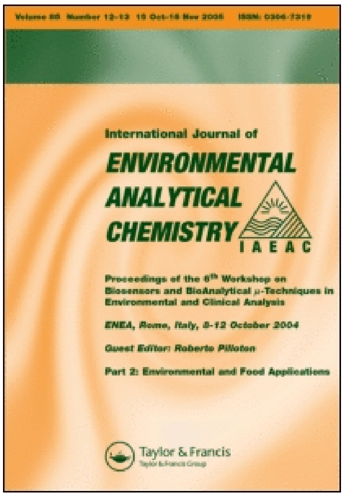

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T. H. Gouw[a]; K. K. Torres[a]; A. J. Ricciardelli[a]
[a] Chevron Research Company, Richmond, California, U.S.A.

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The Modified Oven Drying Technique: A New Method to Determine Oil, Water, and Solids in Oily Waste

T. H. GOUW, K. K. TORRES and A. J. RICCIARDELLI
Chevron Research Company, Richmond, California 94802-0627, U.S.A.

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In processing an oily waste, it is essential to know the relative amounts of water, oil, and solids present. In this method the sample is heated to 110–120°C at about 40 mm Hg absolute in a closed container to drive off moisture and light hydrocarbons into a cold trap. The residue is extracted in a Soxhlet to recover the heavy oils from the solids. Simulated distillation shows that the recovered oil is similar to the original oil in the sample. Relative standard deviations by this method are three to six times better than by the Environmental Protection Agency (EPA)-approved Total Oil and Grease Method.

INTRODUCTION

Oily waste is generally a very complex material. Because of regulatory constraints, characterization is usually directed towards the quantitative determination of specific components in the sample. For process engineering purposes, however, and especially in the development of waste treatment methods, it is necessary to know the relative amounts of oil, solids, and water in the product. Characterization of refinery waste for the Resource Conservation and Recovery Act (RCRA), Part B, waste analysis plans, also requires knowledge of the oil, water, and solids composition of the material.

Most of the methods in current use have serious drawbacks. In general, only two phases are determined and the third phase is calculated by difference. We have recently developed a new and improved procedure called the Modified Oven Drying Technique (MODT) which obviates the most obvious problems and is applicable to a wide variety of waste products. It is now used routinely by us and by several contract laboratories doing waste analysis. An important advantage is that all three phases are recovered separately. This allows for a weight closure check on the analysis; each of the phases can also be subjected to additional analysis and further characterization.

The purpose of this study is to determine the accuracy and the reproducibility of this new method as a function of the composition of the sample. For comparative purposes, several samples have also been analyzed by the Oil and Grease Method.[1]

Other methods

The amount of *water* in oily waste has been determined by: (1) drying the material in an oven and assuming the weight loss to be water, (2) by azeotropic distillation according to ASTM Method[2] D95, or (3) by dissolving the non-solids in a solvent such as tetrahydrofuran (THF) and then using Karl-Fischer titration to determine the water contents.[3] In other methods, the amount of water is calculated as the difference after the direct determination of the oil and solids contents of the sample.

In the standard oven drying step, there is no control on whether all of the water has been removed. Light hydrocarbons will also be lost in this process. The resultant weight loss is thus incorrectly attributed as water content. Splattering during the drying process is also quite common, resulting in further unaccounted loss of material.

In this respect, the ASTM D 95 Method is substantially superior. But since an aromatic solvent is now added to the sample, the oil content has to be determined by other means or by difference.

The amount of *oil* in the sample is conventionally determined by solvent extraction in a Soxhlet apparatus using a Freon or a chlorinated hydrocarbon. The solvent is then removed by distillation, leaving the oil behind as residue. This method is generally not applicable to wet samples. The water forms a barrier which reduces accessibility of the solvent to the oil in the solids matrix. This problem can be circumvented by grinding the sample with a drying agent, such as $CaCl_2$ or $MgSO_4$, prior to extraction.

There are other caveats. A low molecular weight (MW) solvent, such as Freon 113, does not always dissolve all the organic constituents in the sample, especially if they are waxy in nature. With a higher MW solvent, some light solutes can be lost during the solvent removal step unless a high efficiency fractionating column is used.

The amount of *solids* is usually determined directly as the residue from the Soxhlet extraction except in methods where a drying agent is used. In the latter case, the amount of solids may have to be calculated as the difference after direct determination of the water and oil contents.

Applicability of the ASTM D 96 Method to waste samples is limited. Our experience shows that this method often underestimates the amount of water present. With actual waste samples, it is not uncommon to observe four and sometimes five different phases in the centrifuge. Heavy residual oils are often strongly attached to the solids matrix; they cannot be separated by ordinary centrifugation. Porous solids will have entrapped air which reduces its bulk density to unity or less, making centrifugation useless as a separation tool.

An interesting method is to use a Dean and Stark modified Soxhlet for the extraction step. The condenser section of a standard Soxhlet apparatus is modified to trap out the water from the distillate before allowing the reflux to enter the extraction chamber. The typical Dean and Stark head is depicted in ASTM Method D 95.[4] In this method, extraction is carried out overnight with, e.g., dichloromethane. Water azeotropes over and is collected in the Dean and Stark trap, the oily phase dissolves in the solvent and collects in the reboiler, and the residual solids stay behind in the thimble.

For certain sample types, this method is very useful. A drawback is that light hydrocarbons are lost in this process. In many samples, water removal is very slow; dissolution of the oil in the solvent is retarded by the water barrier.

EXPERIMENTAL

Oil and grease method

In this EPA-approved Extraction Method for Total Oil and Grease (OGM), a 20-g sample of the oily waste is first acidified to pH = 2 and then intimately mixed with 25 g of $MgSO_4 . H_2O$. The mixture is ground in a mortar, and the "dried" paste is then extracted with 300 ml of Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane; boiling point 47.6°C) in a standard glass Soxhlet extractor. The Freon is subsequently evaporated in a glass rotary evaporator, and the residual oil is weighed and considered to be the oil in the sample.

The water content is determined by a standard evaporation method, which consists of drying a 2-g sample in an oven for two hours at 105°C. The weight loss is assumed to be from the water in the sample. The amount of solids in the sample is calculated by difference.

THE MODT

a. Oven drying

A schematic diagram of the equipment is shown in Figure 1. In a well-equipped laboratory, this equipment can be assembled for a few hundred dollars. The heart of the system is the modified oven, which consists of two sections. The bottom part is a flat-bottomed glass tube, 50 mm ID and about 18 cm high, which fits the top part, also 50 mm ID and about 5 cm tall, using a standard O-ring seal. Ground glass joints were used in the original version, but we had trouble opening the seals after the oven drying step. We call this part a "modified oven" because it is different in appearance from a conventional laboratory oven.

Standard Whatman cellulose single-thickness extraction thimbles are first dried at 105°C in a conventional laboratory oven overnight and stored in a desiccator. About 25 g of the thoroughly mixed sample are now weighed in a tared thimble and placed in the bottom section of the modified glass oven. A small hole is drilled in the bottom of a second thimble, which is then slipped in the inverted position into the first thimble. The second thimble prevents loss of material by splattering during the drying process. The two parts of the oven are then clamped together with a standard C clamp.

The trend in analytical chemistry is to go to vanishingly small sample sizes. In waste analysis, it is difficult to obtain a small sample which is representative; 20–30 ml are generally adequate to ensure absence of concern on this point.

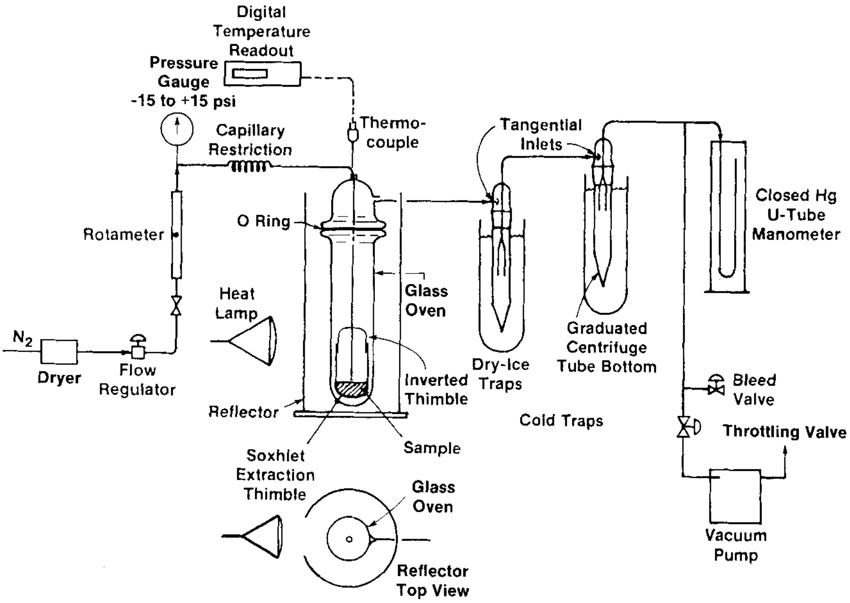

FIGURE 1 Schematic diagram of Modified Oven Drying Technique assembly. The heart of the system is the glass oven heated by an infrared heat lamp.

The other connections are then secured, and the traps are immersed in acetone-dry ice baths. These traps are 100-ml Pyrex centrifuge tubes annealed to 29/42 ground glass joints. The top of the traps has the outlet coming out from the middle. The inlet is mounted at a tangent to induce a rotating flow pattern in the tube to increase trapping efficiency of condensed particles.

The system pressure is then adjusted to around 40 mm Hg (0.8 psia) with the nitrogen flowing at about 15 ml STP/min. Some mechanical vacuum pumps will run hot if operated above ~20 mm Hg, in which case a restriction, such as a needle valve, should be mounted at the inlet of the pump to create a pressure drop. The simplest control is by an air bleed through a needle valve since accurate pressure control is not necessary.

The nitrogen flow rate is adjusted with the regulator mounted after the drier and read of the rotameter. The 10-ft × 0.01-in. capillary restriction is designed to create a pressure drop between the nitrogen source and the system proper.

The outlet of the nitrogen line is about halfway down the bottom part of the oven. The thermocouple tip touches the sample in the thimble.

The reflector is an aluminium plate rolled and bent in the form of a tube with a diameter of about 18 cm and with an open seam, about 14 cm wide, parallel to the axis. This reflector is about 45 cm high. A standard 250-watt infrared heat lamp is used for heating.

The sample is now slowly heated to 110–115°C. The temperature is adjusted by simply moving the heat lamp closer or away from the glass oven. The water and light hydrocarbons evolved in this process are collected in the cold traps. At first some water will condense in the top, colder sections of the oven, but the purge gas will soon evaporate and remove all visible drops of liquid. This is a good visual check to determine whether all water has been removed.

The operational pressure of around 40 mm Hg has been found to be the most convenient to remove the water. The vapor pressure of water is around 13 mm Hg at room temperature. Even though the sample temperature will reach 110–120°C, the partial pressure of water around the sample can be very low, especially at the end of the run when there is just a small amount of residual moisture left. At higher pressures, there is more condensation in the transfer lines and heating of the lines may be required. At lower pressures, gas velocities become higher and trapping efficiencies will be impaired.

This drying step can take from one to eight hours. For most samples, two to three hours are adequate. At the end of the run, when nothing more is observed to distill over, the system is allowed to return to atmospheric pressure. After capping off the openings, the traps are removed and stored in a refrigerator set at 0 to 5°C.

b. Recovery of heavy oil

The bottom thimble is now removed and placed in a standard glass Soxhlet extractor. The oven and top thimble are rinsed with dichloromethane, and the solution is poured through the bottom thimble into the 500-ml round-bottomed flask of the extractor. A squirt bottle is recommended to ensure that all oil and solids in the top thimble are rinsed off. Confirmation is by a careful, visual check. Additional dichloromethane is added to bring the volume to around 400 ml.

With very waxy oils, chloroform or even carbon tetrachloride can be used instead. Extraction is usually carried out for at least four hours and preferably overnight. The tests described in this paper were carried out with dichloromethane.

After the extraction step, the solution is transferred to a glass rotary evaporator where the solvent is removed under a slight nitrogen bleed. Since all the light hydrocarbons have already been recovered in the oven drying step, solvent removal can be performed without concern for possible losses of oil. The recovered oil is weighed and saved.

The use of a heavier solvent such as carbon tetrachloride will necessitate more drastic steps to recover the oil from solution without loss of light ends. We recommend fractional distillation through a short column under a slight vacuum with a very small nitrogen bleed through the sample.

Even with a light solvent such as dichloromethane, care is necessary to remove all traces of this solvent without loss of oil. We use gas chromatography to determine the residual amount of solvent to correct for the recovered oil weight. This step is not routinely performed. The amount of oil recovered in this step can also be calculated as the difference between the gross weight of the unextracted solids after the oven drying step less the weight of the recovered solids.

The thimble containing the dried solids is then weighed to determine the amount of solids recovered. To ascertain whether these solids still contain residual oil, we can subject a sample to thermal gravimetric analysis (TGA).

An alternative to the Soxhlet extraction step is to subject the dehydrated and homogenized sample directly to TGA. A drawback in this case is that no actual oil is recovered for other analytical tests.

c. Recovery of water and light hydrocarbons

Oil and water will have condensed in the traps in a solid matrix. Placing the traps in a refrigerator set at 0 to 5°C allows the ice to melt, and a mixture of oil and water will be observed. If excessive amounts of material are observed on the walls of the vessel, the lower portions of the traps can be centrifuged to force the material into the bottom of the tube. This is usually not necessary. The interface between the two layers should be clear. There are no high molecular weight and/or polar compounds to create emulsions.

The traps are now placed in a freezer set between −20 to −25°C. The water will slowly freeze and during this process eject any hydrocarbons from the solid ice matrix. This process is allowed to take place overnight. The hydrocarbons collect as a liquid layer above the ice; they are recovered by pouring the liquid into another container or by using a syringe equipped with a long needle to transfer out the hydrocarbon layer. These hydrocarbons can be analyzed separately or blended with the heavier oils recovered earlier.

d. Processing time requirement

We have set up five modified oven assemblies and five Soxhlet extractors in our laboratory. A technician working full-time can process five samples a day. Elapsed time per sample is two to three days. To process the same number of samples by the OGM requires about the same amount of time.

Samples and analyses

Samples were prepared by thoroughly mixing deionized water, oil, and soil. The oil was either a refinery sidecut or a blend of sidecuts with a distillation bottom. The blend had an initial boiling point of around 95°C, a 50% point distilled off at around 315°C, and a 95% point distilled off at 540°C. The soil was from landfarm samples which had been dried and extracted with CH_2Cl_2 but had subsequently picked up about 3% moisture. The true values were determined by correcting for this amount of moisture.

Samples were prepared to simulate landfarm soil (Sample A), API separator sludge (Sample B), and unleaded tank bottoms (Sample C). Five synthetic blends were also prepared with varying amounts of the three components (Samples D–H). Four samples were prepared with the same water, oil, and solids composition, but with oils of a different boiling range (Samples T2–T5).

Tables I and II show the composition of the samples tested in this study. The boiling ranges of the cuts are included in Table II.

The three samples resembling refinery waste (A–C) were each

TABLE I

Corrected synthetic sample composition for MODT evaluation study

Sample I.D.	Sample composition Wt % Oil	 Wt % Water	 Wt % Solids
A	7.9	14.8	77.2
B	16.7	75.2	8.1
C	30.0	31.1	38.9
D	49.1	26.1	24.8
E	40.1	50.2	9.7
F	60.3	20.3	19.4
G	53.4	26.6	20.0
H	25.2	60.3	14.5
T2	10.0	10.0	80.0
T3	10.0	10.0	80.0
T4	10.0	10.0	80.0
T5	10.0	10.0	80.0

TABLE II

Oil composition in synthetic sample blends

Sample I.D.	Sidecut no. 1	 2	 3	 4	 5	345°C+, Wt %
A–H, Wt %	20	0	24	0	28	28
T2, Wt %	0	100	0	0	0	0
T3, Wt %	0	0	100	0	0	0
T4, Wt %	0	0	0	100	0	0
T5, Wt %	0	0	0	0	100	0
Boiling range, ASTM D 2887						
IBP, °C	97	150	132	121	159	
10%, °C	128	186	225	243	279	
30%, °C	139	202	258	284	324	
50%, °C	179	249	313	363	429	
70%, °C	202	266	328	382	448	
90%, °C	228	282	348	404	477	
FBP, °C	281	336	407	452	543	

analyzed three times by both the MODT and the OGM. The set of five samples (D–H) and the set of four samples (T2–T5) were analyzed once by the MODT, except for Sample H which was analyzed twice.

RESULTS AND DISCUSSION

Analytical test results are shown in Table III. Since in the OGM the amount of solids is calculated as difference, the sum of the three constituents is always 100%. In the MODT, the amount of each phase is determined separately; hence, workup losses are reflected in the totals. Figures 2–4 show the bias of the measurements as a function of the true weight percent of the component measured. The

TABLE III

Analytical test results—% oil, water and solids, recovered by the OGM and by the MODT

	OGM			MODT		
Sample I.D.	Oil	Water	Solids	Oil	Water	Solids
A	5.7	14.5	79.9	7.3	13.6	79.2
A	5.8	15.3	78.9	7.3	13.7	79.0
A	6.4	16.4	77.2	7.3	13.9	78.8
B	14.5	81.1	4.4	15.5	76.4	7.8
B	16.1	87.1	−3.2	14.0	76.7	7.6
B	19.6	79.5	0.9	18.4	71.5	9.4
C	22.7	40.9	36.4	28.5	31.7	38.8
C	26.4	44.2	29.4	28.6	31.6	39.3
C	23.9	45.2	30.9	29.1	31.9	38.3
D				47.4	27.3	24.6
E				40.0	52.1	8.0
F				64.8	21.6	13.5
G				54.1	28.4	18.7
H				24.7	66.2	8.8
H				20.8	65.2	13.3
T2				9.1	9.7	81.0
T3				9.3	10.0	80.9
T4				8.9	9.1	80.1
T5				9.8	8.4	80.2

bias, or error, is shown here as the actual percent difference between the true and the measured value. This observed bias is obviously a combination of the bias in the method and errors due to sampling.

The curves were fitted using a smoothing technique provided by SAS/GRAPH, a computer program which fits a linear combination of a cubic spline and least square line.[4] The factors governing the relative importance of the two components were adjusted to give the smoothest line.

It is important to note that more data were generated for samples with high solids contents compared to those with high liquids contents. Consequently, there is more uncertainty in the region for high liquid levels.

Oil contents

As shown in Figure 2, the MODT gave good and consistent results for the amount of oil present. Up to 40% oil, the results show a

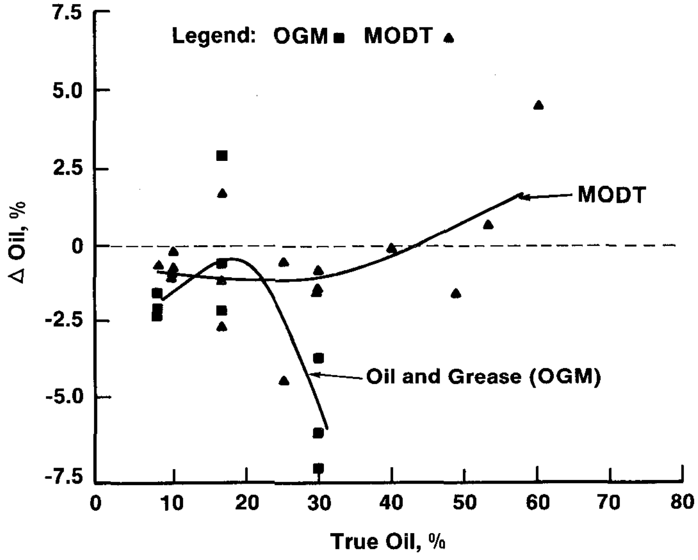

FIGURE 2 Accuracy of oil determinations as function of actual oil contents by the MODT and by the OGM. The vertical axis shows the deviation from the true value in absolute percent.

negative bias of up to 1% absolute. The maximum relative error was 9% and decreased with increasing oil contents.

Losses during the handling of small amounts of material may be the reason for the negative bias at the low oil levels. At the other end, we attribute the large bias to two suspect, unrepresentative samples. Based on the results on the solids as well, it appears that the solids may have settled out of these mostly liquid samples. Thus, the aliquots tested may have been "enriched" in oil and water.

Results by the OGM are significantly poorer. At the higher levels, recovery of the oil becomes incomplete. The highest absolute error observed was 6%; the highest relative error observed was 40%.

Water contents

Figure 3 shows that the MODT reports a slightly negative bias for

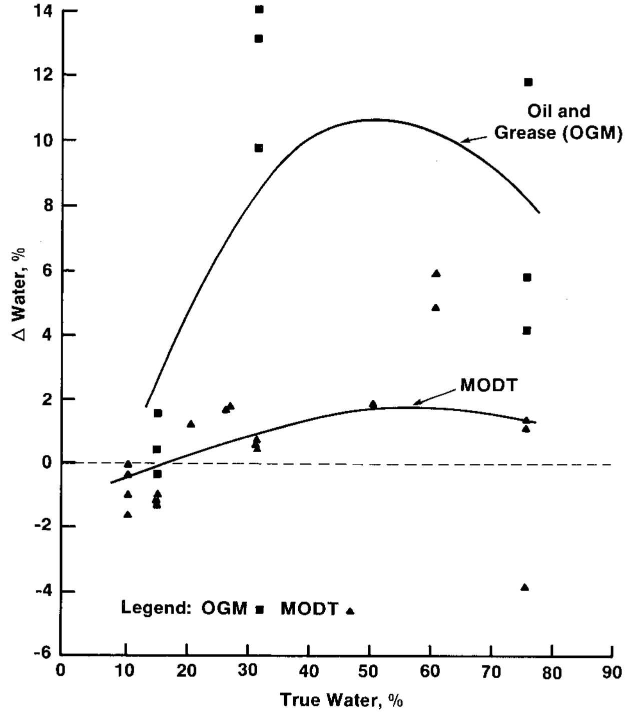

FIGURE 3 Accuracy of water determinations as function of actual water content by the MODT and by the OGM.

samples with low water contents and a positive bias for samples with high water levels. Again, settling of the solids may have enriched those samples with high liquid contents. The absolute error was always less than 2%, and the maximum relative error observed was 8%. The error tapered off as the water contents of the sample increased. The OGM usually showed the presence of more water than actually present. The absolute error varied between 2–10% for samples with 10–75% water. The relative error ranged from 10–20%.

Solids contents

Figure 4 shows there is a negative bias at the lower end and a

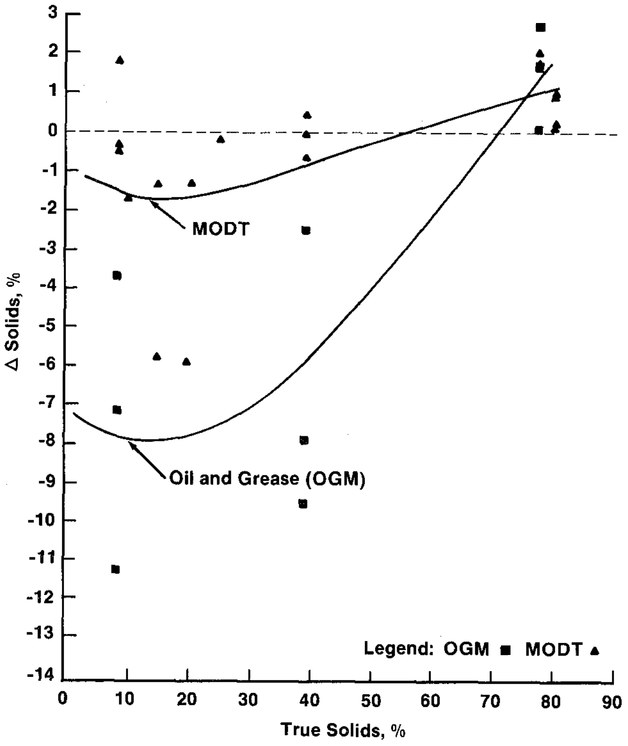

FIGURE 4 Accuracy of solids determinations as function of actual solids content by the MODT and by the OGM.

positive bias at the higher end of the scale. The MODT again showed much better results than the OGM.

Average bias and reproducibility

The maximum and average bias calculated for each of the components are shown in Table IV. Results are based on the 12 samples shown in Table I for the MODT and for Samples A, B, and C for the OGM. The bias shown is hence the average difference between the true and measured values. Values reported are the greatest deviations from zero, as determined by a "parametric spline" correlation available from SAS Institute.[5]

Standard deviations have been calculated in absolute and relative terms for each component. Results are shown in Table V. Included in this table are the results of many duplicate analyses of actual samples of unknown composition. The data base is, therefore, much larger than that used in Table IV. Relative standard deviations by the OGM are three to six times larger than observed with the MODT. It is clear that the MODT gives significantly superior results to the OGM.

Recovered oil properties

Simulated distillation by gas chromatography was used to compare

TABLE IV

Accuracy of oil, water, and solids measurements maximum bias and average bias by the OGM and by the MODT

			Maximum bias absolute % (relative %)			Average bias absolute % (relative %)		
Method	No. of samples	No. of analyses	Oil	Water	Solids	Oil	Water	Solids
MODT	12	19	2 (−9)	2 (−8)	−2 (−20)	−0.6 (−5)	0.6 (−0.3)	−0.4 (−4)
Oil and grease	3	9	−6 (−40)	11 (20)	−8 (−220)	−2.6 (−15)	6.8 (18)	−4.2 (−35)

TABLE V

Standard deviations of oil, water, and solids measurements

Method	No. of samples	No. of analyses	Absolute %			No. of samples	No. of analyses	Relative %		
			Oil	Water	Solids			Oil	Water	Solids
MODT	21	46	1.4	1.7	2.0	4	11	4	1	6
Oil and grease	3	9	1.9	2.7	3.1	3	9	10	6	28

the oils recovered against the original oils in the synthetic blends. Preferential losses of light ends or heavy bottoms would show us an offset in the obtained chromatograms.

Figure 5 shows the simulated distillation curves of an average MODT recovered oil, an oil recovered by the OGM, and the original oil used in the blend. The particular oils shown in the chromatogram were from an OGM analysis of Sample B and a MODT analysis of Sample A. Note that the results from the oil recovered by the MODT very closely parallel the original material. The oil from the OGM, on the other hand, shows a considerable loss of light ends.

At 200°C, the original oil has about 20 wt % lighter boiling constituents. The oil from the MODT still has about 19 wt % 200°C material, while the oil from the OGM only shows about 5% light ends. The tail end of all three curves is similar, indicating that no or

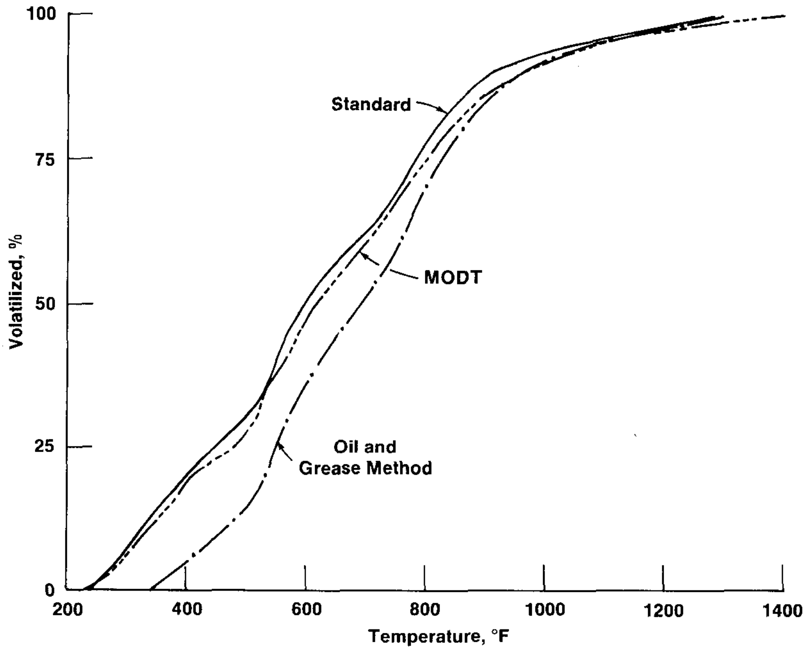

FIGURE 5 GC simulated distillation curves for recovered oils and for standard oil used.

little heavy ends are lost. Similar results were observed from tests with different levels of oil in the sample and from tests with oils of different boiling ranges.

CONCLUSIONS

The MODT is a good method to determine oil, water, and solids in a wide range of oily waste samples. These findings are based not only on the results of this study but on a very large number of samples which we have routinely analyzed by this method.

Extreme care in sampling is still the major factor in obtaining reproducible results. In highly liquid samples, sedimentation of solids may give higher results for the liquids at the expense of the solids.

In comparison, the OGM is not very accurate. It tended to overestimate the amount of water and underestimate the amount of oil and solids present. Most of these errors can be traced to the evaporation step to determine the water level in the sample. Low oil values may also be the result of incomplete extraction; Freon 113 is not as good a solvent as dichloromethane.

Oil recovered by the MODT was representative of the oil in the sample. The OGM recovered oil has less light ends than the original sample. The MODT has the advantage of several built-in checks. All three components are recovered and weighed. Most of the other methods determine two components and calculate the third by difference.

A comparison of the recovered versus the original sample weight gives a rapid indication of the validity of that particular run. Leaks or losses during each stage can be detected by keeping track of the weights. Each of the three separate components can also be characterized by other techniques, e.g., to determine the level of contamination still present in each phase. This allows results to be further corrected for still more accurate results.

Acknowledgements

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