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Gaithersburg, MD 20899

REPORT OF ANALYSIS

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Submitted to:	Mr. Bruce York, Department of Transportation, National Highway Traffic Safety Administration, Office of Defects Investigation, 400 7th Street, SW, Washington, DC 20590
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Title:	Investigation of Ford Speed Control Deactivation Switches – Analytical Chemistry Division Contributions
Constituents:	Chemical Composition of Brake Fluid, Deposits and Switch Parts
Methods:	X-Ray Fluorescence Spectrometry (XRF), Gas Chromatography/Mass Spectrometry (GC/MS), Karl Fischer (KF) Water Determinations, Coulometry, Fourier Transform Infrared Red Attenuated Total Reflectance Spectroscopy (FT-IR/ATR), Nuclear Magnetic Resonance (NMR)
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Background: This report is submitted pursuant to the requirements of a contract between NIST and the National Highway Traffic Safety Administration (NHTSA) covering NIST testing of speed control deactivation switches (SCDS) from Ford vehicles. The NIST Analytical Chemistry Division was contracted to perform a variety of tests and to provide consultation as directed by the NHTSA Office of Defects Investigation. Figure 1 is a schematic drawing of an SCDS, from a Texas Instruments document provided by NHTSA. This report[1] contains descriptions of work performed and test results obtained by the Analytical Chemistry Division (ACD) during the period from about July 1, 2005, until about November 1, 2005, in fulfillment of the contract with NHTSA.

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[1] This report and its contents are not covered by the provisions of the Analytical Chemistry Division Quality Manual

Sample Details: Approximately 80 SCDS were provided to NIST by NHTSA during the course of the investigation. The SCDS were identified only by a serial number assigned by NHTSA. NHTSA categorized them according to damage apparent through visual inspection by NHTSA investigators. SCDS conditions categories are
- Likely Good - no apparent damage to SCDS obtained from a vehicle unlikely to be affected by the problem,
- Likely Bad – no apparent damage to SCDS obtained from a vehicle likely to be affected by the problem,
- Leaker – SCDS leaking fluid at the electrical connection, but no visible damage,
- Light Burn With Brake Fluid (LBWBF) – SCDS with visible heat damage or from a vehicle reported to have a smoking SCDS,
- Burned With Base Remains (BWBR) – SCDS with significant fire damage, but with a portion of the switch base remaining,
- Burned No Base Remains (BNBR) - SCDS completely burned with no remaining switch base.

NHTSA also provided the model and year information. See Excel spreadsheet NHTSA_SCDS_Log_Sheet.xls, which contains a complete listing of SCDS handled by ACD.

Most SCDS were accompanied by a plastic or glass bottle containing brake fluid sampled by NHTSA from the master cylinder reservoir of the vehicle. The fluids were characterized by visual inspection by J. R. Sieber according to their color, opacity, and sediment contents. Then, the bottles were sampled by A. F. Marlow who filled 2 mL amber vials using glass pipettes and provided one vial of each fluid to M. M. Schantz and S. J. Choquette, who later performed gas chromatography/mass spectrometry (GC/MS) and Fourier-transform infrared spectrometry (FT-IR), respectively. Aliquots for X-ray fluorescence spectrometry (XRF) were taken by J. R. Sieber who used glass pipettes to transfer aliquots directly from the original bottles to XRF sample cells. At later dates, selected original bottles were given to K. W. Pratt, T. W. Vetter, and D. K. Hancock for conductivity measurements, water determinations, and nuclear magnetic resonance (NMR), respectively. All fluid samples were taken without disturbing the sediment layer on the bottom of the container. For samples containing sediment, the quantity of sediment increased with time even though the bottles were stored in a closed box to prevent exposure to light.

Four brands of service-fill brake fluid were purchased by J. R. Sieber for comparison to the used brake fluids provided by NHTSA from each vehicle. Three brands of service-fill fluid, Advance Auto Parts, Wearever®, and Prestone®, were purchased off the shelf at a local store. Motorcraft®[2] brand brake fluid was purchased from a local Ford dealer. The parts manager at the dealer stated that the same Motorcraft formulation is used for both service fill and factory fill applications.

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[2] Certain commercial products are named in this report for the purpose of adequately specifying the experimental conditions and the sources of analytical results. Such descriptions do not constitute endorsement by the National Institute of Standards and Technology, nor do they imply that the products are necessarily the best for the purpose.
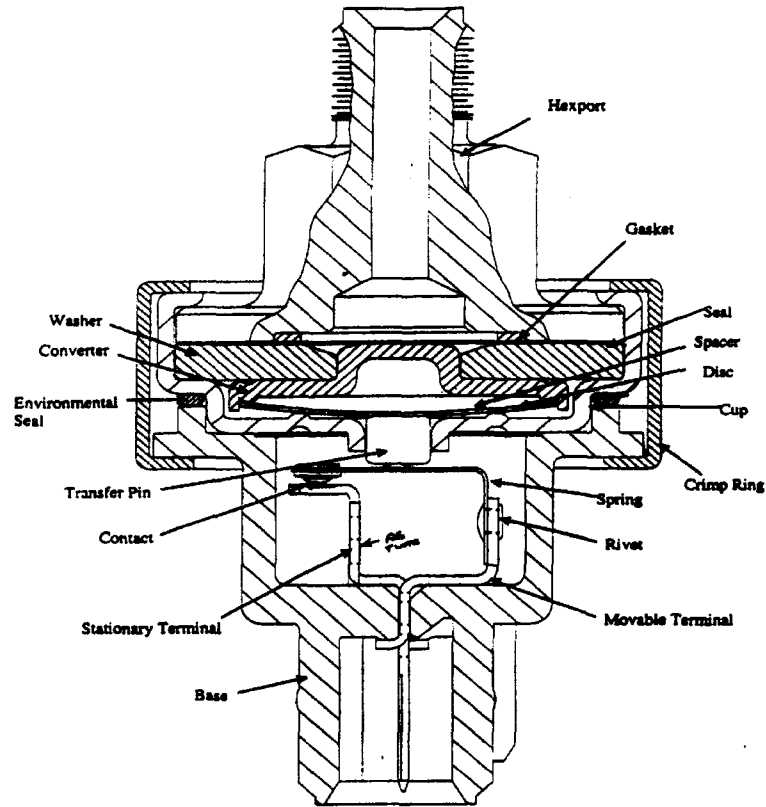
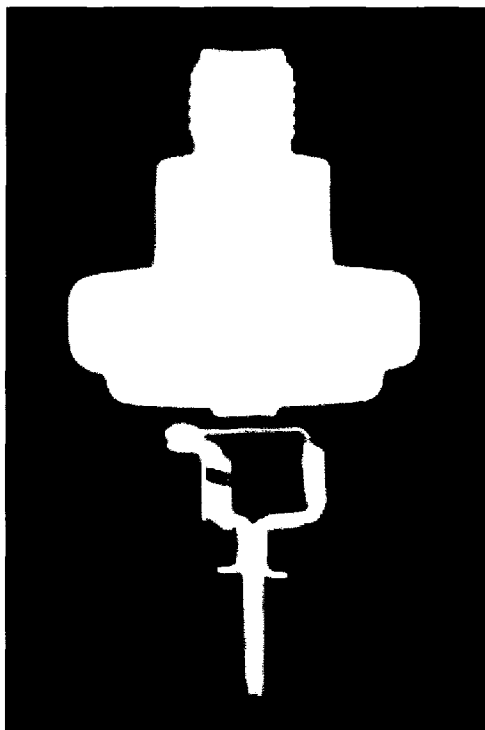Figure 1. Schematic drawing of SCDS.

Figure 2. X-Ray photograph of
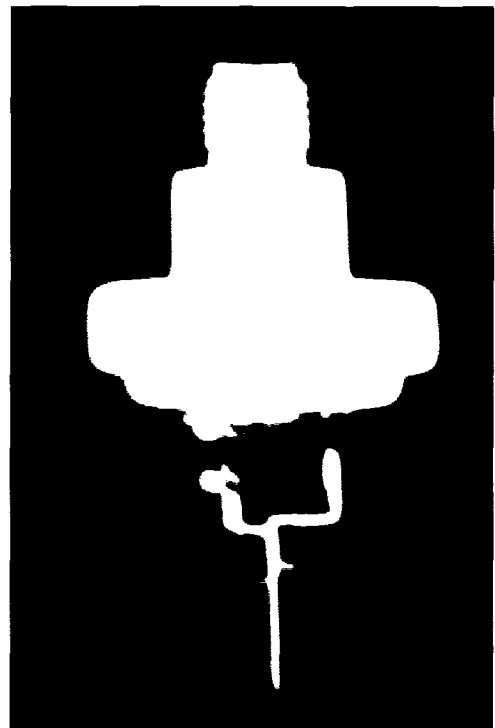SCDS in good working condition.

Figure 3. X-Ray photograph of
SCDS with internal damage.

Disassembly of SCDS

SCDS were disassembled in the NIST Fabrication Technology Division Inspection Room by W. K. Combs and T. A. Butler. Instructions for disassembly and documentation were developed by J. R. Sieber in consultation with G. A. Holmes, NIST Polymers Division. Guidance was obtained from a disassembly procedure obtained from Texas Instruments (manufacturers of the SCDS) by NHTSA. Figure 1 is a schematic drawing of an SCDS, from a Texas Instruments document provided by NHTSA. The instructions for disassembly at NIST included a reporting form, which is provided in Excel spreadsheet NHTSA_SCDS_Log_Sheet.xls.

Before disassembly, X-ray photographs were made of each SCDS at the NIST Radiation Physics facility. Examples are shown in Figure 2 and Figure 3. The X-ray photographs were used to document the condition of the switch parts inside the Base. [SCDS part names are shown in Figure 1.] The Spring is made from thin beryllium copper and can be seen when intact. The Contacts contain silver. The Stationary Terminal and Moveable Terminal are made of a yellow brass alloy. The Cup and Hexport are made of steel. These steel, silver, copper and brass parts are easily seen in X-ray photographs. The Crimp Ring is made of an aluminum alloy and is transparent to the high-energy X rays used to expose the photographs. The complete set of X-ray photographs is available from NIST Polymers Division.

The first step in disassembly was removal of the outer aluminum Crimp Ring. Cutting was accomplished using a handheld, motorized cutter. This allowed separation of the switch Base from the Cup. A sample of fluid in the Crimp Ring, if any, was collected using a glass pipette and placed in a 2 mL amber vial. The contents of the switch Base, any fluids, solids and pastes, were taken from inside the switch Base using a stainless steel spatula and/or glass pipette, and placed in a single 2 mL amber vial. In some cases, loose metal pieces were found. The Cup was cut open using a circumferential cut. The Kapton® Seals were kept in place on the Washer. The Disc was removed for inspection without cleaning. The parts were stored in a divided, plastic box, which was wrapped in the report form held by a rubber band.

Deposits were recovered from switch Bases from SCDS 3, 4, 9, 17, 45, 46, 48, 49, 53, 55, 56, 59, 60, 65, 68, 69, 70, 75, 76, and 80. In addition, brake fluid was found inside the Crimp Rings of SCDS 1,

The SCDS were photographed during disassembly. Photographs were taken of the following items:
* each SCDS as received,
* the inside of the aluminum Crimp Ring,
* the inside of the switch Base viewed from the side in contact with the Cup,
* the Cup face in contact with the switch Base,
* the flexible Disc side in contact with the ceramic Transfer Pin,
* the Kapton® Seals in place on the Washer.
The photographs are provided on a CD-ROM labeled NHTSA081205 Disassembly Photos.

After photography, the Kapton® Seals were marked for relative location and removed, one at a time, to individual zip-closure plastic bags. Seal orientation and location were preserved to

facilitate investigation of the mechanism by which leaks develop. The zip-closure bags were stored in the plastic parts box.

Summary of Analytical Methods and Results

Each analyst provided a summary of the test method for which he/she was responsible. Their summaries are included in this section of the report. Each summary includes the test results obtained using that method.

X-Ray Fluorescence Spectrometry

Measurements were made using the PANalytical PW2404 spectrometer, a research grade instrument equipped with a Rh anode end-window tube, three collimators, eight crystals, and three detectors. The PANalytical method IQ+ was used for semiquantitative analyses with a helium atmosphere. IQ+ is a fundamental parameters method optimized for selectivity and calibrated using a selection of calibration standards provided by PANalytical plus a few NIST Standard Reference Materials® (SRMs) of glass and alloy materials. Brake fluid specimens were weighed into 25 mm inner diameter, polyethylene, liquid cells (Somar brand) with sample masses between 1.0 g and 3.1 g depending on the available quantity of the sample fluid. Brake fluid samples were modeled as a balance compound defined as diethylene glycol diethylether with detected elements calculated in their elemental form and the sum constrained to equal 100 %. Deposits from inside switch Bases were weighed onto polypropylene film (6 μm Spectrolene® by Somar) by spreading with a spatula into a pie wedge shape. The deposit was then covered by a second sheet of polypropylene. Deposits were modeled as a fictitious compound defined as CH_2 containing elements in the elemental form. In addition to the known or assumed chemical information, the IQ+ program uses known sample mass and sample area in its calculations.

Table 1 contains the results of XRF analyses of all brake fluid samples. The top part of the table is devoted to fluids removed from vehicle reservoirs. The reservoir fluids that were tested were found to contain significant contamination from both water (see the section on Water Determinations below) and elements. The bottom part of Table 1 contains results obtained from fresh fluids. Measurements were made on the three fresh service-fill brake fluids purchased at a local automotive parts store. These fluids were found to contain very little in the way of elements detectable by XRF using the IQ+ method. In fact, the Wearever® brand fluid contained no detectable elements. Detection limits for IQ+ are in the range of 10 mg/kg to 100 mg/kg for samples of this nature. This fortuitous discovery allowed the Wearever fluid to be used to create control samples to test the IQ+ method for bias.

One aliquot of Wearever fluid was mixed with 2-ethylhexanoic acid (a stabilizer) and measured to check for contaminants in the 2-ethylhexanoic acid. A test on Prestone fluid stored in a new plastic bottle showed that the bottle and cap did not contaminate the fluid with trace metals. Mixtures of Wearever fluid and 2-ethylhexanoic acid were spiked with known quantities of the elements detected in used brake fluid. The sources of spiking solutions were SRM single element, spectrometric solutions containing 10 mg/g of each element. Three controls were created and measured with the results shown in Table 2. Across the range, Na results are high by approximately 150 mg/kg. Across the range, Al results are high by a factor of approximately 2.

Si results are not quantitative and should be viewed as simply indicative of the presence or absence of trace quantities of Si. S results have a positive bias at the blank level. Across the range, Cl results are high by approximately 20 %. K results are also biased positive at blank level. Cu results are low by approximately 20 % at higher levels. Fe and Zn do not appear to be subject to biases.

Although the results for certain elements in reservoir brake fluid samples are biased, the values can be used to look for trends. The following observations were made.
+ Motorcraft factory/service fill fluid contains Na and K due to buffers added to the formula.
+ Service fill fluids from Wearever, Advanced, and Prestone do not contain Na and K.
+ Most used brake fluids samples from NHTSA contain Na and K.
+ The used fluids contain significant levels of Cu and Zn as expected due to the interactions between brake fluid and vehicle brake lines.
+ The used brake fluids are contaminated with Si, S, Fe, Ni, but only at trace levels.

Deposits and fluid were retrieved from a small number of SCDS Bases. The materials varied in appearance including fluid with small quantities of particles, paste-like material in several shades of dark green, black granular material wet with fluid and gray, brittle material with the appearance of ash. Deposits from just four Bases, 4, 48, 65, and 76, were measured using the IQ+ method. Table 3 contains the XRF results for the four deposits along with descriptions of deposits from other SCDS. The analyzed deposits were found to contain substantial amounts of Cu, Zn, and Ag. This is expected because the metal switch parts are made of these elements and it is known that electrolysis begins to degrade them as soon as brake fluid infiltrates the Base of an SCDS. Iron was measured at elevated levels substantially greater than Fe in used brake fluid. Iron is available from the SCDS Cup surface and the Disc inside the cup. It is interesting to note that deposits found in each Base were also found inside the Cup of the SCDS coating the surface of the Disc. Once the Spring breaks due to corrosion by electrolysis (see Electrochemistry section below), the Transfer Pin becomes dislodged from its hole, and fluids and corrosion products are free to move into the cup.

Table 1. Results of Elemental Analysis by X-Ray Fluorescence Spectrometry and Water Determinations by the Karl Fischer Method.

Brake Fluid from Reservoirs Description	SCDS Code No.	Water (%)	Na (mg/kg)	Al (mg/kg)	Si (mg/kg)	P (mg/kg)	S (mg/kg)	Cl (mg/kg)	K (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Sum
LBWBF	4	4.2	110				10	35	55			110	70	390
LBWBF	48	1.9	290	30			30		180	15		260	120	925
LBWBF	45	1.9		40			30		180	35		370	50	705
LBWBF	46													
LBWBF	76	2.7	850		80	7	220		590	20		420	250	2437
LBWBF	80	1.4	1100	20	100		65		750			620	240	2895
Leaker	3	2.0	730	25		<5	60		420	<5		640	300	2175
Leaker	17	1.7		50			20		120			140	180	510
Leaker	56	1.0		30	100		6		45			20	20	221
Likely Bad	6		620	30	100		45		510			590	270	2165
Likely Bad	30	2.4	1200		100		140	15	590	15		900	340	3300
Likely Bad	32		720			10	40		820			410	170	2170
Likely Bad	61		470				55		520			570	340	1955
Likely Bad	62			35			20		240			230	150	675
Likely Bad	82		1300	30	100		60		600			220	310	2620
Likely Bad	83		190	40	100		30		310			370	130	1170
Likely Bad	84		750		100	6	45		740		9	410	270	2330
Likely Bad	85		890	30	100		85		550			670	330	2655
Likely Bad	86		870	40	100		50		760			340	260	2420
Likely Bad	87		880				45		740			670	320	2655
Likely Bad	88		1400	45	15		50		770			440	350	3070
Likely Bad	89		960		100		85		480			610	300	2535
Likely Bad	90		900	25	5		65		670			750	240	2655
Likely Bad	91		640	35			30		590			480	230	2005
Likely Bad	92		700	50			40		830			230	160	2010
Likely Bad	93		1200	30	100		110		650			700	350	3140
Likely Bad	95		720		100		70		550			420	190	2050
Likely Bad	96		1100		40		65		610			410	210	2435
Likely Good	1		1100				100		700	20		470	650	3040
Likely Good	5		390	20		7	110		400			610	260	1797
Likely Good	7		750	40	100		40		720			320	260	2230
Likely Good	10		530	25			20		220			250	95	1140
Likely Good	14		690	<10	100	4	65	25	530	20		310	420	2164
Likely Good	15		540		100	7	55	50	550			790	300	2392
Likely Good	16	1.4	610				35		380	15		520	370	1930
Likely Good	18		920		100		50		700			200	340	2310
Likely Good	20		1300	25	5		140		610	25		1100	350	3555
Likely Good	26		1100				70		710	15		370	440	2705
Likely Good	27			60			40		700			450	350	1600
Likely Good	28		1200		100	6	80		670	20		670	470	3216
Likely Good	29		1300	30	85	17	120	30	560	60		910	230	3342
Likely Good	34		600		100		50	30	540			560	350	2230
Likely Good	40		870		100	20	65		590	35		640	580	2900
Likely Good	27		1000				45		740			460	380	2625
Likely Bad	92		1100	45			55		800			240	170	2410
Stored vehicle	112	0.9												
Stored vehicle	113	0.9												
Fresh Brake Fluids:														
Motorcraft		0.2	800	30				25	770					1625
Wearever														
Prestone				30							5	8		
Advance					100									
Prestone in New PETE Bottle				35	100									
Wearever + 2-ethylhexanoic acid (9+1)				25										

Table 2. Results from Control Samples Determined Using X-Ray Fluorescence Spectrometry

(All values in mg/kg)

	Na		Al		Si		P		S	
	Known	Found	Known	Found	Known	Found	Known	Found	Known	Found
BF1	0.083	0.11	0.0031	0.0072	0.0087	0.039	0.0016	0.0015	0.0068	0.0072
BF2	0.011	0.017	0.21	0.18	0.0016	0.0030	0.0010	0.0031	0.0012	0.0033
BF3	0.14	0.15	0.0014	0.0038	0.010	0.14	0.0017	0.0023	0.022	0.020

	Cl		K		Fe		Cu		Zn	
	Known	Found	Known	Found	Known	Found	Known	Found	Known	Found
BF1	0.13	0.17	0.055	0.055	0.0033	0.0043	0.048	0.041	0.028	0.028
BF2	0.017	0.024	0.0034	0.0060	0.0019	0.0018	0.0015	0.0018	0.0019	0.0035
BF3	0.22	0.25	0.084	0.071	0.0056	0.0056	0.11	0.090	0.065	0.056

Table 3. Deposits Obtained from SCDS Bases

Part A. Descriptions of Deposits

SCDS Code No.	Description
3	Fluid containing dark particulates
4	Paste, wet with fluid
9	Fluid containing dark particulates
17	Paste, black with clear fluid
45	Paste, black with clear fluid
46	Particles, black , sticky
48	Paste, green color
49	Fluid containing dark particulates
53	Particles, black , sticky
55	Paste, black with clear fluid
56	Paste, black, small quantity
59	Particles, black , sticky
60	Particles, gray and dry
65	Paste and particles, dark green
68	Particles, black , sticky
69	Particles, black and dry
70	Particles, black and dry
75	Particles, black and dry
76	Particles, black , sticky
80	Paste, black with clear fluid

Part B. Results of XRF Analyses of Selected Deposits

(All values in mg/kg)

SCDS Code No.	4	48	65	76
Description	LBWBF	LBWBF	BWBR	LBWBF
Na	100			2400
Al	25	45	35	40
Si	45	45	10	60
P		5	6	15
S	10	20	10	75
Cl	25	15		
K		85		560
Ca	6			
Cr	90	65	80	95
Mn	5			
Fe	190	250	300	260
Ni	8	15	15	15
Cu	6300	6800	7400	5800
Zn	2700	650	1600	3400
Mo			95	
Ag	190		1000	1200
Sn		80		

Gas Chromatography/Mass Spectrometry

Samples of 43 brake fluid samples from reservoirs were received for analysis using gas chromatography/mass spectrometry (GC/MS). The descriptions of the samples are given in the spreadsheet NHTSA_SCDS_Log_Sheet.xls. In order to stay within the linear range of the MS detector, the brake fluid samples were diluted (100 µL of brake fluid to 100 mL of ethyl acetate, ACS grade) prior to analysis. The diluted samples were agitated and then 1.5 mL of the diluted sample was transferred to an autosampler vial for GC/MS analysis.

The GC/MS method employed was similar to that described by Stauffer, et al. (2003). In summary, a non-polar 5 % diphenyl dimethylpolysiloxane phase, 30 m x 0.25 mm (id) and 0.25 μm film thickness, (HP-5MS, Agilent Technologies, Wilmington, DE, serial # US5138051H) was used with the oven temperature as follows: 3 min hold at 60 °C followed by temperature ramp at 5 °C/min to 285 °C where the temperature was held for 15 min. Helium was the carrier gas at a constant flow of 1.2 mL/min. Diluted samples (1 μL) were injected using an autosampler with the injector temperature set at 250 °C, split flow set at 30 mL/min. The transfer line from the GC to MS was maintained at 280 °C. The MS was auto-tuned prior to the start of the analyses with the oven temperature set at 120 °C. For the brake fluid analyses, the electron multiplier voltage was 1647 EMV and the MS was operated in a scan mode from 70 amu to 400 amu at 2.26 scans/sec. A solvent delay of 4 min was used. The brake fluid samples were run in a randomized order with 100 % ethyl acetate samples run periodically to ensure that there was no injection carryover from sample to sample. None was observed.

The results of the GC/MS analyses are summarized in Table 4, which has been split into two parts for presentation. The compounds identified are the most abundant components in the brake fluid as identified from the GC/MS analyses. The samples identified as A (for Advanced), P (for Prestone), and W (for Wearever) were commercial, unused brake fluid samples purchased for method development. The major components are glycols and related compounds. For 33 of the samples, triethylene glycol dimethyl ether, also known as Ansul Ether 161, was the major component identified by GC/MS. For six of the samples, butoxytriethylene glycol, also known as Dowanol® TBAT, was the major component identified by GC/MS. The only correlation noted is that the new brake fluids purchased for method development and the lighter colored fluids in this study, 4 and 56, did not contain identifiable quantities of the longer retained compounds with retention times of 32 minutes and greater. These compounds were not well identified by the MS database as they are closely related compounds to those eluting earlier, probably containing additional aliphatic moieties but exhibiting similar mass fragmentation patterns to the earlier eluting compounds. For future reference, the GC/MS chromatograms are on a CD-ROM accompanying this report.

Reference:
Stauffer, E. and Lentini, J.J., "Contamination of Brake Fluid by Power Steering Fluid," J. Forensic Sci., 2003, Vol. 48, pp. 1-6.

Table 4a. Qualitative GC/MS Identification of Components of Brake Fluid Samples.

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Ret time (min)	most abundant peaks only (X indicates largest) tentative ID based on best match in database	A	P		W	BF 4		BF 16		BF 17		BF 10	BF 45
6.26	diethylene glycol	*	*		*	*		*		*		*	*
9.88	1,2-[2-(2-isopropoxyethoxy)ethoxy]ethanol							*		*		*	*
12.65	butoxyethoxyethanol / butyl diglycol	*	*		*	*		*		*		*	*
13.43	methoxytriethylene glycol	*	*		*	*		*		*		*	*
13.63	triethylene glycol	*	*		*	*		*		*		*	*
15.29	ethyltriethylene glycol	*			*	*				*		*	*
15.85	triethylene glycol dimethyl ether												
16.04	ethyl methyl acetal acetone												
16.46	hexaethylene glycol dimethyl ether												
16.56	same as 16.46												
20.05	butoxytriethylene glycol	X	X		X	X		X		X		X	X
20.74	tetraethylene glycol	*	*		*	*		*				*	*
20.8	tetraethyleneglycol monomethylether	*	*			*		*		*		*	*
21.54	triethyleneglycol dimethyl ether							*		*		*	*
21.78	same as 20.8												
22.09	same as 16.46												
22.3	same as 15.29				*					*		*	*
26.42	3,6,9,12,15-pentaoxanonadecan-1-ol	*	*		*	*		*		*		*	*
26.94	same as above							*		*		*	*
27.1	2,5,8,11,14-pentaoxahexadecan-16-ol	*	*			*		*		*		*	*
27.52	same as above							*		*		*	*
27.63	dimethoxytetraethylene glycol							*		*		*	*
27.84	pentaethyleneglycol dimethyl ether							*		*		*	*
28.04	same as above							*		*		*	*
31.94	same as 26.42	*	*		*	*		*		*		*	*
32.34	same as 26.42							*		*		*	*
32.94	same as 27.1							*					*
33.27	same as 27.84							*					*
36.8	same as 26.42				*			*		*		*	*
37.1	same as 26.42												
37.51	same as 37.1												

Table 4b. Qualitative GC/MS Identification of Components of Brake Fluid Samples.

Ret time (min)	most abundant peaks only (X indicates largest) tentative ID based on best match in database	BF 1	BF 6	BF 26	BF 27	BF 28	BF 29	BF 30	BF 32	BF 40	BF 46	BF 80	BF 84	BF 86	BF 87	BF 88	BF 92	BF 93	BF 95
6.26	diethylene glycol																		
9.88	1,2-[2-(2-isopropoxyethoxy)ethyoxy]ethanol																		
12.65	butoxyethoxyethanol / butyl diglycol						*			*									*
13.43	methoxytriethylene glycol	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
13.63	triethylene glycol						*												*
15.29	ethyltriethylene glycol						*												
15.85	triethylene glycol dimethyl ether																		
16.04	ethyl methyl acetal acetone																		
16.46	hexaethylene glycol dimethyl ether																		
16.56	same as 16.46																		
20.05	butoxytriethylene glycol	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
20.74	tetraethylene glycol	*			*		*	*	*			*	*	*	*	*		*	*
20.8	tetraethyleneglycol monomethylether	*	*	*	*	*	*	*	*	*	*	*		*		*	*	*	*
21.54	triethyleneglycol dimethyl ether	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
21.78	same as 20.8	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
22.09	same as 16.46	*						*				*	*		*		*		*
22.3	same as 15.29	*					*												
26.42	3,6,9,12,15-pentaoxanonadecan-1-ol	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
26.94	same as above	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
27.1	2,5,8,11,14-pentaoxahexadecan-16-ol	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
27.52	same as above	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
27.63	dimethoxytetraethylene glycol	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
27.84	pentaethyleneglycol dimethyl ether	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
28.04	same as above	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
31.94	same as 26.42	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
32.34	same as 26.42	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
32.94	same as 27.1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
33.27	same as 27.84	*	*		*	*	*	*		*	*	*	*	*	*	*	*	*	*
36.8	same as 26.42	*		*	*	*	*	*			*	*	*	*			*	*	*
37.1	same as 26.42	*		*	*	*	*	*		*	*	*	*	*			*	*	*
37.51	same as 37.1	*		*	*	*	*	*		*			*	*			*	*	*

Water Determinations

Procedure: Water was determined in samples of brake fluid in two sets with an interval of about two months between the two sets of determinations. For each sample, a sub sample for analysis was withdrawn using a glass disposable pipette and was transferred to a nominal 1.5 mL brown glass vial and capped.

The first set consisted of four samples of brake fluid solution and one control. The four bottles were labeled 16, 17, 30 and 80. Each solution was green, with sample 30 having a darker tint. The control, Motorcraft high performance motor vehicle brake fluid, barcode 031508265820, was amber in color.

The second set consisted of eight samples of brake fluid solution, the Motorcraft control and one sub sample from the first set (#17). The eight samples were labeled 3, 4, 45, 48, 56, 76, 112, and 113. Samples 4, 56, 112, and 113 had a yellowish amber color; the other samples were a dark green with sample 48 having a less dark color. A new sub sample of the control was taken for the second set, but the original sub sample for 17 from the first set was reanalyzed.

Water in these samples was determined by Karl Fischer titration using a Brinkman/Metrohm 633 Automatic Karl Fischer Titrator and Brinkman/Metrohm Dosimat burette. The titrant (Riedel-deHaen # 34806 Hydranal®-Composite 2 one-component reagent) was standardized against water-saturated 1-octanol and an instrument drift (blank) was recorded. An explanation of the theory of the titration is contained in the instruction manual [1].

Nominal 20 mg 1-octanol standards were withdrawn using a 25 µL glass syringe and 100 mg samples were withdrawn using a 500 µL syringe. The mass of standard or sample titrated was determined from the difference of the mass of the syringe with the sample and the mass after the sample was injected into the titration vessel.

The amount of water in each sample was calculated using a relationship between the standard, drift, and sample with values for the standard and drift determined both before and after the titration of the samples. The water value for the octanol standard was taken from the certificate for SRM 2890, Water Saturated 1-Octanol [2].

First, a moisture factor, F_m, is calculated as shown in Equation 1 based on the mass fraction of water in the standard, w_{std}, the volume of standard titrant, v_{std}, the calculated volume drift per unit time, d, the length of time for the titration, t, the mass of the syringe with sample, m_{s+std}, and the mass of the syringe after injecting the sample, m_s.

$$F_m = w_{std}/((v_{std} - d \cdot t)/(m_{s+std} - m_s)) \qquad (1)$$

The mass fraction of water in the sample, w_{sam}, is calculated as shown in Equation 2 where the volume of sample titrant is v_{sam}, and mass of the syringe with sample is m_{s+sam}.

$$w_{sam} = F_m(v_{sam} - d \cdot t)/(m_{s+sam} - m_s) \qquad (2)$$

The % water was calculated as shown in Equation 3.

$$\% \text{ water} = 100 \cdot w_{sam} \qquad (3)$$

Results and Discussion: The results for all samples are listed in the attached Table 5. Since the values for the control and sample 17 in the two sets of determinations agree within the uncertainty of the measurement, there is no significant bias in the results between the two sets. All values were determined based on standardization against SRM 2890, Water Saturated 1-Octanol. Samples were not spiked with standard or water to determine % recovery since the significance of the difference in the water content between samples was more important than determining a more accurate value for each sample. The uncertainty of all values includes a component with the assumption that the % recovery is 100 % ± 5 %. The estimated relative expanded uncertainty of the samples (last column of Table 5.) with the highest water content (nominally ≥ 2 %) is 11 % and the relative uncertainty increases as the water content decreases. The determined water content in the samples ranged from 0.9 % to 4.2 %. With the exception of sample 4 (yellowish amber, 4.2 % water) there was a correlation between the color of the sample and the water content. The yellowish amber samples had the lowest nominal water content (0.9 %); the green samples had higher nominal water content (1.6 %); and the dark green samples had even higher nominal water content (2.2 %). The quantity U in Table 5 denotes the expanded uncertainty, corresponding to an approximate 95 % level of confidence.

Table 5. Results for water in brake fluid samples

Analysis Date	Set	ID	Color	Water Content mean (%)	s (%)	U (%)	relative U (%)
8/9/2005	1	16	green	1.33%	0.007	0.18	13
8/9/2005	1	17	green	1.68%	0.002	0.23	13
8/9/2005	1	30	dark green	**2.33%**	0.001	0.26	11
8/9/2005	1	80	green	1.36%	0.005	0.18	13
8/9/2005	1	control	amber	0.19%	0.096	0.03	18
10/5/2005	2	control		0.20%	0.045	0.03	16
10/6/2005	2	17	green	1.76%	*	0.24	13
10/6/2005	2	4	yellowish amber	**4.22%**	0.003	0.47	11
10/6/2005	2	45	dark green	**1.91%**	0.004	0.21	11
10/6/2005	2	48	green	**1.91%**	0.004	0.21	11
10/6/2005	2	56	yellowish amber	0.98%	0.004	0.12	13
10/7/2005	2	17	green	1.68%	*	0.23	13
10/7/2005	2	3	dark green	**2.02%**	0.007	0.23	11
10/7/2005	2	76	dark green	**2.75%**	0.011	0.31	11
10/7/2005	2	112	yellowish amber	0.87%	0.009	0.12	13
10/7/2005	2	113	yellowish amber	0.92%	0.013	0.12	14

* only 1 determination, all other values determined in triplicate

Documentation: The raw data for the determinations experiment can be found in notebook #3520 pages 1 to 16.

References:
1. Brinkman/Metrohm, Instructions for use, 633 Automatic Karl Fischer Titrator, 8.622.1003.
2. NIST Certificate of Analysis, SRM 2890, August 25, 1998.
3. ISO, Guide to the Expression of Uncertainty in Measurement, ISBN 92-67-10188-9
   ISO:Geneva, 1993.

Fourier Transform Infrared Red Attenuated Total Reflectance Spectroscopy (FT-IR/ATR)

Samples of 43 brake fluid samples from reservoirs were received for analysis from A. F. Marlow. These samples were held in 2 mL GC vials and numbered from 1 through 96. In addition, samples of as-purchased brake fluids were also provided. These samples were analyzed on a Bruker IFS 66 FT-IR spectrometer using a horizontal attenuated total reflection accessory from Spectra Tech (ARK model). The ATR accessory was installed into the main sampling compartment of the IR and kept under purge. The ATR element used was a 45° ZnSe element that provided a 12-bounce path length. A single bounce accessory was not available at the time of analysis. The system was calibrated with SRM 1921a, Infrared Transmission Wavelength Standard, NIST polystyrene infrared wavelength standard.

An aliquot of 25 µL of each sample was transferred by pipette onto the center of the ATR element. This amount was determined empirically and provided a spectrum of the sample without saturating any bands of its spectrum. Between each measurement, the ATR element was cleaned with a deionized H_2O saturated wipe, followed by a rinse with dry ethanol. A 5 min purge, followed by a baseline measurement were performed for each sample. A liquid nitrogen-cooled MCT (HgCdTe) detector and a KBr beam splitter were used to acquire all spectra. Each spectrum was measured from 6000 cm^{-1} to 600 cm^{-1}, using a minimum of 64 co-added scans with 4 cm^{-1} resolution. A zero-filling factor of 4 was used to provide a final data point spacing of approximately 1 cm^{-1}.

Four neat brake fluids were measured as received from their original containers. These samples were from Prestone (P), Advance (A), Wearever (W), and Motorcraft (M). Brake fluids P, A , and W had essentially identical spectra. The spectra of sample A and sample M are shown in Figure 4. The Motorcraft sample was slightly different from the other neat fluids. The peak of the hydroxyl (O-H) region for this sample was shifted 25 cm^{-1} (3455 cm^{-1} vs. ~3430 cm^{-1}) and showed a medium strong band as 1200 cm^{-1}. This band was absent or very weak in samples A, P, and W. Samples A, P and W show a strong doublet at 1100 cm^{-1} and 1065 cm^{-1} whereas sample M was missing the peak at 1065 cm^{-1}.

A library search indicates a strong correlation to both diethylene glycol monomethyl ether and diethylene glycol dimethyl ether. Both are likely matches as the neat brake fluids are known to be composed of a mixture of triethylene glycol methyl ether and triethylene glycol butyl ether with additional trace additives. Comparison of the library spectra with the neat samples indicates that sample M is predominately the dimethyl ether while samples A, P and W are composed of the monomethyl ethers. Examination of the 43 reservoir samples indicated that 32 appeared to be primarily the dimethyl ether while the remaining 11 were monomethyl glycol ethers. Table 6 shows the identification of the type based upon the band structure centered at 1100 cm^{-1}.

Samples from the reservoirs were grouped into *likely bad* versus *likely good* according to information received in the spreadsheet NHTSA_SCDS_log_sheet.xls. No differences could be observed visually between these two data sets. The only feature that appeared dissimilar was a series of three highly overlapped bands that were centered around 1650 cm^{-1} in the likely bad category. Only one sample, sample 3, showed significant bands at this location, and it must be added that this region shows significant interference from residual atmospheric water in the spectrometer system. This sample is shown in Figure 5. No other identifying features could be used to distinguish *likely bad* from *likely good* samples by this analysis.

Figure 4. Advance vs. Motorcraft Brake Fluid FT-IR/ATR Spectra
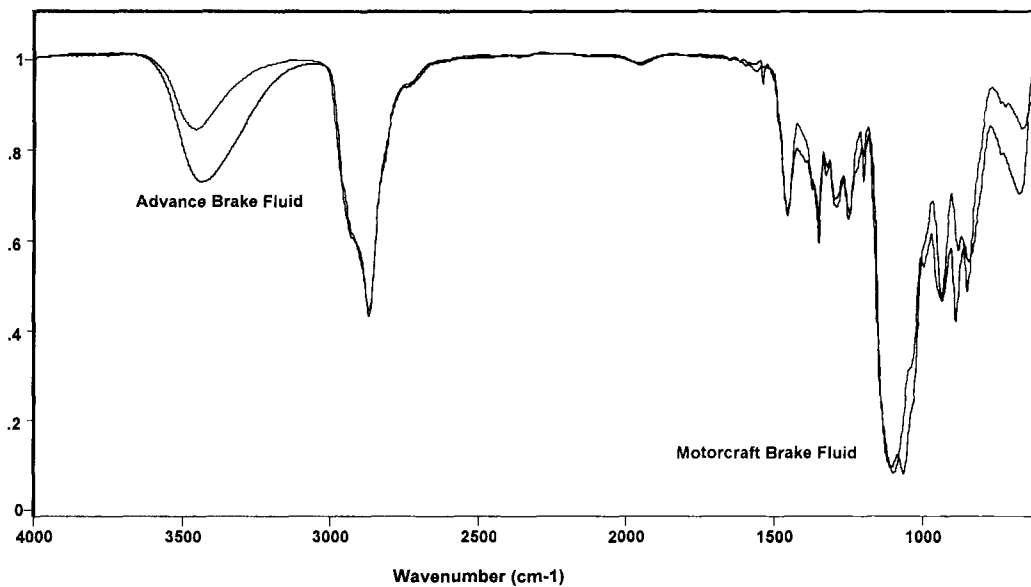
Figure 5. Sample 3 vs. Likely Good Sample.
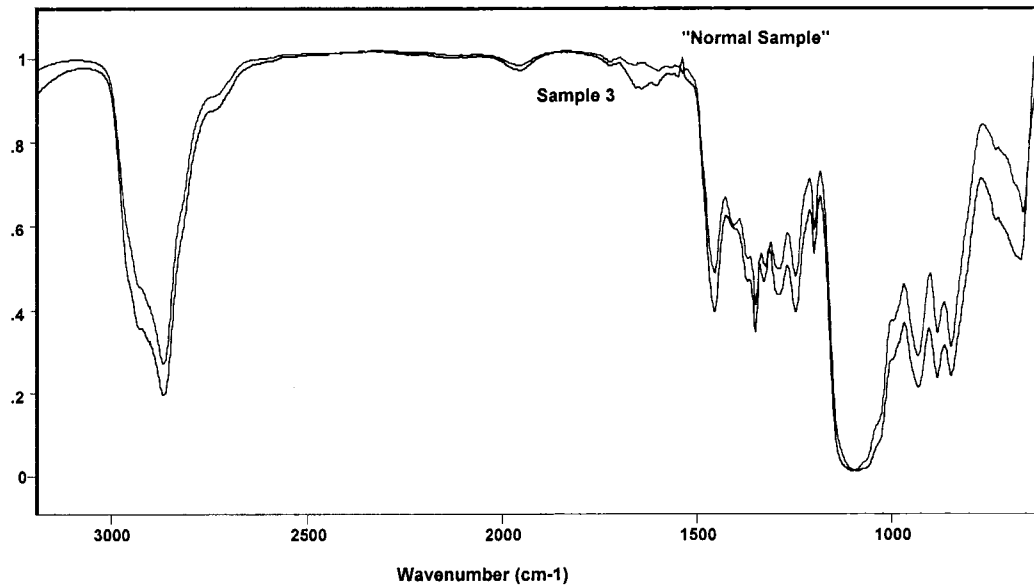
Table 6. Identification of Predominate Type of Glycol Ether Compounds in Reservoir Brake Fluid Samples

Reservoir #	Infra Red Identification	Reservoir #	Infra Red Identification	Reservoir #	Infra Red Identification
1	dimethyl	27	dimethyl	82	dimethyl
3	monomethyl	28	dimethyl	83	monomethyl
4	monomethyl	29	dimethyl	84	dimethyl
5	monomethyl	30	dimethyl	85	dimethyl
6	dimethyl	32	dimethyl	86	dimethyl
7	dimethyl	34	dimethyl	87	dimethyl
8	monomethyl	40	dimethyl	88	dimethyl
10	monomethyl	45	monomethyl	89	dimethyl
14	dimethyl	46	dimethyl	90	dimethyl
15	dimethyl	56	monomethyl	91	dimethyl
16	monomethyl	61	dimethyl	92	dimethyl
17	monomethyl	62	monomethyl	93	dimethyl
18	dimethyl	76	equal*	95	dimethyl
20	dimethyl	80	dimethyl	96	dimethyl
26	dimethyl				

* Sample 76 contained roughly equal amounts of dimethyl and monomethyl glycol ethers.

Nuclear Magnetic Resonance Analysis

Sample Preparation

All samples (Table 7) were prepared in new 5 mm Norell XR-55 NMR tubes that had been washed with water, rinsed multiple times with isopropanol, and oven dried (125 °C, 2 hrs). The Motorcraft and Wearever samples were added drop-wise directly to the NMR tubes using washed and oven-dried Pasteur pipettes. NMR samples of the used brake fluid solutions (W-# 16, W-#17, W-#30, and W-#80) were withdrawn from the upper portion of the solution to avoid bottom precipitates and were syringe-filtered through Whatman 0.45 μm NYL filters (hence the W added to the SCDS number to identify the sample) directly into the NMR tubes (~3 drops/tube). Approximately 750 μL of chloroform-D-"100%" with 0.03 % *v/v* tetramethylsilane (TMS) (CIL, Andover, MA, DLM-29TC-10x0.75, PSO 5b-348) was added to each tube. Tubes were capped with Norell Teflon® caps, sealed with Parafilm® and labeled, then sonicated to ensure complete mixing of the sample.

Experimental

NMR experiments were performed on a Bruker AVANCE 600 MHz spectrometer operating at 600.13 MHz and 300 °C and equipped with a 5 mm inverse broad-band probe. The system was controlled with Bruker's TopSpin software (Bruker, Rheinstetten, Germany). Experimental parameters were: spectral window 8200 Hz; acquisition time 3.997 s; relaxation delay 4s; pulse width (30°) 2.5 μs; transients 7200; data points 64 K. Experiments were performed in non-spinning mode to eliminate spinning sidebands. Prior to Fourier transformation, the free induction decay (FID) signals were multiplied by an exponential multiplication function with a line broadening of 0.3 Hz. Transformed spectra were phased manually, and a manual base line correction was applied. Ranges for integration of signals were set manually to exclude 13C satellites. Integration was referenced to the TMS reference peak set at 1.00. Chemical shifts are reported in parts per million (ppm) relative to TMS at 0 ppm.

Results

The major ether components of the samples have been identified, but due to sample complexity, peak overlap, and hydrogen exchange the exact nature of the polyalkylene glycol portion of the molecules was indeterminable. The identified components are presented in Table 8. Although the scope of this study was not quantitative in nature, relative concentrations of components in a given sample could be determined. Table 8 provides a summary of the relative amounts of the identified components in a given sample.

Samples W-#30 and W-#80 appear to be nearly identical, while the other four samples vary in both composition and relative proportions of the identified components. In addition to the major components present in these samples, there are multiple, low-level aromatic components. Table 9 provides a listing of the NMR signals and their integrated intensities along with information on the multiplicities of the signals. The ID's in the last column of this table are the ID's defined in Table 8. It should be noted that most of the minor components have yet to be identified.

The minor aromatic components present in these samples may well be brake fluid stabilizers and additives. 5-Methyl-1H-benzotriazole was identified in the Wearever brake fluid sample based on the chemical shifts indicated in Table 9. This additive is present at ~1 % of the monomethyl

ether peak (E-1), with peaks roughly comparable to the 13C satellite of that peak. The single sharp peak at 2.906 ppm suggests that piperazine may also be present in the Wearever sample. Considerable effort was made to identify the other minor components. Literature was searched to assemble a list of known brake fluid additives and the spectra were analyzed for the presence of these compounds. The remaining peaks could not be definitively correlated with known brake fluid additives, although for the most part these additives appear to be proprietary in nature and few are listed in the product MSD information.

The final row in Table 9 gives the integral across the entire spectral range for each of the samples. Although NMR samples were prepared by adding three drops of the brake fluid sample and 700 µL of deuterated chloroform to each NMR tube the sample concentrations do vary. The drops dispersed from the Whatman filters (W-#16, W-#17, W-#30, and W-#80) were larger than those from the capillary pipette. Because of this difference, peak integration values should only be compared for peaks within the same sample.

In conclusion, the NMR analysis of these samples shows that with the exception of W-#30 and W-#80 the composition and proportions of the main components differ from brake fluid sample to sample. The samples contain low levels (1 % or less) of aromatic materials that differ between samples. 5-Methyl-1H-benzotriazole was present in, and only in, the Wearever sample. Although further NMR experiments might allow additional identification of the minor components, this search would be greatly aided by more definitive information on the possible additives we are looking for. In a sample mixture such as these, it is not possible to distinguish between the diethylene, triethylene, tetraethylene, and polyethylene glycols as the ethylene signals overlap. The ether moieties are however readily identified.

Table 7. NMR Brake Fluid Samples

File Name	Date	Solvent	Scans	Sample Description (prior to dilution)	Sample :
	Prepared		Summed		CDCl$_3$ Vol (mL)
Wearever Brake Fluid	8/30/2005	CDCl$_3$	1600	Clear colorless	10 drops:700
Wearever Brake Fluid	8/30/2005	CDCl$_3$	800		
Ford Motorcraft Brake Fluid	8/31/2005	CDCl$_3$	800	Clear, gold tint	10 drops:700
Dilute Ford Motorcraft Brake Fluid	9/1/2005	CDCl$_3$	1600		3 drops:750
Dilute Wearever Brake Fluid	9/2/2005	CDCl$_3$	1600		3 drops:750
Dilute Brake Fluid W-#80*	9/2/2005	CDCl$_3$	1600	Dark olive green, no sediment	3 drops:750
Brake Fluid W-#30*	9/2/2005	CDCl$_3$	1600	Brownish-olive green, opaque, sediment	3 drops:750
Brake Fluid W-#16*	9/3/2005	CDCl$_3$	1600	Dark green, cloudy, sediment	3 drops:750
Brake Fluid W-#17*	9/4/2005	CDCl$_3$	1600	Yellow-brown, clear	3 drops:750

* Brake fluid sample was filtered through a Whatman 0.45 mm syringe filter prior to NMR sample preparation

Table 8. NMR Analysis Summary of Identified Components of Brake Fluid Samples

Numerical values in this table are based on peak integral values divided by the number of protons contributing to the peak signal. Hence the values for a given sample provide relative molar ratios for each identified component. Due to sample complexity, overlap of peaks, and proton exchange, the exact nature of the polyalkylene glycol portion of the molecule was indeterminable.

Components	ID	Motorcraft	Wearever	W-#16	W-#17	W-#30	W-#80
CH$_3$O-	E-1	2.23	0.51	3.68	2.05	6.50	6.69
CH$_3$CH$_2$O-	E-2		1.93		1.33		
(CH$_3$)$_2$CHO-	E-3	7.76		2.45	0.52	4.00	4.08
CH$_3$CH$_2$CH$_2$CH$_2$O-	E-4	0.85	3.58	5.98	6.38	2.40	2.49
5-Methyl-1H-benzotriazole	A-1	o	0.0048	o	o	o	o
Piperazine	A-2	?	o	o	o	o	o
1,1'-iminodi-2-propanol		u	u	u	u	u	u

+ Present   u Undetermined due to overlap
o Absent   ? Evidence but not conclusive

Table 9. NMR Peak Analysis Summary

Integrated peak areas are listed in decending frequency order relative to the area of the TMS standard peak. Multiplicity of the peak is indicated by letter designations: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, d of d=doublet of doublets. The letter u indicates the signal is not resolved; therefore the integration value is questionable. Numbers in ( ) for identified peaks are the per proton integral values, hence are relative to the number of moles.

Chemical Shift (ppm)	Peak Integration Values Motorcraft	Wearever	W-#16	W-#17	W-#30	W-#80	ID
9.846			s-0.0010				
9.815				s-0.0010			
9.796					d-0.0006	d-trace	
8.675	s-0.0007						
8.245				s-0.0010			
8.203				s-0.0012			
8.143			s-0.0035	s-0.0175			
8.114			s-0.0152	s-0.0175	s-0.0194	s-0.0254	
8.104			s-0.0029				
8.091			s-0.0058	s-0.0017	us < 0.0077	s-0.0085	
8.073					us 0.0051	s-0.0085	
8.068	d-0.0269		um-0.0035				
8.064					us-0.0055		
8.051			s-0.0018	um-0.0099		?	
8.029	s-0.0015		?	um-	ud?	um	
8.016					us	?	
7.913				s-0.0006			
7.890				d-0.0008			
7.853				s-0.0009			
7.801 and 7.787		d-0.0048		um-0.0011			A-1
7.727			s-0.0048	us-0.0010?			
7.710			s-0.0025	um-0.0020?			
7.687				d-0.0020			
7.640 and 7.626		d-0.0033		ud-0.0021			
7.586		s-0.0048					A-1
7.546				d-0.00			
Broad 7.415, 7.530, 7.538, 7.524			hump 0.0179	hump < 0.0094	hump < 0.059	hump << 0.108	
7.503 and 7.490			d-0.0014	um-0.0073	d- << 0.0107	d- << 0.0156	
7.458					broad s- 0.043		
7.440	t-0.0143						
7.431						broad s-0.040	
7.376	t-0.0271						
7.336		t-0.0039	t-0.0038		t-0.0051	t-0.0066	
7.306	s-0.147	s-0.144	s-0.151	s-0.151	s-0.150	s-0.147	CHCl₃
	(at 7.273)	(at 7.284)	(at 7.306)	(at 7.308)	(at 7.301)	(at 7.300)	
7.235 and 7.221		d-0.0054			um 0.0048	d or q? 0.0044	A-1
7.164 and 7.154		d-0.0228					
7.062				s-0.0017			
7.055 and 7.041			d-0.0368	d-0.0048			
6.959		s-0.0228		s-0.0091			
6.927				ud-0.0027			
6.893				u d of d?,0.0025			
6.802				ud-0.0023			
6.732 and 6.717			d-0.0357	d-0.0048			
6.893	d-0.0004						
6.696				ud-0.0012			
6.566				s-0.0012			
6.506			s-,0.0027	s-,0.0035			
6.512, 6.500, 6.489, 6.478	d of d-0.0014	d of d-0.0135	d of d- < 0.0138	d of d- < 0.0221	d of d- 0.0044	d of d- 0.0146	
6.456				q? < 0.0031			
6.397		um-0.0006					
6.304 and 6.290	d-0.0006						
6.197				d of d ? 0.0007			
6.159				um ? 0.0012			
5.931 and 5.904	m? 0.0009				um? 0.0028	um?	
5.757				0.0004			
5.717				s 0.0002			
5.698, 5.684, 5.669				s,s,s 0.0019			
5.555, 5.545, 5.527, 5.514			uq? 0.0285	q 0.0070	q 0.0541	um 0.0534	
5.572,5.560, 5.542, 5.530	q 0.0198						
5.479, 5.468, 5.450, 5.441	m? 0.0040						
5.426, 5.414, 5.399,			uq? 0.0338	um ? 0.0078	q 0.0604	um 0.0636	
5.418, 5.406, 5.388, 5.376	q 0.0219						
5.362	s < 0.0009						
5.339, 5.332	m 0.0087		um-0.0223	um ? 0.0036	um 0.0185	um 0.0233	
5.283, 5.370, 5.254			um 0.0037		m? < 0.0027	(d of d?) < 0.0036	
5.274	s 0.0014						
5.208, 5.190	d 0.009						
5.205, 5.188, 5.175, 5.158			um 0.0083		d of d? 0.0064	d of d? 0.0059	
5.021				s 0.0042			
5.003		s 0.0117					
4.900, 4.889, 4.879, 4.868, 4.857	p 0.0034				t? < 0.0064	up? 0.0085	
4.842, 4.833, 4.824				up? <0.0047			
4.778		s 0.0015					
4.752, 4.743		s 0.0009		d? < 0.0047	ud < 0.0031		
3.973	m 1.62 (1.62)	hump	m 2.53 (2.53)	um << 1.04 (1.04)	um 4.76 (4.76)	um 4.94 (4.94)	E-3
3.752		um 11.26	um 14.74	um 1.17	um 1.23		
3.723	um 2.67	um 5.29	um 15.02	um 23.80	um 7.90	um 7.77	
3.65-3.68	um 31.83	um 15.19	um 86.91	um 81.27	um 94.92	um 99.62	
3.611	um 2.61	um 6.32	um 23.40	um 33.28	um 7.61	um 7.92	
3.586	um 1.83	um 3.36	um 12.16	um 19.03	um 5.20	um 5.47	
3.555	um 4.78		um 8.28	um 5.61	um 13.70	um 14.52	
3.530		uq < 4.77 (2.38)		uq 2.35 (1.18)			E-2
3.550	d of d 2.00			um 5.61			
3.490					d of d? 6.19	d 6.20	
3.462	um < 2.70	t 6.9 (3.45)	ut 15.11 (7.55)	t 13.36 (6.67)	ut < 7.51 (3.7)	ut 8.13 (4.06)	E-4
3.381	s 6.69 (2.23)	s 1.52 (0.51)	s 11.05 (3.68)	s 6.16 (2.05)	s 19.49 (6.50)	s 20.04 (6.68)	E-1
3.279	t 1.66		t 4.07	t 1.79	t 4.91	t 5.12	
3.180			uhump				
3.080				uhump 8.20			
2.960					hump 14.62	hump 12.86	
2.906	us << 0.10						A-2
2.741				uhump 6.08			
2.660	hump 4.93	hump 8.77					
1.565	m 1.64 (0.82)	m 7.21 (3.60)	11.96 (5.97)	m 12.72 (6.36)	m 4.69 (2.35)	m 4.95 (2.47)	E-4
1.361	m 1.75 (0.87)	m 7.12 (3.56)	m 11.83 (5.92)	m 12.66 (6.33)	m 4.88 (2.44)	m 5.13 (2.56)	E-4
1.214			t 5.80 (1.93)	t 400 (1.33)			E-2
1.128	d 7.76 (1.29)		d 14.68 (2.45)	d 3.14 (0.52)	d 23.97 (4.00)	d 24.50 (4.08)	E-3
0.914	t 2.45 (0.86)	t 10.76 (3.58)	18.18 (6.06)	t 19.37 (6.46)	t 7.20 (2.40)	t 7.29 (2.43)	E-4
0.000	1.000	0.996	1.000	1.000	1.000	1.000	TMS
-0.50 to 10.00	82.75	150.75	281.61	286.54	241.58	247.23	Total Integration

Electrochemistry

Conductivity Measurements: Values for the electrolytic conductivity, κ, of NHTSA-supplied samples of used brake fluid and NIST-supplied samples of new factory-fill and service-fill brake fluids, of samples of the paste-like deposit obtained from the switch cavity of several SCDS units with observed leakage, and of samples of graphite and copper oxide (CuO) in slurries with brake fluid were determined with a small-volume conductivity cell.

The conductivity cell was constructed from two disks of Pt metal of nominal diameter 0.63 cm affixed with insulating, double-sided adhesive tape to the barrel faces of a micrometer. The spacing between the Pt electrodes, 0.127 cm, was fixed by setting the micrometer at the same spacing for each measurement. The micrometer setting corresponding to zero spacing was obtained as the point at which nominal zero resistance was recorded on a DC ohmmeter connected to the electrodes. Measurements of κ were obtained with an Altex conductivity bridge at a frequency of 1 kHz. The cell constant, K_{cell}, 0.53 cm^{-1}, was obtained by calibrating the micrometer cell with 0.01 mol kg^{-1} HCl, using κ calculated from the Onsager equation applicable to aqueous HCl. The accuracy of the cell was verified by measurements of κ for the current lot of SRM 3199, with a nominal κ of 15 μS cm^{-1}, which was in the range obtained for the new brake fluid samples. The value of κ was obtained from the measured conductance, G, by Eq. 4:

$$\kappa = GK_{cell} \qquad (4)$$

The micrometer was mounted with the barrel axis vertical. Sample was introduced from a micropipette onto the lower (stationary) face. The sample volume was 40 μL to 50 μL for each sample. For the liquid brake fluid samples, three separate measurements were performed following three rinses with water followed by a preliminary rinse with the same sample. The available quantity of the paste samples limited the number of replicate measurements to two with no preceding rinse, and the average of both measurements was reported. Measurements were performed at ambient temperature, 22.7 °C ± 0.2 °C for the brake fluid samples and 22.3 °C ± 0.4 °C for the paste samples.

The reproducibility for the brake fluid samples was on the order of 5 % to 10 % (standard deviation, $n = 3$). The reproducibility of the measurement was on the order of 25 % for the paste samples (standard deviation, $n = 2$). The overall uncertainty is estimated as 20 % (30 % for pastes) and is limited by the reproducibility of the surface area of the electrodes that is wetted.

The obtained values are presented in Table 10 and in Figures 6 and 7. Values of κ for the brake fluids ranged from 1.9 μS cm^{-1} to 17.4 μS cm^{-1} for unused NIST brake fluid samples and 4.9 μS cm^{-1} to 52 μS cm^{-1} for the NHTSA used brake fluid samples (obtained from vehicle reservoirs). For sample 76base, the paste sample was dry, and 20 μL of brake fluid from reservoir 76 was added to obtain a paste suitable for measurement. When adding sample 76base and closing the micrometer, it was noted that there were granular particles present. The recorded value of κ was a factor of 2000 higher than the κ for the next-higher sample, 65base. These facts are consistent with the presence of highly conductive particles of Cu metal from the corroded, disintegrated moving contact in the collected 76base sample.

Measured κ values for the graphite slurry were 11,800 μS cm^{-1} and 29,800 μS cm^{-1} for separate replicates. The κ value increased on vibration, presumably owing to contact of the graphite particles when the slurry was vibrated (as in a carbon microphone). The κ value for the CuO was 87 μS cm^{-1}, slightly greater than the largest κ value for used brake fluid. The value for the CuO slurry was not vibration-sensitive.

Corrosion Forecasts: The elapsed time from filling of the switch cavity in an SCDS Base to dissolution of the moving contact (called Spring in Fig. 1), assumed to be Cu, was calculated from the measured κ values. These calculations were based on the constants listed below. Eq. 5 yields the "cell" resistance, R_{SCDS}. Eq. 6 yields the current, $I_{corrosion}$, that flows through the SCDS "cell" when the switch cavity is filled with the given brake fluid. Eq. 7 yields the time, t, corresponding to total corrosion of the moving contact. The t values shown in Table 10 are converted to days and years: 1 d = 86,400 s and 1 yr = 365.25 d.

K_{cell} for SCDS switch: 1.1 cm^{-1} (0.5 cm spacing, l; 0.45 cm^2 area, A; $K_{cell} = l/A$)
Applied potential, E: 12 V (positive to SCDS moving contact, negative to ground)
Dimensions of moving contact: 1.0 cm x 0.45 cm x 0.0127 cm (L x W x T)
Density of Cu, ρ_{Cu}:   8.92 g cm^{-3}
Atomic weight of Cu, A_{Cu}:   63.546 g mol^{-1}
Faraday constant, F: 96,485.3383 C mol^{-1}
Anode corrosion reaction: $Cu \rightarrow Cu(II) + 2e^-$ (i.e., electron number z = 2)

$$R_{SCDS} = K_{cell}/\kappa \tag{5}$$

$$I_{corrosion} = E/R_{SCDS} \tag{6}$$

$$t = LWT\rho_{Cu}zF/A_{Cu}I_{corrosion} \tag{7}$$

The $I_{corrosion}$ values are of the same order of magnitude as values reported by NHTSA for other SCDS units at the progress meeting on October 12, 2005 at NIST. Values of t from Eq. 5 ranged from 9 days to 89 days for unused brake fluid and 5 days to 34 days for used brake fluid. These corrosion estimates start from the point in time corresponding to filling of the SCDS switch cavity with brake fluid, *not* from the initial application of potential (which occurs when the vehicle is new).

Table 10. Conductivity, κ; SCDS Resistance, R_{SCDS}; Corrosion Current, $I_{corrosion}$; and Predicted Corrosion Time, t, for Moving Contact (Spring) in SCDS.

Sample	$\kappa/(\mu S\ cm^{-1})$	$R_{SCDS}/k\Omega$	$I_{corrosion}/mA$	$I_{corrosion}/mA$	t/s	$t/days$	t/yr
4	24.2	45.9	0.26	2.6E-04	5.9E+05	6.9	0.019
16	33.6	33.0	0.36	3.6E-04	4.3E+05	4.9	0.014
17	15.0	74.2	0.16	1.6E-04	9.6E+05	11.1	0.030
30	31.4	35.4	0.34	3.4E-04	4.6E+05	5.3	0.014
45	21.4	52.0	0.23	2.3E-04	6.7E+05	7.8	0.021
46	51.6	21.5	0.56	5.6E-04	2.8E+05	3.2	0.009
48	22.4	49.7	0.24	2.4E-04	6.4E+05	7.4	0.020
56	4.9	226.3	0.05	5.3E-05	2.9E+06	33.8	0.093
76	33.6	33.1	0.36	3.6E-04	4.3E+05	4.9	0.014
80	23.9	46.5	0.26	2.6E-04	6.0E+05	6.9	0.019
112	18.7	59.3	0.20	2.0E-04	7.7E+05	8.9	0.024
113	18.9	58.9	0.20	2.0E-04	7.6E+05	8.8	0.024
Advanced	12.7	87.6	0.14	1.4E-04	1.1E+06	13.1	0.036
Motorcraft	17.4	63.7	0.19	1.9E-04	8.2E+05	9.5	0.026
Prestone	9.2	121.0	0.10	9.9E-05	1.6E+06	18.1	0.049
Wearever	1.9	593.4	0.02	2.0E-05	7.7E+06	88.6	0.243
48base	22	49.6	0.24	2.4E-04	6.4E+05	7.4	0.020
4base	22	50.2	0.24	2.4E-04	6.5E+05	7.5	0.021
65base	59	19.0	0.63	6.3E-04	2.4E+05	2.8	0.008
76base + 20 µL BF	131933	0.008	1425	1.42	109	---	
graphite slurry 1	11813	0.094	128	0.13	1213	---	
graphite slurry 2	29811	0.037	322	0.32	481	---	
CuO slurry	87	12.8	0.94	9.4E-04	1.7E+05	1.9	0.005

Figure 6. Measured Conductivities, κ, for Brake Fluid Samples[a,b].

Conductivities of Brake Fluid Samples
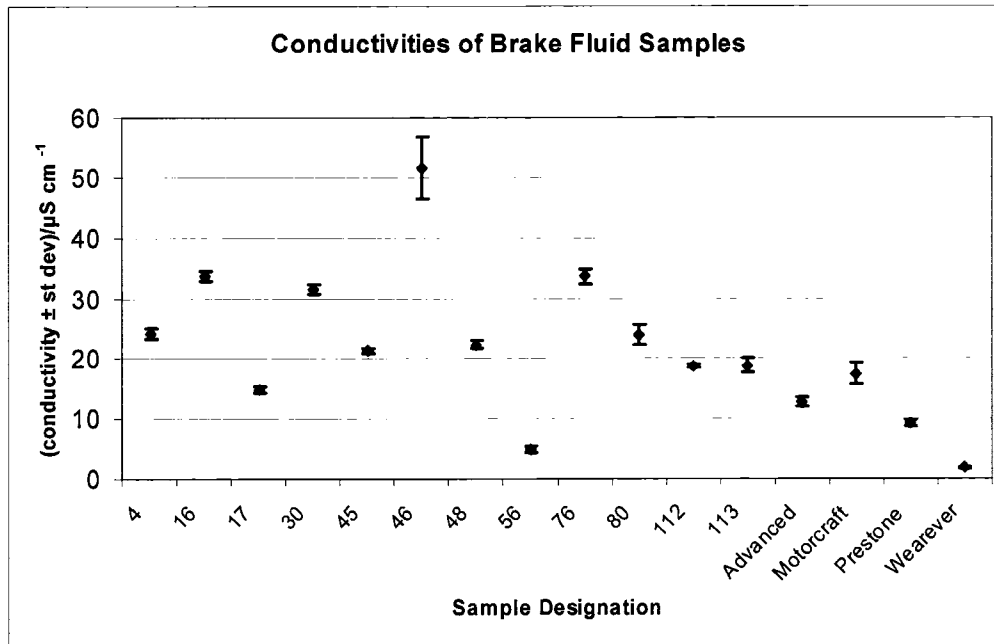
[a] Samples denoted by numbers denote NHTSA reservoir samples. Samples denoted by brand names denote NIST-purchased unused brake samples.
[b] Error bars denote ±1 standard deviation of the mean ($n = 3$).

Figure 7. Measured Conductivities, κ, for NHTSA SCDS Paste and NIST Slurry Samples[a,b].

Conductivities of SCDS Paste Samples and NIST Slurries
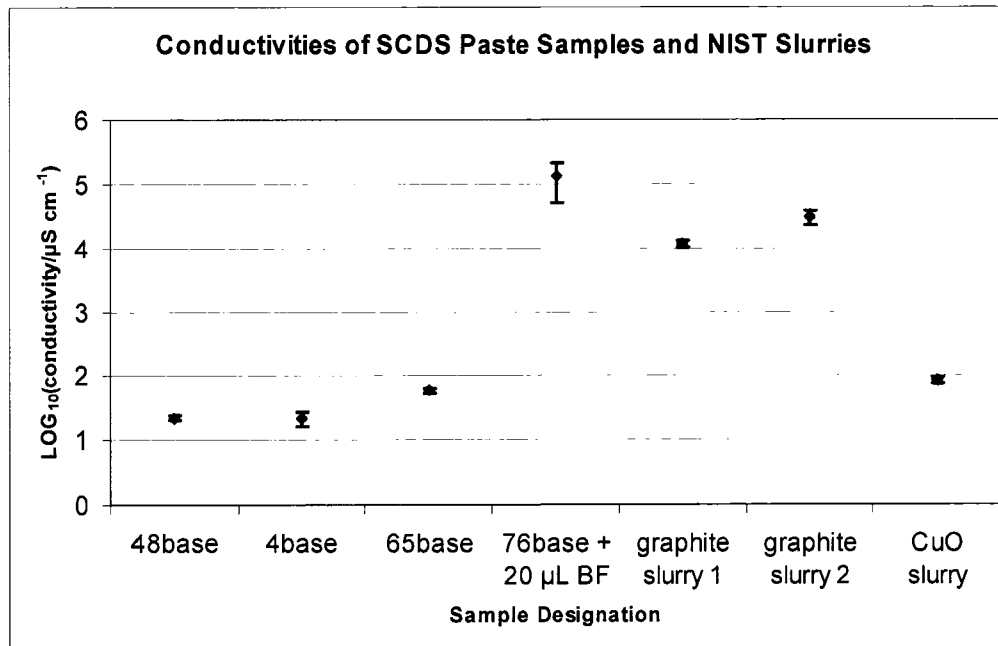
[a] Conductivity is on logarithmic scale. Values are presented in Table 10 (see above).
[b] BF = brake fluid from reservoir sample 76.

Discussion: This report is presented in partial fulfillment of the requirements for work by the NIST Analytical Chemistry Division. Since the work was part of an investigation, the work plan was modified as the investigation proceeded. Significant changes included the following:

- Design of a modified procedure for disassembly and photo-documentation of SCDS with sampling and packaging of fluids and deposits,
- Corrosion forecasts of the destruction of metallic parts during electrolysis inside a switch base,
- Analysis of selected brake fluid samples by NMR,
- Analysis of selected brake fluid samples for water content,
- Dropped plan to perform pH measurements when electrolysis was shown to be the mode of destruction of metal switch parts.

The authors did not attempt to capture in this report the discussions held with NHTSA investigators and NIST Polymers Division. Notes on these discussions are included with observations recorded in the notebooks kept by the authors. All documentation (paper and electronic), specimens, and photographs accompany this report into the custody of NHTSA. Electronic messages pertaining to this investigation were copied onto electronic media and deleted from the authors' computers. Measured data was either exported to electronic media the deleted or simply deleted from the operating systems of all analytical instrumentation.
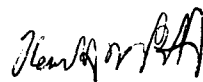
Documents and Materials: Itemized below are all items given over to NHTSA along with this report of analysis.

- This report of analysis,
- CD-ROMs containing data, photographs, and document files created by the authors,
- Vials containing brake fluid or deposits associated with the SCDS,
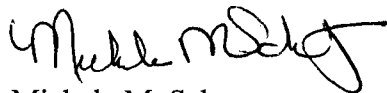- Bottles of brake fluid marked with the code numbers of the associated SCDS.
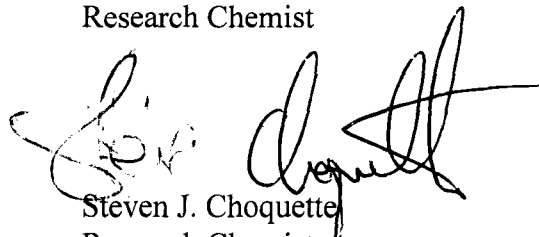
Reported by

John R. Sieber
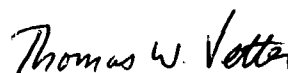Research Chemist

Kenneth W. Pratt
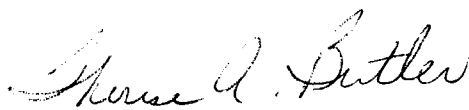Research Chemist

Michele M. Schantz
Research Chemist

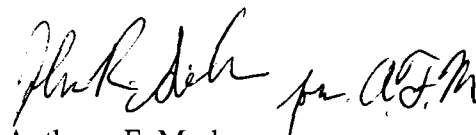Steven J. Choquette
Research Chemist

Diane K. Hancock
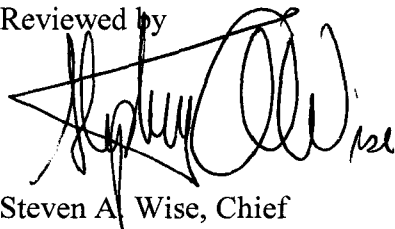Research Chemist

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