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Measurement of water by oven evaporation using a novel oven design.

1. Water in water-saturated 1-octanol, coal, cement, and refined oils

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Abstract Using an automated oven evaporation technique combined with the coulometric Karl Fischer method, the mass fraction of water has been measured in cement, coal, and refined oil samples. The accuracy of this method was established by using SRM 2890, water-saturated 1-octanol that was added to white oil. The samples were analyzed for total reactive Karl Fischer reagent (KFR) material, for interfering materials, and for material that does not react with the aldehyde–ketone KFR. All of the samples yielded volatile material that reacted with the standard KFR. None of the samples contained significant masses of material that reacted with iodine. The cement and coal SRMs contained no material that reacted with methanol and very little material that did not volatilize at 107°C. The refined oils contained some material that was volatile at 107°C and some at 160°C. However, none of this material reacted with the aldehyde–ketone reagent. These results show that the material in the solid samples is water and that the material in the refined oils is a material other than water which reacts with methanol to form water.

Keywords Water · Karl Fischer · Oven evaporation · Coal · Portland cement · Solvent neutral oils

Introduction

The accurate measurement of water in insoluble samples and lubricating oils cannot be accomplished by using the

standard method of titration with Karl Fischer reagent (KFR). Coal and cement samples can contain occluded water and non-aqueous volatile substances that may or may not react with KFR. Motor oils usually contain additives that react with the KFR and cause a spurious increase in the measured water content. The usual method for measuring the water in solids such as coal and cement is to heat them in an oven to constant mass, measuring the loss in mass, and attributing it all to the loss of water [1]. This is satisfactory as long as non-aqueous volatile materials are not present in the sample.

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. Reaction with water of synthetic oils containing dibasic esters and phosphate esters can cause the formation of destructive acids. For oils that contain sulfurous additives and phenolic antioxidants, the acid byproducts resulting from the action of water can cause corrosion and excessive wear of soft metals used in bearings. Even a small amount of water can have a significant effect [2]. The measurement of water in some lubricating oils is a special problem because some of the sulfur-containing additives can react with the KFR, producing a result that is indistinguishable from that of water [3]. The water in oils can be measured by the crackle test [4], reaction with calcium hydride in a pressure chamber [4], use of a relative humidity sensor [5], or infrared spectroscopy [6, 7]. Some of these methods are not very sensitive or are only qualitative or semi-quantitative.

Tubular ovens in which the sample is heated to 105–110°C or higher have been designed to flush the evaporated moisture with a dry gas into a Karl Fischer coulometric instrument that then measures the amount of evaporated water. These ovens have a relatively large volume and are recommended for the coulometric titration of water content from 0.5 to 3.0 mg g⁻¹. When lower masses of water are measured, a significant bias is introduced by atmospheric water that enters the sample chamber when it is opened, and by the condensation

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deposited on the walls of the oven and the tubes conducting the flushing gas to the Karl Fischer apparatus [3].

Several companies distribute automated ovens that will handle multiple samples placed in bottles (≈ 10 mL) with Teflon septa that are crimped in place. The bottles are heated and the moisture is flushed with a dry gas through heated lines. This type of instrument has several advantages: it is automated; suitable calibrants, standards and blanks can be analyzed under the same conditions as the samples; the sample environment remains constant; and a sample can be analyzed every 2–15 min depending on sample size and water content. The use of the Karl Fischer coulometric instrument for measurement of water eliminates the positive bias in mass-loss studies that is introduced by non-aqueous volatile compounds. With lubricating oils it eliminates the positive bias introduced by reaction of the non-volatile additives with the KFR. This method enables the measurement of water that is removed at temperatures $\geq 100^\circ\text{C}$ as a result of chemical reactions, as azeotropes, as occluded water, or as other stable physical species that evaporate or are released at temperatures $\geq 100^\circ\text{C}$. It also enables the use of a variety of coulometric reagents that detect volatile non-aqueous materials, such as sulfides, ketones, and aldehydes, that react with the standard KFR.

The purpose of this study, the first published study using this new type of instrument, is to demonstrate the bias and accuracy of this automated method using water-saturated 1-octanol. This method was also applied to the measurement of water in solid samples, such as coal and Portland cement, and in refined oils using the standard coulometric KFR (Coulomat A) [3], the aldehyde–ketone coulometric KFR (Coulomat AK) [3], and the sulfur dioxide-free interference reagent [8].

Experimental

The Coulomat reagents were purchased from Brinkmann Instruments (Westbury, NY, USA). Coal SRM 1632c 1635, and 2684a; Portland cement SRM 1880a and 1886a; and water-saturated octanol (WSO) SRM 2890 were certified at NIST for distribution through the NIST SRM program. Direct water-mass measurements were made with a Metrohm 737 or Metrohm 756 coulometer using either a one- or two-compartment cell (Brinkmann Instruments). The reagents used for the two-compartment cell were Coulomat AG-H, Coulomat A, or Coulomat A plus a volume fraction of 30% chloroform in the anode compartment and Coulomat C in the cathode compartment. Coulomat AK in the anode compartment was used with Coulomat CK in the cathode compartment. The reagent used in the one-compartment cell was Coulomat A. Calibration materials and samples were prepared and coulometric measurements were performed as previously described [9]. For water measurements made by oven evaporation, a

Metrohm 774 Oven Sampler was connected to a Model 756 Coulometer with either a one-compartment or two-compartment cell (Brinkmann Instruments).

The titration conditions for the coulometer attached to the oven were: dynamics = 70 mV, stop drift = $20 \mu\text{g min}^{-1}$, time interval = 8 min, maximum rate of titration = $2000 \mu\text{g min}^{-1}$, extraction time = 60 s, polarization current = $10 \mu\text{A}$, minimum rate of titration = $10 \mu\text{g min}^{-1}$, start drift = $20 \mu\text{g min}^{-1}$, and end-point voltage = 30 mV. The titration data were collected using the Brinkmann Titrino Workcell software version 4.0 (Brinkmann Instruments). The oil, cement, and coal samples (total mass ≈ 30 – 250 mg) were weighed to the nearest milligram into 9-mL Brinkmann sample vials and Teflon septa were tightly crimped on to the vials. Standards were prepared by adding different amounts of WSO to crimped vials containing 2.0 mL Drakeol 35 oil (Fisher Scientific, Pittsburgh, PA, USA), after the oil samples were pre-dried in the Model 774 oven system. Calibration solutions were prepared by injecting 2–10 μL WSO [9] into the pre-dried oil through the septum. A series of measurements on empty vials and vials containing WSO-in-oil standards were performed with each experiment. In all oven studies the temperature increased at a rate of 5°s^{-1} .

The presence of interfering substances was evaluated using the sulfur dioxide free reagent (containing no xylene) in the coulometric cell attached to the oven [8, 10, 11]. When measuring the interfering substances, the oil samples were heated in the oven at 160°C with a 5 min extraction period. The coulometric reagent for measuring the interferences was reagent 1 [8]; the measurement conditions were the same as those previously described [8]. All of the determinations reported in the tables have been corrected for the water–mass blank contributed by the atmosphere trapped in the sealed vial. The curves illustrated in Figs. 2, 3, and 4 have not been corrected for the blank values that are illustrated in Fig. 1.

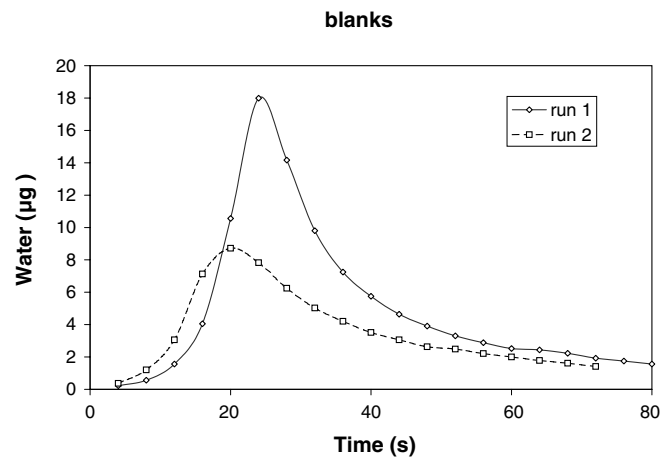


Fig. 1 Progress curves for the titration of atmospheric water in blank vials. Each curve represents an evaporation cycle over an oven temperature range of 20– 107°C

Safety considerations All KFR 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 regard 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 measurement of water in some materials cannot be performed by direct addition to the KFR. These materials may contain substances that modify the response to the KFR either by modifying its pH [3], by reacting with one or more of its components [8], or by modifying its polarity and changing its sensitivity to water [11]. Some materials also contain occluded water that is not accessible to the Karl Fischer reagent. The oven sampling apparatus provides an alternative method for measuring the mass of water in these types of sample. Non-automated tubular ovens have been used previously for these types of measurement. However, these tubular ovens have large volumes (several hundred milliliters), often their transfer lines are not heated, and they must be opened after each sample is analyzed. The new automated oven-evaporation instruments that incorporate a carousel eliminate these limitations. Each sample is placed in a small glass container (≈ 9 mL) with a Teflon septum. Empty vials can be analyzed to correct for the relatively constant but significant mass of atmospheric water trapped in the vials or trace levels of water present in the sparging gas. The transfer lines are heated to minimize condensation. Also, the carousels hold between 24 and 35 samples which are analyzed automatically.

Instrument calibration

Before any method can be used it must be calibrated. Table 1 illustrates the calibration (accuracy and linearity) of the Karl Fischer coulometric method with SRM 2890, WSO which was certified to contain a water concentration of 39.24 ± 0.85 mg mL⁻¹. The accuracy of the Karl Fischer method, using the Model 756 coulometer to which the Model 774 oven was connected, was compared with results obtained with the Model 737 coulometer which was used to certify SRM 2890 [9]. Samples having volumes 1, 2, 4, 6, 8, 10, 20, and 30 μ L of SRM 2890 were analyzed using three different KFR and either a one- and two-compartment cell. All plots of the sample volume vs. water mass were linear ($R^2 > 0.999$), the intercepts were close to zero indicating that the bias was small, and the measured water-mass concentration (slope) in SRM 2890 was within the certified value of 39.24 ± 0.85 mg mL⁻¹ [9]. Thus under all test conditions the responses are linear and accurate over the range of 39–1177 μ g water, the range over which all water determinations were made.

When the Model 756 coulometer was connected to the Model 774 oven, the performance of the coulometric measurement decreased (see Table 1 without oven vs. Table 2 with oven). Specifically, the slope of the response of the instrument to increasing masses of water added to a dried Drakeol 35 matrix was more variable and the intercept increased by a relatively large mass. In these studies 1, 2, 4, 6, 8, or 10 μ L WSO was added to 2 mL of dried white oil (Drakeol 35). Initial studies in which we tried to deposit 2–10 μ L quantities of WSO into empty crimped vials gave highly variable results. This was probably because of a variable amount of sample (1–2 μ L of sample) remaining on the tip of the syringe. Depositing the WSO standard in dry white oil gave more consistent results (Table 2). It also ensured that the WSO sample was deposited more consistently into the vial and simulated as closely as possible the evaporation of the water from a known matrix.

In these measurements on WSO, a positive bias was observed that was attributed to the atmospheric moisture that was introduced into the 9-mL vial when the vial was initially capped. This bias was identified by determining the mass of water in a series of empty vials to be 87 μ g (SD = 1.6 μ g of water, $n = 20$). However, this value

Table 1 Results of measurements of mass concentration of water in WSO obtained by using various coulometric instruments and reagents

| Sample | Instrument model | Cell type | Coulomat reagent | Water | | R^2 | n |
|--------|------------------|-------------|------------------------|--|--|-------|-----|
| | | | | Slope ^a c (water) (mg mL ⁻¹) | Intercept ^a m (water) (μ g) | | |
| WSO | 737 | Membrane | A + 30 vol% chloroform | 38.15 | 2.68 | 0.999 | 18 |
| WSO | 737 | No membrane | AG-H | 39.86 | -3.07 | 0.999 | 12 |
| WSO | 756 | No membrane | A | 39.50 | -0.45 | 0.999 | 10 |

R^2 regression coefficient, n number of WSO samples measured

^a c (water) the mass concentration of water, m (water) the mass of water. Certified value of water in WSO = 39.24 ± 0.85 mg mL⁻¹

Table 2 Results of measurements of water in matrix standards containing different masses of WSO added to 2 mL Drakeol 35 oil in experiments measuring water in different oils

| Sample oven temperature ^a | Water | | R^2 | n |
|--------------------------------------|---|--|-------|-----|
| | Slope ^b c (water; mg mL ⁻¹) | Intercept ^b m (water; μ g) | | |
| Experiment 1. Drakeol 35 | | | | |
| WSO 107 °C | 46.77 | 76.03 | 0.996 | 11 |
| WSO 160 °C | 40.67 | 77.71 | 0.994 | 11 |
| WSO 160 °C | 39.65 | 68.99 | 0.995 | 11 |
| Experiment 2. SRM 1848 | | | | |
| WSO 107 °C | 37.51 | 60.38 | 0.994 | 10 |
| WSO 125 °C | 37.85 | 65.21 | 0.991 | 10 |
| WSO 160 °C | 40.01 | 73.76 | 0.998 | 10 |
| Experiment 3. Motor oils | | | | |
| WSO 107 °C | 42.23 | 74.29 | 0.991 | 11 |
| WSO 125 °C | 44.61 | 75.65 | 0.991 | 11 |
| WSO 160 °C | 42.70 | 59.38 | 0.967 | 11 |

R^2 regression coefficient, n number of WSO samples measured

^aMeasurement conditions: instrument model 756+774, Cell type no membrane, Reagent Coulomat A

^b c (water) the mass concentration of water, m (water) the mass of water. Certified value of water in WSO = 39.24 ± 0.85 mg mL⁻¹

Table 3 Results of analysis of water in solid samples

| Sample | Heating at 107°C | | | | Heating at 160°C | | | |
|-----------------|--------------------------------------|------------------------|-------|-----|--------------------------------------|------------------------|-------|-----|
| | Water | | R^2 | n | Water | | R^2 | n |
| | Slope (mass; mg g ⁻¹) | Intercept mass (mg) | | | Slope (mass; mg g ⁻¹) | Intercept mass (mg) | | |
| Coal | | | | | | | | |
| SRM 1632c | 19.935 | 0.034 | 0.999 | 3 | 21.114 | 0.050 | 0.998 | 7 |
| SRM 1635 | 168.915 | 0.037 | 0.999 | 3 | 166.157 | 0.016 | 0.999 | 7 |
| SRM 2584 | 33.105 | 0.035 | 0.999 | 3 | 35.084 | 0.038 | 0.997 | 7 |
| Portland cement | | | | | | | | |
| SRM 1880a | 4.118 | 0.065 | 0.998 | 3 | 4.109 | 0.063 | 0.999 | 7 |
| SRM 1886a | 4.587 | 0.066 | 0.998 | 3 | 4.742 | 0.062 | 0.997 | 7 |

R^2 regression coefficient, n number of samples measured from a single bottle

is subject to some variation associated with the daily variation in the relative humidity. Repetition of this measurement on the same set of vials yielded 54 μ g of water (SD 7.7 μ g, $n = 20$). These results are caused either by water that is present in the carrier gas that remained in the vial or water accumulated on the needle while it was exposed to the air during the process of transfer from the conditioning vial to the sample vial.

These sources of bias are independent of the temperature to which the vial is heated in the oven. This is demonstrated by the relative consistency of the intercepts of the WSO standard regression lines of the sample volume vs. water that were run as calibrants for various water-in-oil studies at various temperatures (Table 2). These intercepts are also independent of the length of the extraction period (1 and 5 min extractions yield the same values). All values reported in Tables 3 and 4 have been corrected for the bias calculated from the value of the intercept. The source of the variation observed in the slopes of the WSO regression lines of the sample volume vs. water is not dependent on the 756 coulometer and

appears to be attributable to the combination of the oven and coulometer. These sources of error limit the accuracy of the measurement, particularly for samples containing small masses of water.

Measurement of water in solid samples

Insoluble materials such as coals and cement must be heated to release any occluded water that might be difficult to measure by direct titration in the KFR. The oven method also provides an alternate method for measurement of water in the presence of other volatile substances that might be released upon heating the sample to constant mass but do not react with the KFR [1]. Coal and cement samples of increasing mass (30–240 mg) were used to assess the linearity of the evaporation of the water from the sample and to measure the positive bias resulting from the atmospheric water as described above. The mass of the samples was dependent on the mass of water in the sample and for any given

Table 4 Results of analysis of water in oils with no additives

| Sample | Water (mg kg ⁻¹) | | | | | | | | | |
|------------|------------------------------|----|-------------------------|----|--------------------------|----|-------------------|----|------------------------------|----|
| | 774 oven with 756 coulometer | | | | | | | | 737 coulometer membrane cell | |
| | 20–107°C (Column A) | | 107–160°C (Column B) | | Sum of column (A + B) | | 20–160°C | | | |
| | Mean ^a | SD | Mean ^a | SD | Mean ^a | SD | Mean ^a | SD | Mean ^a | SD |
| Polyol | | | | | | | 641 | 15 | 582 ^b | 10 |
| Drakeol 35 | 30 | 17 | ND | | 30 | 17 | 32 | 3 | 30 ^c | 4 |
| SNO 450 | 16 | 6 | 60 | 9 | 76 | 7 | 88 | 9 | 41 ^d | 3 |
| SNO 600 | 28 | 3 | ND | | 28 | 3 | 63 | 9 | 52 ^d | 6 |
| SNO 850 | 0 | | 159 | 20 | 159 | 20 | 182 | 35 | 56 ^d | 8 |

ND none detected

^an = 4^bAnode reagent = Coulomat A^cAnode reagent = Coulomat A + 30% chloroform^dAnode reagent = Coulomat AG-H

coal or cement sample the masses fell within a fivefold range of the lowest mass. Table 3 summarizes the results obtained for several coal and Portland cement SRM. All samples were at room temperature before they were inserted into the oven and heated to the temperature of the oven. One set of samples was heated from 20 to 107°C. A second set of samples was heated from 20 to 160°C. This enabled measurement of the effect of temperature on the completeness of the evaporation of the free water. The results demonstrate that nearly all of the available water was removed at 107°C and that the small additional mass measured at the higher temperature might be occluded water. The water in the coal samples has been independently measured by heating the samples at 107°C to constant mass by Mann et al. [1] and the measurements in Table 3 agree with these measurements. Thus, all of the volatile material removed from these coal samples by heating to a constant mass represents water and not other volatile materials.

The absence of non-aqueous materials that interfere with the Karl Fischer method was confirmed by substituting the reagent used for measuring interfering substances described by Margolis et al. [8] for the Coulomat A reagent in the coulometer. The samples were extracted for 5 min to ensure that all possible volatile interfering materials were removed; none was detected. Also no substances that generated water by reacting with methanol were detected by the Coulomat AK Reagent. Thus all of the material that was measured was volatile water. Portland cement contains approximately 0.01 mass fraction CaO (free lime) which can react with water to form Ca(OH)₂. However, Ca(OH)₂ decomposes to CaO at 580°C, thus none of the water measured at 160°C arises from the decomposition of any Ca(OH)₂ that might be present in the cement samples.

Measurement of water in white oil and in solvent-neutral oils (SNO)

Some oils such as motor oils and other lubricants contain a variety of additives that may or may not form

volatile substances that interfere with the Karl Fischer reaction [3]. Some oils contain a small amount of these interfering substances and others, such as sour crude oil, contain relatively large amounts of substances that increase the apparent water mass concentration when added directly to the coulometric titration vessel [8]. This oven method provides a procedure for measuring water in those materials that contain both volatile and non-volatile substances that interfere with the Karl Fischer reaction. For this reason it is necessary to establish the performance of this measurement technique with oils that contain little or no non-aqueous material (< 2 water-mass equivalents) [8] that reacts with the iodine in the KFR. (A *water mass equivalent* is the mass of a non-aqueous material that reacts with iodine in the Karl Fischer method and corresponds to a mass of water reacting with an equivalent amount of iodine, see Ref. [8].)

Because the Drakeol 35 oil and the SNO oils have been shown to contain very small amounts of these interfering substances [8], these oils were used to demonstrate that water can be measured in oil by this oven method (Table 4). Each analysis included a calibration curve of WSO (range of total water mass = 78–392 µg). The volume of the oil samples varied from ≈0.5–≈2.0 mL. In each case the mass of water was proportional to the mass of the oil sample. The response curves were linear and the regression coefficients (*R*²) were greater than 0.995. This study was designed to measure the mass of water released between 20 and 107 °C (Fig. 2) and any additional KFR-reactive material that might be released from the same sample between 107 and 160°C (Fig. 3). A second set of samples was heated only from 20 to 160°C (Fig. 4). The water in a third set of samples (Drakeol 35 and SNO oils) was measured by the standard method of direct addition of the oil into the coulometric reagent. It is important to keep in mind that the curves in Figs. 2, 3 and 4 have been normalized to 1.7 g (≈2 mL) sample and have not been corrected for the atmospheric water as illustrated in Fig. 1.

It is clear from Table 4 and Figs. 2 and 3 that in Drakeol 35 and SNO 600 oils material that reacted with

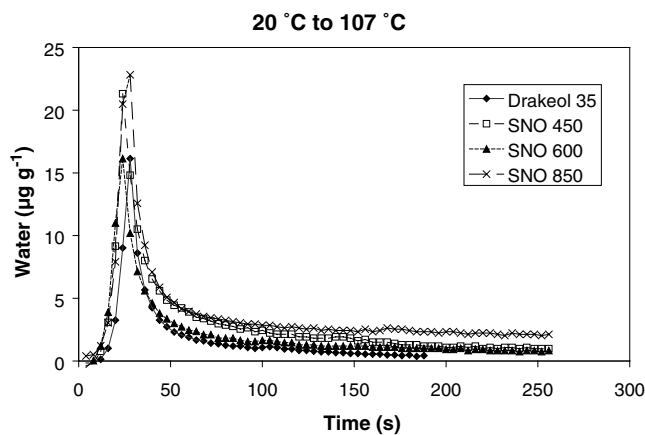


Fig. 2 Progress curves for evaporation of water from Drakeol 35 and SNO oils. Each curve represents an evaporation cycle over an oven temperature range of 20–107°C. These curves are normalized to 1.7 g oil, but are not corrected for the blank value in Fig. 1

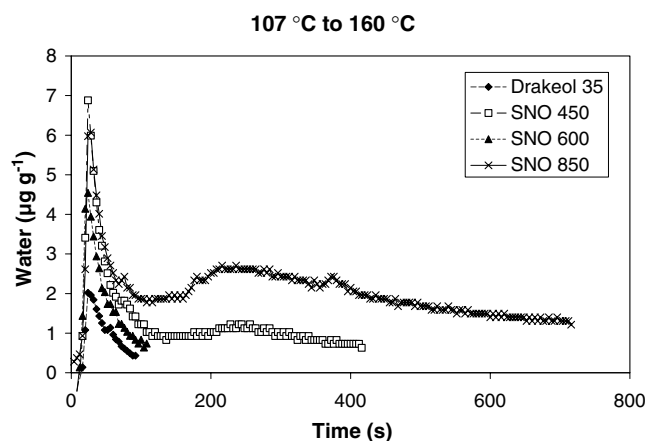


Fig. 3 Progress curves for evaporation of water from Drakeol 35 and SNO oils. Each curve represents an evaporation cycle over an oven temperature range of 107–160°C. These curves are normalized to 1.7 g oil, but are not corrected for the blank value in Fig. 1

KFR evaporated between 20 and 107°C and no additional material was removed by subsequently heating the same set of samples to 160°C (Table 4, 107–160°C). SNO 450 released KFR-reacting material at both 107°C and between 107 and 160°C, and SNO 850 released KFR-reacting material only between 107 and 160°C. With the exception of Drakeol 35 oil, additional material was also released when a second set of oil samples was heated from 20 to 160°C and more material was measured by the oven method than by direct addition of the sample to the KFR. For Drakeol 35 oil the mass of material measured as water by heating one set of samples from 20 to 107°C or a second set of samples from 20 to 160°C was very similar to that measured by direct addition of the sample to the KFR. It is evident from Fig. 3 that additional water-like material evaporated from SNO 450 and SNO 850 after the sample had

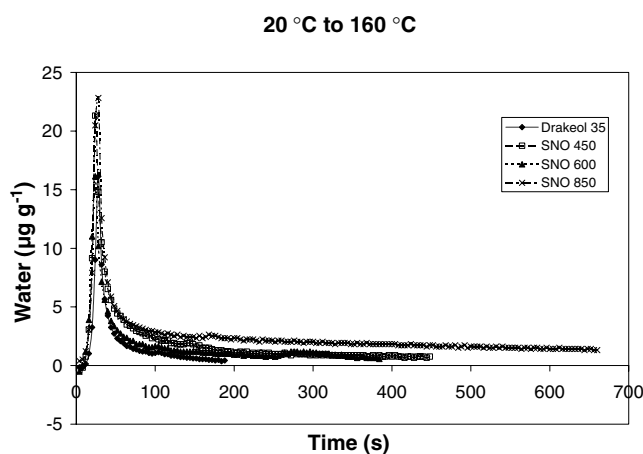


Fig. 4 Progress curves for evaporation of water from Drakeol 35 and SNO oils. Each curve represents the first evaporation cycle of a second set of samples over an oven temperature range of 20–160°C. The *insert* represents the expansion of the progress curves. These curves are normalized to 1.7 g oil, but are not corrected for the blank value in Fig. 1

been heated for about 3 min. The evaporation of this additional material is also observed at 160°C (Fig. 4). However, at 160°C this additional water-like material has partially merged with the initial peak. Another peak of material was observed evaporating from SNO 600 at about 260 s; this represents the additional water-like material in Table 4 that evaporated when the sample was heated from 20 to 160°C.

Reaction of a substance that is volatile at 107°C or higher with the coulometric KFR (Coulomat A) does not prove that it is water. It might be a reducing substance or any other substance that reacts directly with iodine yielding the same endpoint product and increasing the apparent water content. Alternatively, this volatile substance might be a low-boiling aldehyde, ketone, acid, amine, or siloxane that reacts with methanol forming water. By replacing the standard KFR in the coulometer used with the oven with a sulfur dioxide-free reagent [8], we tested the oils and the solid samples for substances that are volatile below 160°C and that react with iodine. None was detected.

In another series of experiments the standard KFR was replaced with Coulomat CK and AK using a two-compartment cell. The solid samples yielded the same mass-concentration of water as the Coulomat A KFR at both temperatures and no water was measured in any of the oil samples at either 107 or 160°C. In this series of experiments the curve for the WSO external standards (2–10 µL) added to a Drakeol 35 oil matrix was linear and accurate (slope = 39.23 mg mL⁻¹, intercept = 27.975 µg, $R^2 = 0.987$) and the atmospheric water in the sample was 90 µg, SD 5 µg. The maximum sample size was 2.1–2.3 mg and was large enough to detect water if it was present in the samples shown in Table 4.

These results clearly indicate that the material present in these four oil samples reacts with the standard KFR

either directly when added to the titration cell, or indirectly when evaporated into the titration cell. It does not react with iodine or iodide, and it does not react with demonstrably active ketone–aldehyde reagent when evaporated into the titration vessel. Thus the material detected by the standard KFR (Coulomat A) seems to be water generated by chemical reaction of volatile materials with the KFR, but does not appear to be free water. The absence of any significant change in the sample mass demonstrates that very little of the oil sample is vaporized and eliminates the possibility that addition of hydrocarbons is modifying the reagent in the titration vessel. This excludes the possibility of the oil altering the properties of the Karl Fischer reaction as suggested by Cedergren and Lundstrom [10]. The relatively low vaporization temperature indicates that the material has a relatively low molecular mass and might be a low-boiling aldehyde, ketone, acid, amine, or siloxane that reacts with methanol forming water, but does not react with diethyleneglycol monomethylether [3]. The exact nature of this material remains unknown and headspace-GC–MS analysis of the volatile material might assist in the identification of this material.

Conclusion

The data and progress curves demonstrate that the oven technique described herein can measure the mass-concentration of water in solids and oils. The water in the coal and Portland cement samples evaporated as a single entity. However, the materials in the oils clearly did not evaporate as a single entity but as multiple entities and at different temperatures as seen in the progress curves. This provides clear evidence that the volatile material in oils that reacts with the KFR is not present as a single

entity. Samples evaluated by the NIST interference assay [8] did not contain, or degrade to, volatile materials that reacted with a sulfur dioxide-free reagent similar to the KFR. In the solid samples the same amount of water was measured with both the Coulomat A and Coulomat AK KFR. However, all of the substances in the refined oils only (not the solid samples) that reacted with the standard KFR (Coulomat A) did not react with the aldehyde–ketone reagent (Coulomat AK). Thus the material measured in the solid samples was most probably water whereas the material in the oils that reacted with the Coulomat A KFR was probably not water, but substances that generate water in the Coulomat A reagent by reacting with methanol.

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