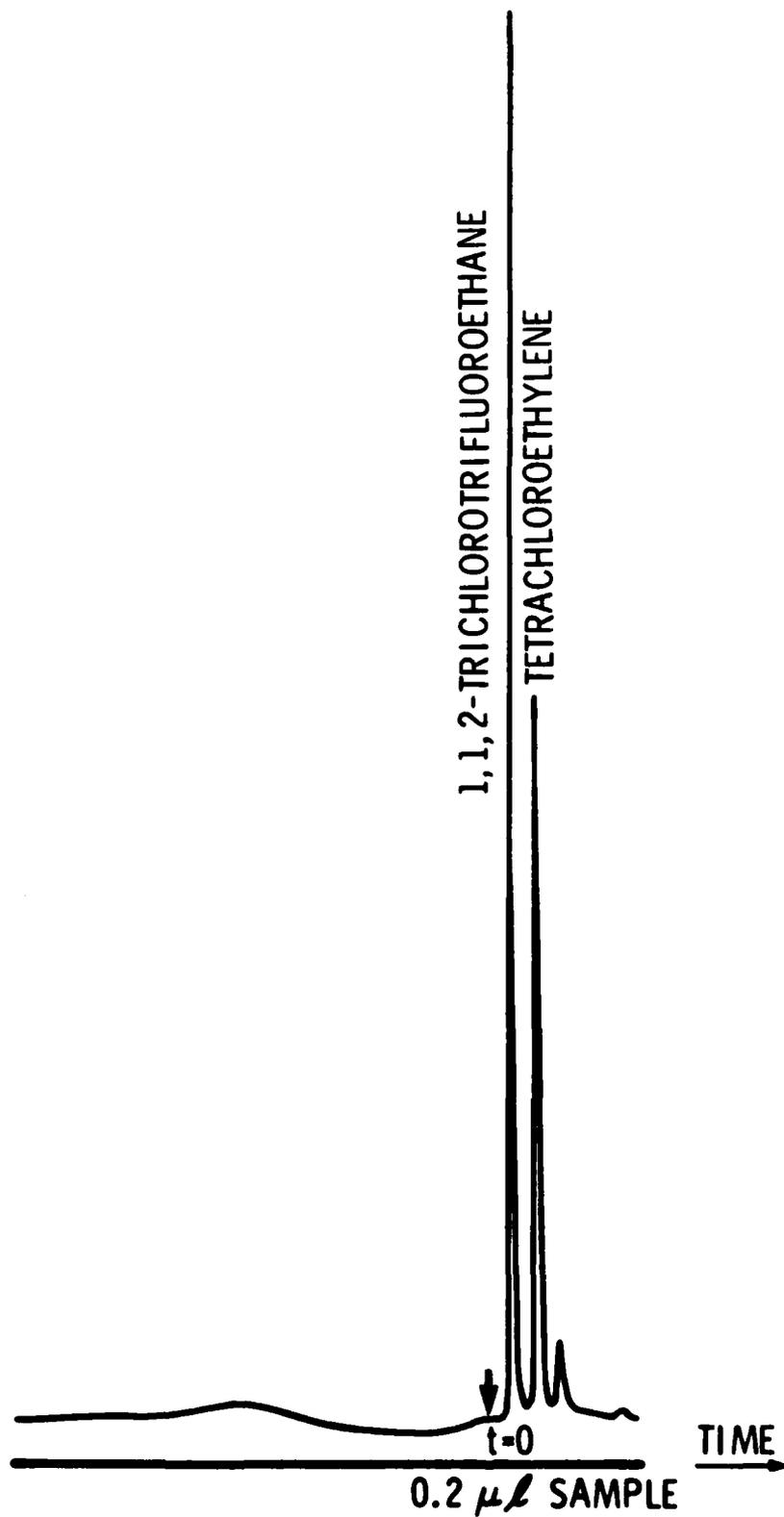


Figure B-1. Separation of 1,1,2-trichlorotrifluoroethane and tetrachloroethylene

$$D = \frac{T}{S_A}$$

Where: D = dilution

T = Total weight (oil and sample)

S_A = weight of sample to be analyzed

Note 4.3.7.9 for example calculation. The dilution factor times the concentration of chlorine as 1,1,2-trichlorotrifluoroethane equals this concentration in ppm. The first dilution to the sample prepared should be around 100 to 1 to avoid possible overload of the electron capture detector.

- c. Then 0.2 μ l of the sample prepared in part (b) of this section is injected into the gas chromatograph under the chromatographic conditions stated in 4.3.3. Duplicate runs should be made.

The concentration of the diluted sample should fall within the range of the standards made prior to evaluation of this sample. If the dilution results in a chromatogram with peak areas outside this range, another dilution should be made until the value falls within the standard range. The linear range of the chromatographic system with an electron capture detector is dependent on several variables including: column type, column temperature, carrier gas purity and compound type. Therefore, to obtain reliable quantitative data, the samples should be run within the standard limits set prior to analysis.

- d. Calculate the concentration of chlorine as 1,1,2-trichlorotrifluoroethane in the hydraulic fluid and take into account dilution factor.

4.3.7 PRECISION

- a. The following criteria should be used for determining the reliability of the results.

Dilutions

Sample Number	AA01
Sample	Type of Fluid
Tare w/cap	5.000
Tare + Oil	7.000

Tare + Oil + Sample	7.0200
Wt. Oil	2.000
Wt. Sample	0.02
Total Wt. Oil + Sample	2.0200
Dilution Factor	
(Total/Sample)	101

- (1) Repeatability - Duplicate results by the same operator should be suspect if the value differs by greater than 5 percent.

REFERENCES

1. "Combined Meeting No. 81 of SAE Committee A-6, Aerospace Fluid Power and Control Technologies of the SAE Aerospace Equipment Division with Hydraulic Engineers of Industry and Government," Oct 4 to Oct 8, 1976. pp 47, 48.
2. Report No. NADC-73183-3, 16 Nov 1973, "Corrosion of Steel Components of the P-3 Aircraft Hydraulic System in the Presence of MIL-H-5606 Hydraulic Fluid, Freon and Water."
3. SAE Aerospace Information Report #1416, "Phosphate Ester Aircraft Hydraulic Fluid Contamination with Chlorine Containing Compounds," Jan 1977.