

Feature Article

Application

Introduction of Oil Measurement Applications using Oil Content Analyzer

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Oil is a commonly used material which is essential for mankind's activity. Thus, it is necessary to measure and control oil content for its effective use. HORIBA's OCMA-500 series and OCMA-550 series have achieved easy and accurate measurements by extracting oil to a solvent. In this article, we introduce some applications of oil extraction and measurement using OCMA-550 series, discussing the significance of each case. Specifically four difficult samples that require special technique for the extraction, which are oil in soil, residual oil on metal parts after being cut, residual oil on surgical instruments and oil in rice (rice balls from a store), are shown with detailed explanation regarding the setting of extraction time and removal of detergent-like substances.

Introduction

It is important for humans to measure and control water quality in order to use water resources sustainably. There are many water quality parameters such as pH, Chemical Oxygen Demand (COD), Dissolved Oxygen (DO) and turbidity, etc. and various methods for measuring them have already been established, but it is difficult to measure oil content accurately without pretreatment because oil and water are immiscible. Even though oil is a substance which is used in every aspect of life and essential for human activities, improper use of oil could cause pollution. Oil pollution not only contaminates utilizable water resources directly but also affects organisms living around it, leading to the destruction of ecosystem. Therefore, it is essential to measure and analyze oil to understand the usage and pollution situations, and this also leads to the conservation of the global environment.

HORIBA group offers a lineup of OCMA-500 series oil content analyzers that enable to measure oil content easily and accurately. (Table 1) Simply delivering discharged water to the device enables to easily measure the oil content in the discharged water.^[1] We also produced earth-conscious OCMA-550 series products that achieved low running cost by reducing the solvent usage per measurement to one-third or lower. (Figure 1) In the lineup of this series, we mainly offer OCMA-555 using

Table 1

| Model | OCMA-500 | OCMA-505 | OCMA-550 | OCMA-555 |
|-----------------|-----------|---------------|------------------|------------------|
| Solvent | S-316 | H-997 | S-316 | H-997 |
| Extraction | Automatic | Automatic | Manual operation | Manual operation |
| Country of sale | Overseas | Mainly Japan* | Overseas | Mainly Japan* |

*...sold in Japan and China.

H-997 as an extraction solvent for Japanese markets and OCMA-550 using S-316 for other markets. With OCMA-550 series products, measurements can be performed by extracting the oil into the solvent by means of manual agitation of a sample and the solvent, putting the solvent into which the oil is extracted in the measurement cell,



Figure 1 OCMA-550 series

Table 2 The example of the oil measurement technique in soil.

| | Measurement time | Advantage | Fault |
|--|------------------|---|--|
| Hydrogen flame ionization gas chromatograph (GC-FID) | 30 min. | Distinction of the grade of crude by a carbon number is possible. | Knowledge is required to read data. A hydrogen cylinder is required. |
| Extractive substance in normal-hexane | 2 hours~ | Regulating method (JIS) | Detection of volatile oil is impossible |
| Infrared absorption spectrophotometry | 3 min.~ | Operation is simple. | Distinction of a grade of crude is impossible. |

and placing the measurement cell in the device. However, there are many points to be noted when extracting oil. In this paper, examples of the measurements of oil content in soil, residual oil on industrial parts, oil attached to medical instruments, and the oil attached to food (rice) using OCMA-550 series are introduced and the points of attention during measurement are explained in detail.

Measurement of Oil in Soil

Outline

Old gas station sites may have soil pollution problem caused by the gasoline leaked from tanks and pipes. The Soil Contamination Countermeasures Act is not applied to pollutions arising from oil, but the Ministry of the Environment published the Guidelines for the Countermeasures against Oil Contamination in 2006.^[2] In addition, some local governments require investigating the oil content in the soil of old business facility sites such as gas station. In this way, the public’s awareness of oil pollution is growing. Generally, for the measurement of oil content in soil, gas chromatography with hydrogen flame ionization detector (GC-FID method), weight method (normal hexane extracts), and infrared absorption method (IR method) are available. Table 2 shows the characteristics of each method. The infrared absorption oil content analyzers (“OCMA” series in HORIBA) is a method for quantitating oil by the use of infrared absorption of 3.4 – 3.5 μm that is attributable to carbon-hydrogen stretching vibration. Although this method cannot distinguish oil types such as plant oil or mineral oil, it is advantageous in which it enables easy extraction, does not require special knowledge for data reading, and has high detection sensitivity.

Procedures for extraction

Soils contain organic substances, microorganisms and moisture as well as a lot of stones and sands. For this reason, when extracting the oil, organic substances and microorganisms in the soil may exhibit surfactant activity to emulsify a sample, preventing accurate extraction of the oil. Therefore, a salting-out effect is used to mitigate the effects of organic substances. The salting-out effect utilizing the property of ions which attract moisture strongly is expected to bring about the following effects:

- Mitigating the emulsification of samples caused by organic substances
- Improving the isolation between a water layer and a solvent layer
- Preventing the oil from remaining in a water layer
- Preventing a solvent from being dissolved in a water layer

As a concrete way of using the salting-out effect, adding not only a sample and a solvent but also saturated saline when extracting the oil enables to prevent the emulsification and to extract the oil accurately. In addition, repeating the operation of discarding the saturated saline layer after extraction and adding the equivalent amount of saturated saline several times makes it possible to extract oil more accurately. In this case, it has already been confirmed that no oil is contained in the saturated saline layer disposed.

Example of a practical measurement

As a contaminated soil sample, the soil made by adding a certain amount of fuel oil B to commercially-available leaf soil was used. To extract the oil content from the soil, the procedures shown in Figure 2 were used. If the soil is stiff, it is desirable to loosen it before extracting the oil content. In addition, if it is too difficult to separate the solvent layer due to emulsification, this problem can be solved by reducing the amount of soil used for extraction or by increasing the amount of extraction solvent. The

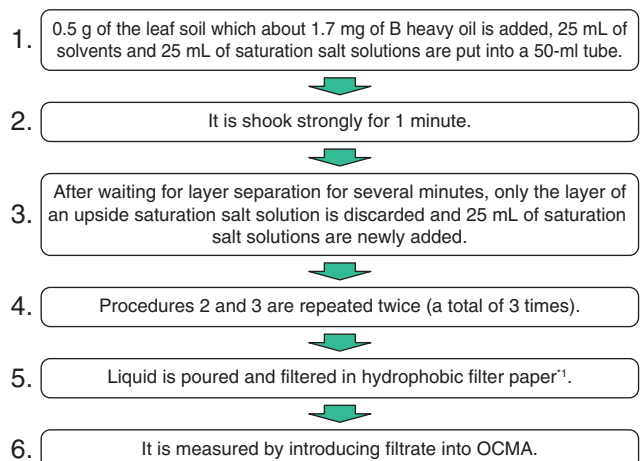


Figure 2 Operation flow of measurement of the oil in soil

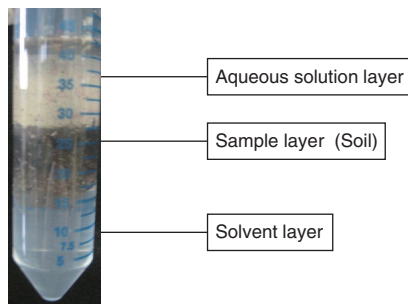


Figure 3 Example of extraction of the oil in soil.

leaf soil without fuel oil B was also used for comparison. Figure 3 shows the measurement situation and Table 3 shows the measurement result.

As a result of the measurement with OCMA, the oil content in the leaf soil and the one with 1.7 mg of fuel oil B were approximately 17 mg/L (A) and 70 mg/L (B) respectively. The calculation of the amount of oil contained in 0.5 g of both soils showed the oil content of approximately 0.40 mg (A') and 1.8 mg/L (B') respectively. Comparing these results, approximately 17 mg/L (A) and 70 mg/L (B), the leaf soil with fuel oil B was clearly distinguishable from the leaf soil without fuel oil B. Furthermore, Table 3 shows the extraction rate (ρ) with respect to the additive amount of fuel oil B. The extraction efficiency (ρ) with respect to the additive amount of fuel oil B is approximately 80 – 90 %, meaning sufficient extraction. The reason why the oil was detected in the leaf soil with no fuel oil B was the oil contained in fallen leaves and tree barks was extracted. In this way, using OCMA, the oil contained in the soil could be measured and the soil contaminated with oil could be distinguished. Therefore, measuring the oil contained in samples which are taken from several places is considered to make it possible to specify the location causing the pollution.

*1: Filter paper No. 2200-125 made by Whatman

Measurement of Residual Oil Content on Industrial Parts

Outline

In recent years, OCMA has been commonly used in the control of the residual oil content attached to electronic components and machined metal parts. Cutting oils used when machining metals for reducing friction and cooling are essential for machining process. However, a process for washing cutting oil away after machining process is required because residual cutting oil on industrial parts may generate odor and noise, causing troubles such as electronic component failure. Controlling the residual oil content on industrial parts after the washing process enables to prevent various troubles attributable to residual cutting oil. In addition, it also makes it possible to know the degradation level of the wash solution used in the washing process to use it as an indicator of the bath life. In the measurement with OCMA, the oil can be extracted just by immersing the parts in the solvent. The measurement of residual oil content using OCMA is becoming a de facto standard because the operation is very easy. Therefore, in this paper, the key points and precautions of the measurement are introduced with an example of the measurement of the oil attached to typical metal parts.

Procedures for extraction

A: For small industrial parts such as screws and electronic components

If H-997 is used, it is desirable to use a screw-top jar with a wide-mouth lid because the solvent volatilizes easily. It is generally preferable not to use containers made of resin except for PTFE in order to prevent the incorporation of plasticizing agent and the swelling of container due to the solvent. In this measurement, parts samples are placed in PTFE containers, and H-997 or S-316 is poured into the containers using a measuring cylinder to immerse the parts samples completely and then the containers are sealed. (Figure 4a) Since the extraction time depends on the parts shape and oil adhesion amount, they need to be immersed first to see how long time it takes to reach to suitable concentration. It is preferable to immerse for an hour shaking occasionally and extend the time according

Table 3 The measurement result of the oil extracted from soil.

| Extraction object | S-316 | H-997 | |
|--|-------|-------|------------------------|
| Soil extract : Measured value (mg/L) | 17.7 | 16.4 | A |
| The amount of oil in the soil 0.5 g : Calculated value (mg) | 0.44 | 0.41 | A' = A/(1000/25) |
| Soil extract which 1.7 mg of B heavy oil is added : Measured value (mg/L) | 77.6 | 69.4 | B |
| The amount of oil in the soil 0.5 g which 1.7 mg of B heavy oil is added : Calculated value (mg) | 1.94 | 1.74 | B' = B/(1000/25) |
| The extraction rate (ρ) over B heavy oil addition (%) | 88.09 | 77.94 | $\rho = (B' - A')/1.7$ |

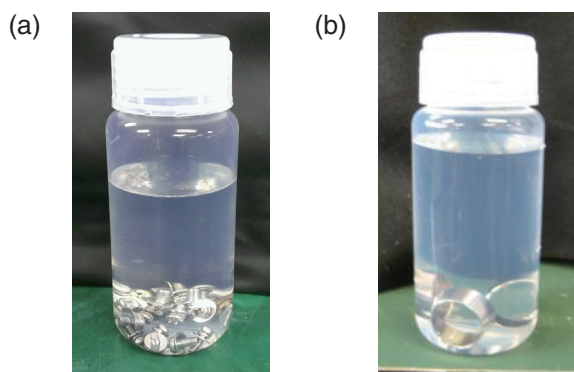


Figure 4 The example of oil extraction of parts (a) and the cut parts (b)

to conditions. Then, leave at rest for the same period of time as the extraction time. If it takes long time for extraction, irradiating ultrasound waves for one to three minutes enables to shorten the extraction time. However, since H-997 generates high vapor pressure and evaporates easily, it is necessary to prevent H-997 from being high temperature. If any particles such as iron powder are contained in the solvent after extraction, it is needed to remove them using glass funnel and ashless-grade cellulose quantitative filter paper^{*1} (Particle retention: 8 μm). The filter paper should be dried after washed with the solvent.

Calibration should be performed using solvent standard solution only. If moisture is contained in this solution, it may cause an error because water isn't used for extraction from samples. If sample solvent is irradiated with ultrasonic waves, also irradiating the standard solution with similar ultrasonic waves enables to reduce errors. With OCMA-550 series, calibration should be performed according to the same procedures for conventional extraction using a separatory funnel. Following the calibration, the measurement should be performed after sufficient prewashing of the interior of the device or cells using a solvent after extraction. It is preferable to use mg/PC (PC = piece, the oil content per a piece of part) as a measurement value unit.

*1: Filter paper No. 2200-125 made by Whatman

B. For large parts

Large parts cannot be put into usual screw-top jars. Therefore, a given amount of solvent needs to be poured over part samples placed in a deep tray made of PTFE, etc. to extract the oil. If it is too difficult to extract the oil in one go due to the shape of them, the solvent needs to be poured several times. However, since H-997 is easily volatilized, it is preferable to perform this operation in a room which is well ventilated and temperature-controlled. Subsequent measurement procedures are the same as

Table 4 The remains oil measurement result of the parts by OCMA-550 and OCMA-555.

| | S-316 | H-997 |
|---------------------------|-------|-------|
| Washing parts (mg/PC) | 0.0 | 0.1 |
| Not washing parts (mg/PC) | 2.0 | 3.0 |

those for small part samples.

An example of a practical measurement using machined metal parts

We measured machined metal parts with OCMA-550 and OCMA-555. Three washed metal parts and three unwashed metal parts were placed separately in PTFE containers and then the containers were sealed as shown in Figure 4b after pouring 100ml each of S-316 or H-997 solvents. After an hour of immersion, the oil was extracted into these solvents as samples. "Washed parts" were washed with surfactant. Table 4 shows the result of the measurement of the oil content in the samples after calibrating OCMA-550 and OCMA-555 with 0 and 200mg/l of fuel oil B or OCB mixed standard substance solution^{*2}, respectively. For OCMA-555, the result shows that the amount of oil attached to washed parts was 0.1 mg/PC and that attached to unwashed parts was 3 mg/PC. The difference between washed parts and unwashed parts is obvious like this, and OCMA are useful for checking if a part is sufficiently washed or not.

*2: A mixture of Isooctane : Cetane : Benzene = 3:3:2

Measurement of the Cleanliness of Medical Instruments

Outline

Human sebum and blood, etc. are attached to used medical instruments. Although most of them are disposed, some of them such as the handle of a scalpel and tweezers may be reused. They need to go through cleaning, sterilizing and drying processes for reuse, and oil content is used as one of the cleanliness control indicators. In this section, an example of the measurement of the oil attached to medical instruments is introduced as a cleanliness control example.

Procedures for extraction

The extraction procedures are the same as those for washing parts. Pick out some instruments which went through cleaning, sterilizing and drying process place in a PTFE container, etc. Pour H-997 or S-316 solvent into a container in which a medical instrument sample is placed using a measuring cylinder to immerse it, seal the container and immerse it for an hour shaking up occasionally. It is preferable to extend the time according

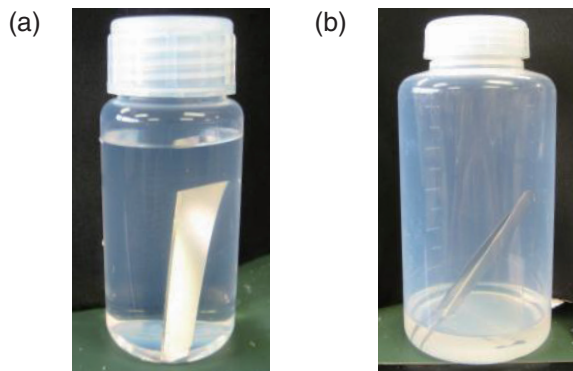


Figure 5 The example of immersion of the edge of a cutter (a) and tweezers (b)

to conditions if it has complicated shape or is extremely dirty. Then, leave at rest for the same period of time as the extraction time. If it takes long time for extraction, irradiating ultrasonic waves for one to three minutes enables to shorten the extraction time.

Calibration should be performed using only a solvent standard solution as it is for washing parts. If moisture is contained in this solution, it may cause an error because water isn't used for extraction from samples. If a sample solvent is irradiated with ultrasonic waves, also irradiating the standard solution with similar ultrasonic waves enables to reduce errors in the preparation concentration of the standard solution. Following the calibration, measurement should be performed after sufficient prewashing of the interior of the device or cells using a solvent after extraction.

An example of a practical measurement

An example of a measurement using tweezers and a cutter blade as medical instrument samples on OCMA-550 and OCMA-555 respectively is introduced. A piece of pork meat used as an alternative for human tissue was cut using two tweezers and two cutter blades. A sample washed with surfactant and an unwashed one were placed in PTFE containers separately, 100 mL each of S-316 or H-997 were poured into each container, and the containers were sealed as shown in Figure 5a and 5b. After immersing the samples in solvent for approximately twelve hours, the oil on them was extracted. Table 5

Table 5 The cleanliness measurement result when OCMA-550 and OCMA-555 are used

| | With Washing | With no washing |
|---|--------------|-----------------|
| Tweezers : Extract by S-316 (mg/L) | 0.0 | 93.0 |
| The amount of oil adhering to tweezers. (mg) | 0.0 | 9.3 |
| Cutter edge : Extract by H-997 (mg/L) | 0.0 | 6.0 |
| The amount of oil adhering to a cutter edge. (mg) | 0.0 | 0.6 |

shows the result of the measurement of the oil on the tweezers and the cutter blades performed after calibrating OCMA-550 and OCMA-555 with zero and 200 mg/L each of fuel oil B or OCB solution. As Table 5 shows, no oil was detected from the washed samples, but the unwashed tweezers and cutter blades showed the oil content of 93.0 mg/L and 6.0 mg/L respectively. As long as samples are washed sufficiently like this, no oil is detected. Therefore, the check of oil content is sufficient for use in controlling the cleanliness of medical instruments. In addition to medical applications, this is also considered to be useful in random sampling inspections of washed dishes and cooking utensils at restaurants.

Measurement of the Oil Attached to Rice

Outline

Food oil may be added to rice in boxed lunches and rice balls sold at supermarkets, etc. at the time of cooking. Adding food oil when cooking rice is effective in preventing cooked rice grains from attaching to measuring containers in the manufacturing process, in enhancing the yield and workability of the manufacturing line, and in preventing the adhesion between a rapping film and rice grains. In addition, a small amount of oil improves taste, preserving property and gloss, but adding an excessive amount of food oil deteriorates the taste. For this reason, it is required to manage the additive amount properly. However, since oil floats on water, there was a case where a concentration gradient of food oil was generated in a rice cooker, resulting in uneven finishing of cooked rice. Therefore, measuring the oil content attached to rice grains enables to check if a proper amount of food oil is attaching to cooked rice grains.

Procedures for extraction

Generally, polished white rice is used as food. Table 6 shows the nutritional components of refined white rice.^[3] Since refined white rice contains carbohydrate and protein, the affinity of these organic substances and the oil content on the rice grain surfaces prevents the extraction of oil content into a solvent. Therefore, saturated saline is added to perform complete extraction, similar to the measurement of the oil content in the soil.

Table 6 The ingredient of polished rice. (Per 100g)

| | |
|--------------|--------|
| Moisture | 60.0 g |
| Protein | 2.5 g |
| Lipid | 0.3 g |
| Carbohydrate | 37.1 g |
| Ash | 0.1 g |

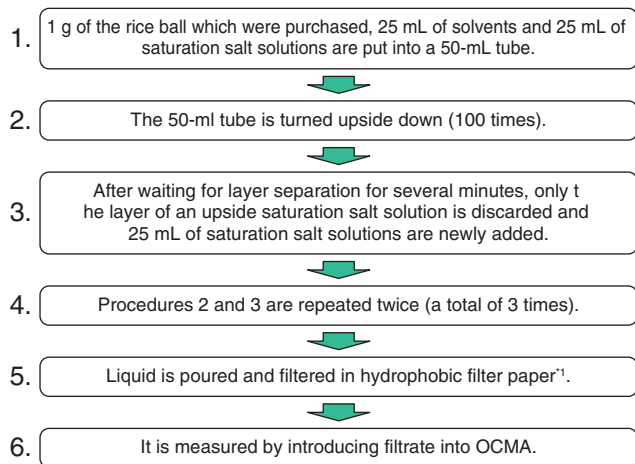


Figure 6 Operation flow of measurement of the oil in rice.

An example of a practical measurement

The amount of oil contained in a commercially-available rice ball was investigated. To extract the oil from the rice ball, the procedures shown in Figure 6 were followed.

The procedure 2 is to prevent rice grains from being broken due to agitating operation, so the tube should not be shaken so fast (Since the measurement focuses on surface oil, they don't need to be broken). In addition, white rice cooked without oil was also used as a reference. In the measurement, OCMA-550 and OCMA-555 which were calibrated with zero and 200mg/L each of fuel oil B or OCB mixed standard substance solution^[3] were used. Figure 7 shows the extraction situation and Table 7 shows the measurement results.

Based on the result of the measurement with OCMA, the amount of oil contained in one gram of white rice or rice ball was also calculated. This experiment showed that approximately 3 – 3.6 mg of oil was attached to one gram of white rice taken from the purchased rice ball. Although white rice also contained oil, it was considered to be due to lipids originally contained in the white rice (triglyceride and fatty acid). In addition, the readings vary depending on whether which solvent is used, S-316 or H-997, due to the difference in oil type and extraction solvent. This is because the extraction efficiency depends on the oil type

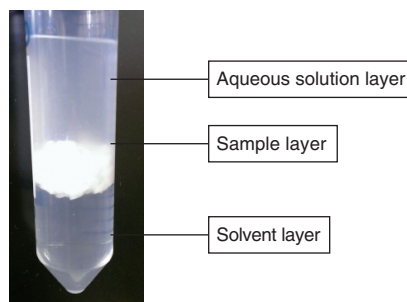


Figure 7 Example of extraction of the oil from rice.

or because of the variation in the oil contained in the sample or the influence of a substance with surfactant action. In this way, the measurement with OCMA oil content analyzer enabled to confirm that commercially-available rice balls contained oil. In addition, the amount of milk fat contained in milk can also be measured. In this case, salt is added to milk until it becomes saturated before performing the extraction operation. As above, OCMA can be used for measuring the amount of oil contained in foods.

Conclusion

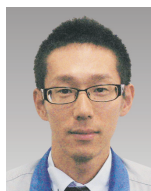
We introduced several examples of typical measurements using OCMA as shown above including the points for successful measurements. There are also many other measurement applications such as oil drilling site, biofuel field and measurement of oil contained in ballast water, etc. Since OCMA can measure a low level of oil content easily, it must have more applications. We believe we can contribute to the global environment protection, though it is in small portion, by offering our oil content measurement tools and applications.

Table 7 The measurement result of the oil extracted from the grain of rice.

| The candidate for extraction | S-316 | H-997 | |
|--|-------|-------|--------------------|
| Polished-rice extract : Measured value (mg/L) | 20.4 | 22.1 | C |
| The amount of oil in 1 g of the polished rice : Calculated value. (mg) | 0.51 | 0.55 | $C' = C/(1000/25)$ |
| rice-ball extract : Measured value (mg/L) | 119 | 144 | D |
| The amount of oil in 1 g of the rice ball : Calculated value. (mg/g) | 2.98 | 3.60 | $D' = D/(1000/25)$ |

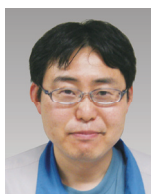
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