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Measurement of water by oven evaporation using a novel oven design. 2. Water in motor oils and motor oil additives

Abstract The measurement of water in lubricating oils is important because water accelerates the corrosion of metal parts and bearings in motors. Some of the additives added to lubricating oils to improve their performance react with the Karl Fischer reagent (KFR) causing a positive bias in the water measurement. A new oven evaporation technique for measuring water in oils has been developed that is automated, requires less sample handling, is easily calibrated, and is capable of measuring relatively small mass fractions of water (≥50 mg/kg sample). A series of motor oils was analyzed with the standard KFR, a reagent that detects interfering substances that reduce iodine, and the aldehyde–ketone reagent that does not detect substances that react with methanol and form water. The oil samples were heated to 107°C and then reheated to 160°C. At both temperatures, material was measured by both KFRs, but only zinc dithiophosphate released sulfur compounds that would react with the reagent that detects interfering substances. Mass fractions of between 20 and 70% of the volatile material released at either temperature were measured with the standard KFR but not with the aldehyde–ketone reagent. These results demonstrate that there are a number of sources of positive bias in the measurement of water in motor oils and that the standard KFR cannot be used to measure water in motor oils and motor oil additives. These results also indicate that some of the material reacts with methanol to form water. Finally, these results suggest that some of the material that is volatile at 160°C and not at 107°C may be water that is physically occluded or may be substances that react with diethyleneglycol monomethylether to produce water.

Keywords Water · Karl Fischer · Oven evaporation · Motor oils · Motor oil additives

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Introduction

The accurate measurement of water in lubricating oils cannot be accomplished using the standard method of titration with the Karl Fischer reagent (KFR). Motor oils in particular contain materials that interfere with the KFR and cause a positive bias in the water measurement. The measurement of water in lubricants is particularly important. Water can cause corrosion of metals. It can also increase the rate of oxidation of the oil tenfold particularly in the presence of catalytic metals. In synthetic oils containing dibasic esters and phosphate esters, the reaction with water can cause the formation of destructive acids. In oils that contain sulfurous additives and phenolic antioxidants, the acid byproducts resulting from the action of the water can cause corrosion and excessive wear of soft metals used in bearings. Even small amounts of water may have a significant effect [1].

Lubricating oils contain additives that react with the KFR to produce a result indistinguishable from that of water. The water in motor oils can be measured by the crackle test, reaction with calcium hydride in a pressure chamber [2], a relative humidity sensor [3], or infra red spectroscopy [4, 5]. Some of these methods are not very sensitive or are only qualitative or semi quantitative.

Tubular ovens in which the sample is usually heated to 105–110°C or higher have been designed to flush the released moisture with a dry gas into a Karl Fischer coulometric instrument that measures the water. These ovens have a relatively large volume and water can condense on the walls and (in some instruments) the tubes conducting the flushing gas to the Karl Fischer

apparatus. Several companies distribute automated ovens that will handle multiple samples. One of the systems uses 9-mL bottles with Teflon septa that are crimped in place as sample holders. The bottles are heated in the oven and moisture is flushed with a dry gas through heated lines. This instrument has several advantages: it is automated, suitable calibrants and blanks can be analyzed using an oil matrix, and a sample can be analyzed every 2–15 min depending on the sample size and the water content.

The use of the Karl Fischer coulometric instrument for the measurement of water eliminates the positive bias in mass studies that is introduced by non-aqueous volatile compounds. In lubricating oils it eliminates the positive bias introduced by the reaction of the non-volatile additives with the KFR. This method permits the measurement of the water that is removed at temperatures above 100°C either as the result of chemical reactions or as azeotropes or other stable physical species with boiling points above 100°C. Finally, it permits the use of various coulometric reagents that permit the detection of volatile non-aqueous materials that react with the standard KFR.

In recent studies, Cedergren and Nordmark [6] and our laboratory [7] have demonstrated that oils can contain significant amounts of materials that react with iodine resulting in a positive bias in the water measurement. These substances can be measured by replacing the standard KFR with a SO_2-free reagent [6–8]. Other materials such as low-boiling aldehydes, ketones, acid amines, or siloxanes that react with methanol forming water can also cause a positive bias in the water measurement [9]. Methanol-free reagents such as Coulomat AK can be used in the coulometric detector to determine the presence of the materials that introduce this type of positive bias.

We have recently used this automated oven evaporation technique to measure the water in coal, Portland cement, and refined oils. We have demonstrated that only the refined oils contain materials that cause a positive bias in the water measurement [10]. The purpose of this study is to extend our observations to the measurement of water in lubricating oils and motor oil additive packages, samples in which the water cannot be measured by directly adding the sample into the KFR.

Experimental

Hydranal reagents were purchased from Brinkmann Instruments Inc. (Westbury, NY, USA). SRM 1848 (Lubricating Oil Additive Package) and SRM 2890 (water-saturated 1-octanol, WSO) were prepared at NIST for distribution through the NIST SRM program. The motor oil and additive package samples were part of an ASTM interlaboratory study for elemental analysis by ASTM method D 4927 [11]. The motor oils were: Exxon 10–30, Castrol 5–30, Havoline 10–30, Quaker 10–30, Penzoil 30, Valvoline 10–40, FGR 7.37 w/WO and

MO-1.44x w/WO, and MO-G. The additive packages were: A6933, FGR, Conostan blend 1, Conostan blend 2 and MO-F. The zinc dithiophosphate, and SNO oils (solvent neutral oils) were research samples sent to one of us (JRS).

Methods

Water measurements made by oven evaporation were performed using a Metrohm 774 Oven Sampler connected to a Model 756 Coulometer with either a one-compartment or two-compartment cell (Brinkmann Instruments Inc., Westbury, NY, USA). The carrier gas was dry nitrogen (flow rate = 70 mL min^{-1}). The oven was equilibrated at 107, 125, or 160°C. The heating cycle started upon the transfer of the sample (at room temperature, 20°C) from the sample tray to the oven. The rate of heating was not controlled, but was estimated to be about 5°C s^{-1}. The lower temperature (107°C) was use to measure the free water, and the higher temperatures (125 and 160°C) were used to assess the existence of additional occluded water, water produced by chemical reaction, or substances that interfered with the KFR. The reagent used for the one-compartment cell was Coulomat A. The reagent used for the two-compartment cell was Coulomat AK in the anode compartment and Coulomat CK in the cathode compartment. Calibration materials and samples were prepared and coulometric water measurements were preformed as previously described [12]. The coulometric conditions for the oven measurements using the Coulomat A and Coulomat AK reagents in the coulometer were: dynamics = 70 mV, stop drift = 20 µg min^{-1}, time interval = 8 s, maximum rate of titration = 2,000 µg min^{-1}, extraction time = 60 s, polarization current = 10 µA, minimum rate of titration = 10 µg min^{-1}, start drift = 20 µg min^{-1} endpoint potential = 30 mV. The presence of interfering substances was evaluated using the sulfur dioxide free reagent (containing no xylene) in the coulometric cell attached to the oven [6–8]. The oil samples for the interference measurements were heated in the oven at 160°C with a 5-min extraction period. The coulometric measurement parameters were the same as those previously described [7]. Every experimental sequence consisted of a standard curve of five WSO samples (2–10 mL) in 2 mL of dry Drakeol oil, two dry Drakeol oil blanks, two empty vial blanks, and a sequence of motor oil samples. The dry Drakeol oil and the two dry Drakeol oil blanks were prepared by pre-drying Drakeol oil at 107°C in a single cycle through the oven and adding the WSO into the dried oil with a microliter syringe. All of the determinations reported in the tables have been corrected for the water blank contributed by the atmosphere trapped in the sealed empty vial. The curves illustrated in the figures have not been corrected for these blank values.

The moisture (Karl Fischer reacting material) in three or more samples of increasing volume (WSO) or mass (oil) was measured in each analysis. The moisture content

(ordinate) was plotted against the volume or mass (abscissa), the linear regression of the data was calculated, and the slope and intercept were determined.

Safety considerations All KFRs contain methanol or diethyleneglycol monomethylether and an organic base (imidazole). Some reagents also contain hydroiodic acid, chloroform, and/or xylene. These compounds are all toxic to varying degrees with respect to inhalation, ingestion, and/or eye irritation. Several compounds (methanol and chloroform) are flammable. In addition, imidazole is an in vitro mutagen and chloroform is an animal carcinogen. Standard laboratory safety precautions and protective equipment were employed throughout this study. The reagents were handled in a chemical hood and disposed of according to OSHA regulations by the NIST Health and Safety Office. The oils used in these studies were free from chlorinated biphenyl compounds but were also disposed of by the NIST Health and Safety Office.

Results and discussion

The automated oven sampling apparatus provides a method for measuring the water in materials such as lubricating oils that cannot be performed by direct addition to the KFR. The tubular ovens that have been used in the past for this type of measurement are not automated; they have large volumes (several hundred milliliters), their transfer lines are not heated, and they must be opened after each sample is analyzed. The new types of automated oven-evaporation instruments incorporating a carousel eliminate these limitations. Each sample is placed in a small glass container (≈9 mL) with a Teflon septum. The atmospheric water in empty sealed vials can be analyzed to correct for the atmospheric water trapped in the vials or trace levels of water present in the sparging gas. The advantages of this new method are: the transfer lines are heated to minimize condensation; 24–35 samples placed in a carousel can be analyzed automatically; and an appropriate set of standards can be analyzed with the samples under the same analytical conditions.

The evaluation of the performance of this method with WSO indicated that the response was linear and the humidity trapped in the sample vial when the sample was pipetted into the sample containers introduced a significant bias to the measurement [10]. This bias was determined either by measuring the water contained in the air in a blank vial or by measuring the water in a series of four samples of increasing mass. The mass fraction of water in the sample was equivalent to the slope of the regression line calculated for the four samples and the bias was equivalent to the intercept of the regression line. Separate sets of samples of three solvent-neutral oils and a white oil were examined. "Water-like" substances that reacted with the standard KFR but not with the aldehyde–ketone reagent (Coulomat AK) were detected when the sample sets were heated to 107°C and heated a second time to 160 °C [10]. This study has been extended herein to motor oils and various additive packages.

Motor oils, which are formulated from base stock oils such as the SNO oils, also do not release all of their KFR-reactive material when heated at 107°C (Tables 1 and 2). Nine different engine oils that were examined released only 40–70% of their water at 107°C and additional "water-like" material was released when they were heated or reheated to 160°C. When the oil was only heated to 160°C, it invariably released less water than the sum of the water released by samples analyzed by heating to 107°C and then reanalyzed by heating to 160°C (Table 1). The stepwise release of water was observed

Table 1 Results of the measurement of water evaporated from motor oils and additive packages over two temperature ranges using a one-compartment cell and Coulomat C reagent

Sample name	Sample type	20–107°C Column A[b]		107–160°C Column B[b]		Column A + B	20–160°C Column C[b]		Column A + B−C
		Mean[a]	SD	Mean[a]	SD	Mean[a]	Mean[a]	SD	Mean[a]
Exxon 10–30	Engine oil	489	47	455	14	944	877	49	67
Castrol 5–30	Engine oil	402	8	337	19	739	674	21	65
Havoline 10–30	Engine oil	256	36	392	11	648	625	30	23
Quaker 10–30	Engine oil	354	45	425	22	779	660	34	118
Penzoil 30	Engine oil	417	68	416	45	833	694	5	139
Valvoline 10–40	Engine oil	582	108	428	17	1,010	834	16	177
A6933	Additive pack	1,420	50	2,634	107	4,050	3,814	119	240
FGR	Additive pack	2,157	136	3,540	79	5,697	5,556	82	141
SRM 1848	Additive pack	1,261	259	2,407	115	3,668	3,024	237	644
Conostan blend 1	Metal sulfonate	577	17	124	25	701	594	28	107
Conostan blend 2	Metal sulfonate	6,272	148	488	422	6,760	6,026	198	734
Dithiophosphate	Zn salt	529	78	d					

[a] The mean represents the average of three measurements
[b] Oven temparature range
d decomposition

with three of the oils when separate sets of samples were heated either to 107, 125, or 160°C (Table 2).

Together these observations indicate that some substance(s) that reacts with the KFR is either more firmly physically associated with the oil components, has a boiling point above 107°C, or undergoes degradation above 107°C. The substances detected as water were not substances that reacted with iodine because we detected no material using our interference assay in which we substituted the SO_2-free reagent for KFR in the coulometric cell of the model 756 coulometer that was attached to the oven [7].

The possibility that this KFR-reactive material was associated with the additives was examined by measuring the evaporation of this material from seven different additive formulations. The pattern of the evaporation of this material from the complete additive packages was similar to that observed for the engine oils and suggests that this may be the source of these substances. In contrast, the Conostan blends (mixtures of metal sulfonates) released the majority of their KFR-reactive material at 107°C.

When heated alone, zinc dithiophosphate, a compound that is used in additive packages of some oil products, released some KFR-reactive material at 107°C and decomposed when reheated to 160°C. At least one of the substances generated from zinc dithiophosphate by the heating process reacted with the KFR and this reaction coincided with the release of sulfur-containing compounds. At this point the heating was terminated and the sample was removed because of its degradation to H_2S and other possible sulfur compounds that might have been toxic. Zinc dithiophosphate was the only sample that lost a significant amount of mass ($\approx 40\%$). The total mass fraction loss for each of the other oil samples and additives was $< 0.2\%$.

The reaction of a substance that is volatile at 107°C or higher with the standard coulometric KFR does not prove that it is water. It may be a reducing substance or any other substance that reacts directly with iodine. The regeneration of this iodine by the generating electrode of the coulometer results in the increase in the apparent water content as is the case with zinc dithiophosphate. The volatile substance also may be a low-boiling aldehyde, ketone, acid amine, or siloxane that reacts with methanol forming water [9].

Experiments were performed on the motor oils and the additive packages, in which the standard KFR was replaced with aldehyde–ketone reagent (Coulomat CK and AK) using a two-compartment cell and the samples were heated to 107°C and then reheated to 160°C (Table 3). This ketone reagent measured 27–47% less KFR-reacting material than the standard KFR (Coulomat A) in all the engine oils. The measurements on the additives yielded similar results, 21–71% reduction in KFR-reacting material. The only exception was Conostan blend 2 that yielded a 29% increase in KFR-reacting material when reheated to 160°C. This distinc-

Table 2 Results of the measurement of water evaporated from motor oils and an additive package at increasing temperatures

Sample name	Sample type	Mass of water (μg g^{-1})					
		20–107°C[b]		20–125°C[b]		20–160°C[b]	
		Mean[a]	SD	Mean[a]	SD	Mean[a]	SD
FGR 7.37x w/WO	Engine oil	638	57	786	27	1,067	46
MO-1.44x w/WO	Engine oil	673	100	827	65	957	51
MO-G	Engine oil	130	18	172	22	253	73
MO-F	Additive pack	1,246	92	1,495	98	1,777	47

[a] The mean represents the average of four measurements
[b] Oven temparature range

Table 3 Results of the measurement of water evaporated from motor oils and additive packages over two temperature ranges using a two-compartment cell with Coulomat AK and CK reagents

Sample name	Sample type	Mass of water (μg g^{-1})					Percentage decrease from data in Table 1		
		20–107°C Column A[c]		107–160°C Column B[c]		Column A + B			
		Mean[a]	SD	Mean[a]	SD	Mean[a]	Column A	Column B	Column A + B
Exxon 10–30	Engine oil	335	11	242	65	577	31	47	39
Castrol 5–30	Engine oil	268	14	240	27	509	33	29	31
Havoline 10–30	Engine oil	179	14	279	44	458	30	29	29
Quaker 10–30	Engine oil	212	11	244	26	456	40	42	41
Penzoil 30	Engine oil	238	16	288	39	524	43	31	37
Valvoline 10–40	Engine oil	413	15	206	44	618	29	52	39
FGR 7.37x w/WO	Engine oil	469	12	226	12	694	27	47	35
A6933	Add pack	1,034	18	1,763	12	2,817	27	32	31
FGR	Add pack	1,498	66	2,708	127	4,296	31	21	25
SRM 1848	Add pack	371	45	1,231	84	1,602	71	49	56
Conostan blend 1	Metal sulfonate	450	19	98	16	547	22	21	22
Conostan blend 2	Metal sulfonate	4,859	267	989	337	5,848	23	(107)[b]	17

[a] The mean represents the average of four measurements
[b] Parentheses indicate an increase from the data in Table 1
[c] Oven temparature range

tive measurement may reflect only the large standard deviation (SD) in this measurement or it may be the result of the differences in the metal compositions of the two blends. From these results it is evident that these oils contain non-aqueous material that reacts with the standard KFR (Coulomat A) and not with the aldehyde–ketone reagent (Coulomat AK). In these experiments the standards (slope = 39.2 mg mL^{-1}, intercept = 28.0 μg, $R^2 = 0.987$) showed that the measurement system is in control and responding properly to water.

Evidence for multiple species

Examination of the progress curves for the release of KFR-reactive material from the various samples indicates that some of the standard KFR-sensitive materials have different boiling points and that some react with methanol to produce water. This would suggest that they may exist in different physical states within the matrix or have different chemical structures. Previously, we demonstrated that only the coal, cement, and Drakeol 35 oil samples released the same amount of water when these samples were heated either to 107 or 160°C [10]. The progress curves of all SNO oils revealed the occurrence of a multistage evaporation of standard KFR-sensitive material in dual heating experiments in which this material in each sample was determined by heating the sample to107°C, then re-determined by heating the same sample to 160°C.

Figure 1 illustrates the simple, smooth, single-peak progress curve for the blank vials that had only room air in them. The larger curve is for the first evaporation cycle at 107°C. This represents the relative humidity at time that the samples were sealed in the sample containers. The smaller curve represents a second evaporation cycle 3 h later on the same vial and this water probably represents the residual water in the dried nitrogen carrier gas that remained in the vial after the first evaporation cycle. Since the amount of atmospheric water was variable and depended on the humidity on the day the analysis was performed, the curves depicted in
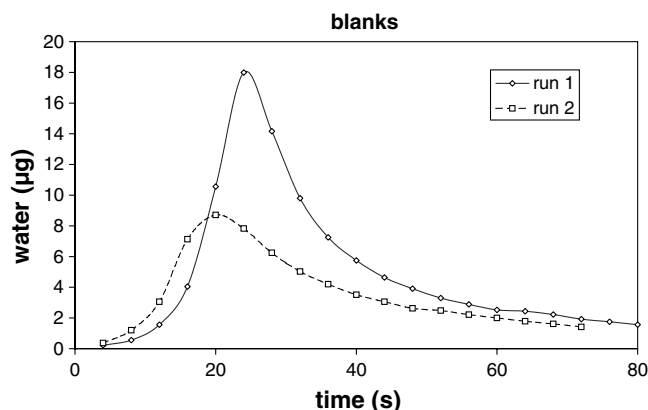

Fig. 1 Progress curves for the titration of atmospheric water in blank vials using the Coulomat A reagent. Each curve represents an evaporation cycle over an oven temperature range of 20–107°C

the figures were not corrected for this blank. However, the data in Tables 1, 2, and 3 were corrected for this blank using the intercept obtained from the regression analysis of each group of oil samples (three or four samples increasing in mass). Thus a significant amount of KFR-sensitive material in the first peak at 25–30 s in the oil samples represents atmospheric water. Additional peaks, not observed in the curves for the blank vials, were observed in the progress curves of the oil samples at ≈110, ≈180, ≈300 s, and in a few cases at ≈600 s (Fig. 2a). Furthermore, the shoulder that appeared at 110 s at 107°C probably did not arise from the same physical material as that which appeared at the same time in the progress curve for the samples that were heated to 160°C after being heated to 107°C. Similar results were observed with the additive packages (Fig. 3a). These results suggest that, in addition to the water, one or more KFR-sensitive materials are present in the motor oil samples and additive packages, and may exist in more than one physical state. This physical state may be an azeotrope or other physical entity such as a micelle or some other lipid–water complex. It may also be the result of a temperature-dependent chemical reaction that produces water [8], the degradation of additives such as zinc dithiophosphate (Fig. 4), a relatively low molecular weight organic acid, or a low molecular mass volatile ketone, aldehyde, or other organic compound that reacts with methanol under acidic conditions to yield water [9].

The results in Tables 1 and 2 indicate that in the motor oils and additive packages some of the KFR-sensitive material is not free to evaporate at 107°C, but does evaporate when the same samples are reheated to 160°C. This observation supports the existence of several types of material. This evaporation occurs in two distinct stages (Table 1 and Figs. 2 and 3). When separate oil samples are heated at 107, 125, or 160°C, different masses of material are released. This suggests that there are several different species of non-free water or non-aqueous material that react with the KFR (Table 1). Examination of the progress curves of the motor oils (Fig. 2) indicate that, when the oil that was heated to 107°C was then reheated to 160°C, additional material was evaporated in at least two distinct stages. There also was an indication of possible additional stages in the production of "water-like" material. These curves include three distinct peaks. One peak occurs at ≈20 s, which probably represents atmospheric water, one at ≈150 s, and one at ≈220 s (Figs. 2 and 3). It is important to note that these peaks may represent more than one compound.

Chemical evidence of volatile compounds other than water

The additional chemical species may arise from a number of sources including: (1) substances that react with iodine or methanol, (2) water that evaporates at higher temperatures because of unknown physical associations
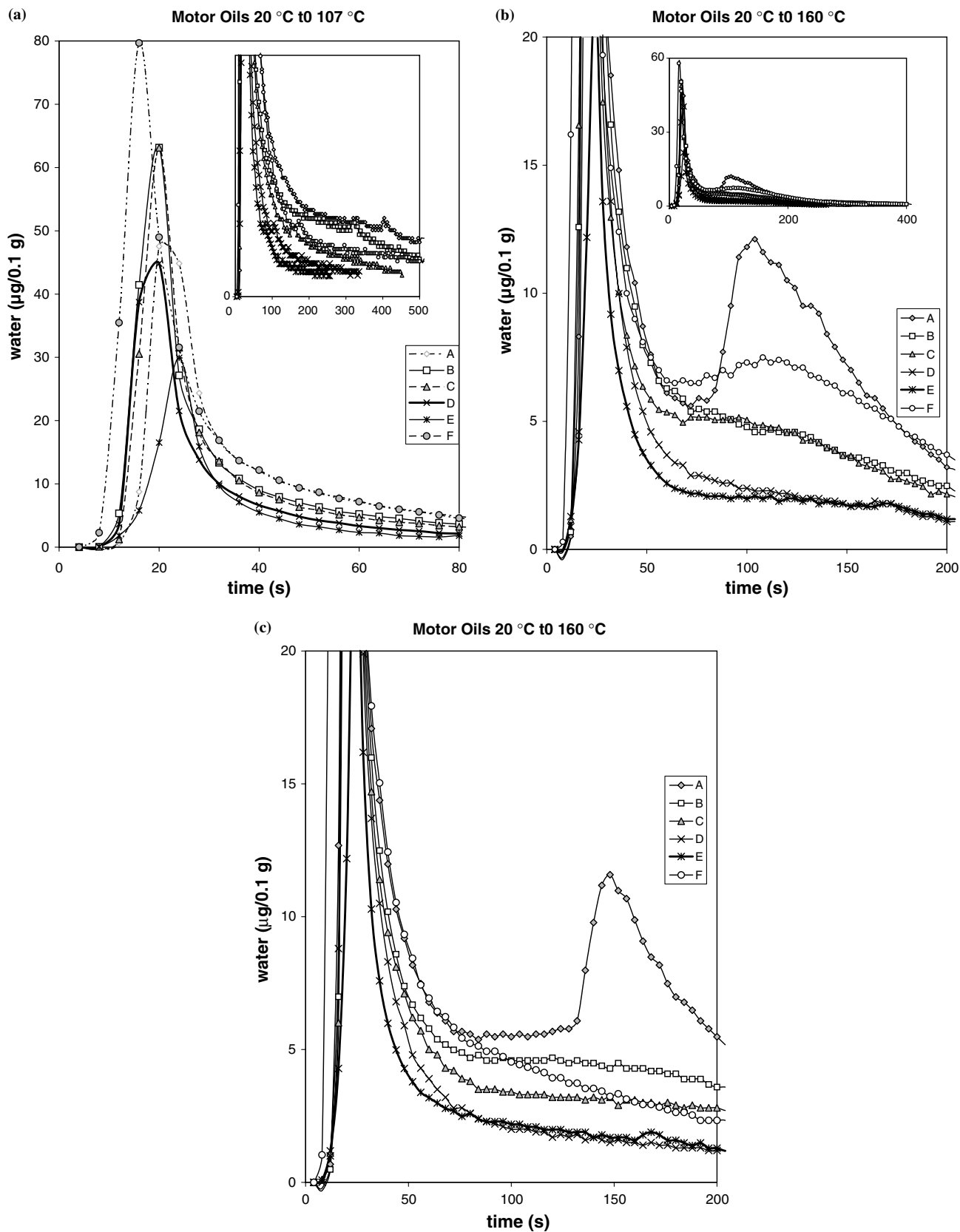
(a) Motor Oils 20 °C t0 107 °C

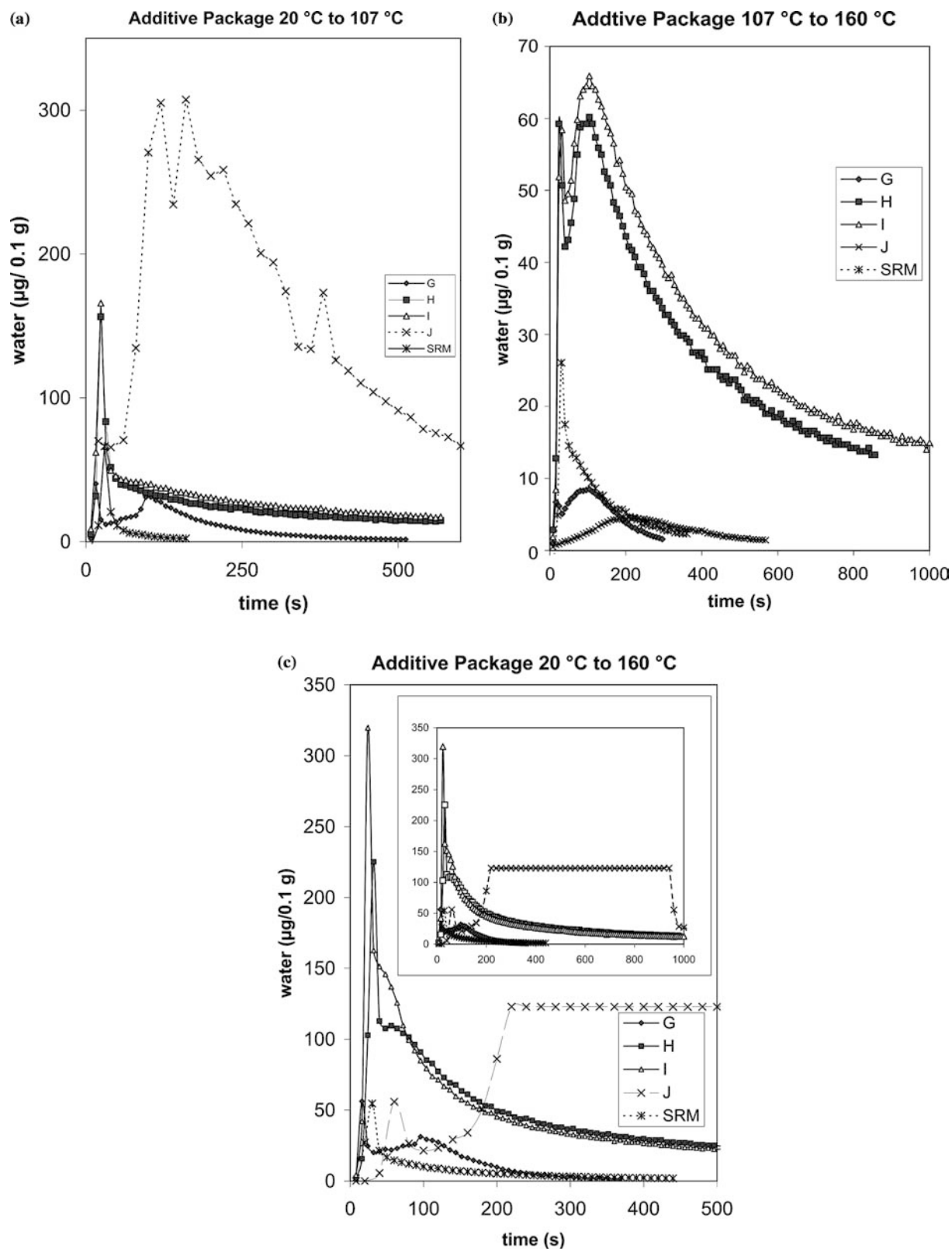**(b)** Motor Oils 20 °C t0 160 °C

(c) Motor Oils 20 °C t0 160 °C

Fig. 2 Progress curves for the evaporation of water from motor oils using the Coulomat A reagent: *Panel A* first evaporation cycle over an oven temperature of 107°C; *Panel B* second evaporation cycle at 160°C; *Panel C* first evaporation cycle on a second set of samples at 160°C. Each curve represents one of the engine oils listed in Table 3. *Inset* represents the complete progress curves. The samples tested were: *A* Exxon 10–30, *B* Castrol 5–30, *C* Havoline 10–30, *D* Quaker 10–30, *E* Penzoil 30, and *F* Valvoline 10–40

Fig. 3 Progress curves for the evaporation of water from motor oil additive packages using the Coulomat A reagent: *Panel A* first evaporation cycle over an oven temperature of 107°C, *Panel B* second evaporation cycle at 160°C, *Panel C*, first evaporation cycle on a second set of samples at 160°C. Each curve represents a motor-oil additive-package listed in Table 3. *Inset* represents the complete progress curves. The samples tested were: *G* Conostan blend 1, *H* A6933, *I* FGR, *J* Conostan blend 2, and *SRM* 1848

Zn Dithiophosphate
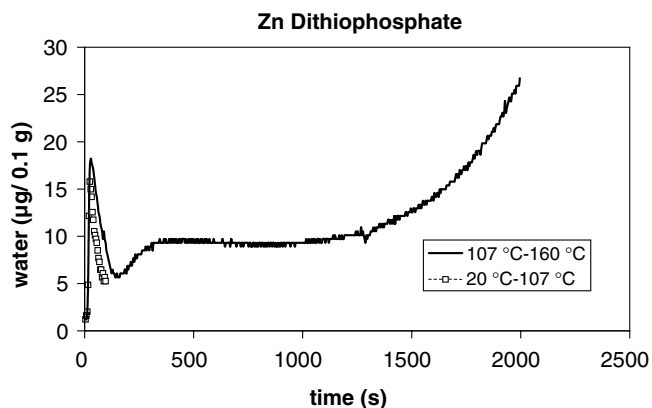
Fig. 4 Progress curves for the evaporation of water from zinc dithiophosphate using the Coulomat A reagent. Each curve represents an evaporation cycle over a different oven temparature range

with other substances in the oils, or (3) water that is formed by chemical reaction, thus inflating the measured water content. Using the method recently developed at NIST for measuring the substances in crude oils that

Fig. 5 Progress curves for the evaporation of water from motor oils using the Coulomat AK reagent: *Panel A* first evaporation cycle over an oven temperature of 107°C, *Panel B* second evaporation cycle at 160°C. Each curve represents one of the engine oils listed in Table 3. The samples tested were: *A* Exxon 10–30, *B* Castrol 5–30, *C* Havoline 10–30, *D* Quaker 10–30, *E* Penzoil 30, *F* Valvoline 10–40, and *K* FGR 7.37 w/WO
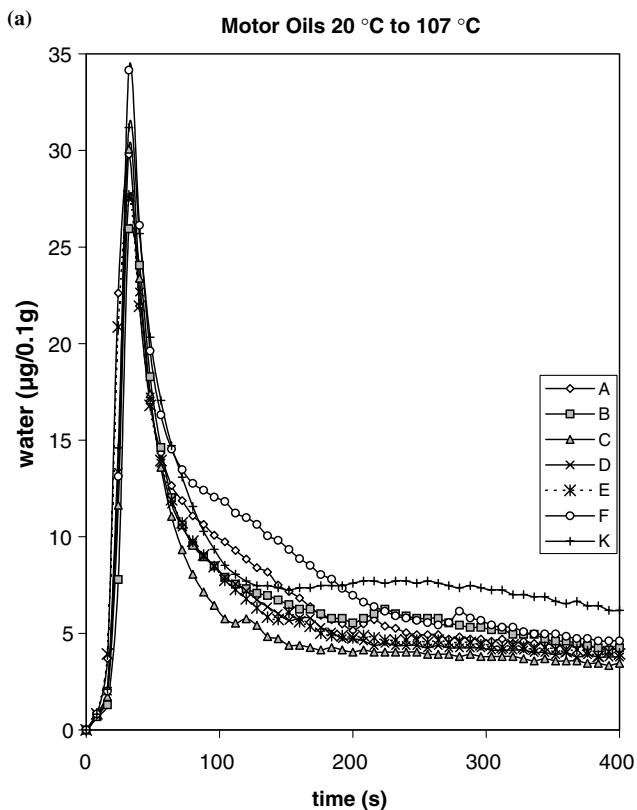
interfere with the KF reaction [7], we have demonstrated that Drakeol 35 and the SNO 850 oils do not contain levels of the interfering substances that can account for the positive bias in the water measurements [7]. This same reagent that detects interfering substances was used in the model 756 coulometer that was attached to the model 774 oven. In this manner, we measured the amount of interfering substances that evaporated from the oil at 160°C during a 5-min extraction period (i.e., a time period covering the time when the majority of the water and water-like material was volatilized). No measurable mass of interfering material was detected. It is important to note that zinc dithiophosphate decomposes at 160°C (Fig. 4) to yield one or more sulfur compounds that react with the KFR, but this oil additive does not decompose at 107°C. Furthermore, this decomposition at 160°C begins at 25 min (Fig. 4) which is after the evaporation of all of the material that is volatile at 160°C has occurred in both the motor oils and the other additive packages (Figs. 2 and 3).

A major concern is the source and nature of the non-iodine-reactive material that evaporates between 107 and 160°C. Cedergren and Lundstrum [8] hypothesized that this material is water generated by a temperature-dependent chemical reaction such as esterification. The determination of the water in the three SNO oils indicates that this may not be the case. Independent measurements indicate that substances that react with the iodine in the KFR did not evaporate into the Karl Fischer vessel and only trace amounts of interfering substances were detected by direct titration in Drakeol
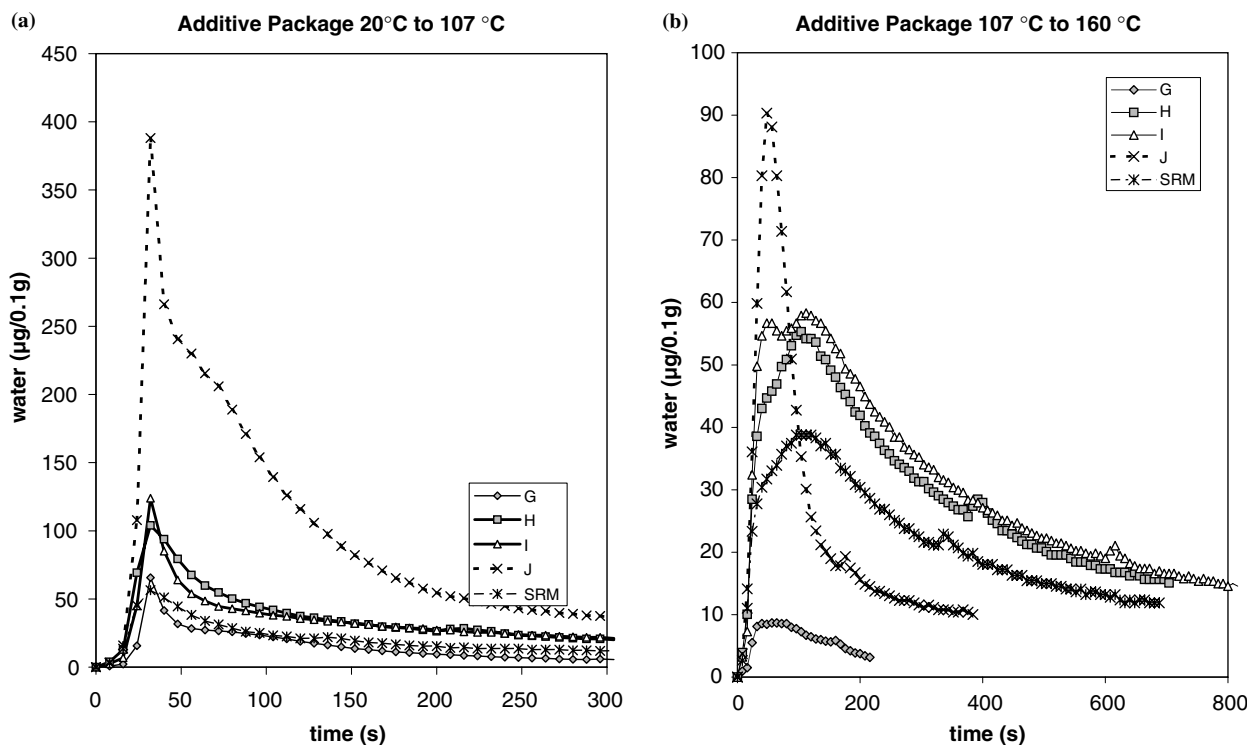
(a)

Motor Oils 20 °C to 107 °C

(b)

Motor Oil 107 °C to 160 °C
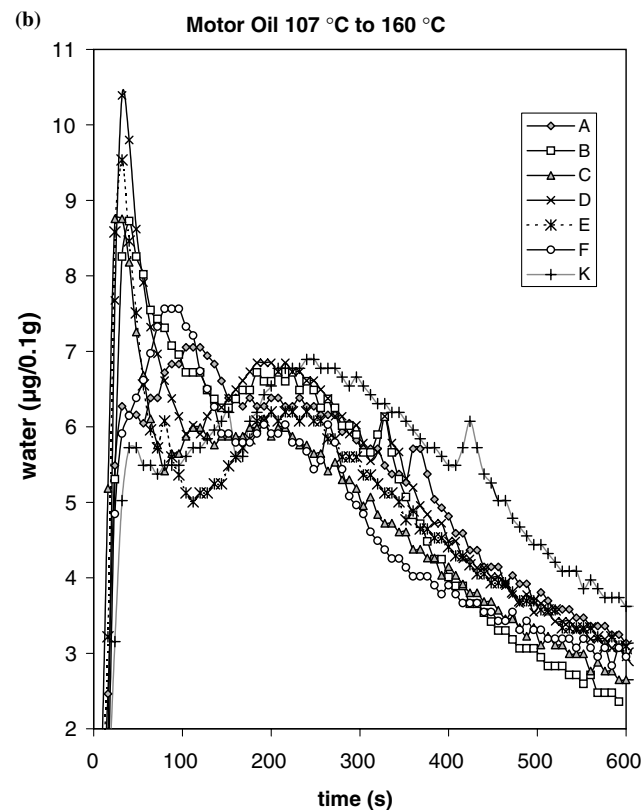
Fig. 6 Progress curves for the evaporation of water from motor oil additive packages using the Coulomat AK reagent: *Panel A* first evaporation cycle over an oven temperature of 107°C, *Panel B* second evaporation cycle at 160°C. Each curve represents a motor-oil additive-package listed in Table 3. The samples tested were: *G* Conostan blend 1, *H* A6933, *I* FGR, *J* Conostan blend 2, and *SRM* 1848

35 and SNO 850 (< 1 μg/g oil) [7]. Furthermore, the masses of the samples did not change upon heating. This indicates that significant amounts of hydrocarbons or other materials that could modify the biamperometric signal did not evaporate into the Karl Fischer vessel [6]. Finally, no KFR-reactive material was detected in the Drakeol 35 or SNO oils when the standard KFR (Coulomat A) in the model 756 coulometric detector was replaced with the aldehyde–ketone reagent (Coulomat AK). This indicates that all of the volatile material consisted of compounds other than water that reacted with the methanol in the Coulomat A to produce water [10]. This clearly demonstrates that some of the material that may be stripped from the oil at 107°C may not be water. The results obtained with the motor oils and motor oil additives were similar except for the zinc di-thiophosphate which degraded to yield sulfhydryl compounds. The other motor oil samples did not contain volatile substances that reacted with iodine. They did however contain significant amounts of material that reacted with Coulomat A but not with Coulomat AK (21–71 mass% of the amount measured at a given temperature, Table 3). The progress curves for the measurements made with Coulomat A (Figs. 2, 3, and 4) and Coulomat AK (Figs. 5 and 6) demonstrate the presence of multiple peaks and show that KFR-reactive

material was measured in samples heated to 107°C and then reheated to 160°C.

It is clear that not all of the KFR-reactive material in the oil samples is free to volatilize at either 107 or 125°C (Table 2). All of the KFR-reactive material in the oil samples may not even be volatile at 160°C. All of the material present in the cement and coal samples but none of the material that was measured in the refined oil samples was measured as water when Coulomat AK was used in the coulometer [10]. Thus, the refined oils most probably contained materials that reacted with methanol to form water, but did not react with diethyleneglycol monomethylether, the solvent used in Coulomat AK. In the case of the motor oils a mass fraction of 21–71% of the volatile materials reacted with methanol and not with diethyleneglycol monomethylether. The remaining water or water-producing material evaporated in several distinct stages (i.e., the progress curves at both temperatures for both coulometric solvents were composed of several peaks). Some of this material may be substances that react with both methanol and diethyleneglycol monomethylether to yield water. Alternatively, some of this material may be "bound" water that interacts in an aprotic manner with aromatic hydrocarbons or other hydrocarbons present in the oil. This material may also be water that is associated with micelles, forms azeotropes, or forms other physical water–lipid species whose dissociation constants and/or boiling points are higher than that for free water.

We have not tested for the possible existence of material that evaporates above 160°C. This decision was based on our concern about approaching the flash

point of some of the hydrocarbon components and of the likely formation of toxic compounds resulting from the rapid thermal decomposition of some of the components. However, these results demonstrate the existence of a significant source of material in oils that yields water by reacting with methanol or that modifies the KFR reaction which leads to a positive bias in the measurement of water in oils by the Karl Fischer method. All of the samples were weighed after each evaporation procedure was completed and the mass loss was less than 2 mg in every case except when the zinc dithiophosphate was tested. Thus, significant amounts of materials that might modify the kinetics of the KF reaction as described by Cedergren and Nordmark [6] were not volatilized. This is supported by the lack of change in the slope of the standard curves that were run after the oils samples were analyzed.

Conclusion

The data and progress curves demonstrate that the oven technique used herein can measure water, materials that yield water by chemical reaction, and materials that react with iodine that are present in motor oils and motor oil additives. Newly recognized sources of bias in this measurement have been found. Heating oil samples at 107°C produces more than one species of KFR-reactive substance as shown by the several peaks of material in the titration progress curve. Some of these substances react with methanol to form water (detectable with the Coulomat A reagent but not the Coulomat AK reagent). The process of reheating the same samples to 160°C produces similar results. Additionally, the zinc dithiophosphate additive degrades at 160°C to yield a sulfhydryl compound that reacts with iodine and causes an increase in the apparent water content. Multiple species are still observed at both temperatures even when the Coulomat AK reagent is used. This observation is consistent with the presence of compounds that react with diethyleneglycol monomethylether to yield additional water or physical structures that entrap water and prevent its evaporation.

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