

732 Methods of Testing for Chlorinated Compounds in Used Oil

by Dexsil Corp.

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Introduction

In order to reduce the amount of hazardous halogenated compounds in the atmosphere, federal regulations (40 CFR 266 recodified at 40 CFR 279; see 9[510) place strict limits on the amounts of halogenated materials that are allowed in used oil burned for energy recovery. Used oil may contain up to 1,000 parts per million (ppm) total halogens or, in some cases, up to 4,000 ppm if it can be shown that the source of the halogens is non-hazardous.

With millions of gallons of used oil being collected every year for reuse as a fuel, there is a great need for reliable test methods to determine if a batch of oil is in compliance with the regulations. Several methods exist for determining the amounts of halogenated compounds in used oil. Some of the methods can be used on site and some require that a sample be sent to a laboratory. Even though the regulations limit the concentration in used oil of all halogenated compounds, they only require that testing be done for chlorinated compounds, so all of the methods discussed here test for chlorinated compounds only, unless otherwise noted.

The six methods of analysis that will be discussed include:

- microcoulometry;
- x-ray fluorescence;
- gas chromatography;
- Beilstein test;
- halogen sniffers; and
- Chemical test kits.

The first three methods use sophisticated instruments and generally require that they be performed in a laboratory. The latter three are field methods that are portable enough to be used on site. The laboratory methods require a greater level of operator expertise, but supply a higher level of precision as well as a lower limit of detection.

MICROCOULOMETRY

Microcoulometers are capable of testing almost any type of material for total chlorine content. A small amount of sample (less than 10 milligrams) is either injected or placed into a quartz combustion tube where the temperature ranges from 600' to 1,000' C. Pure oxygen is passed through the quartz tube and any chlorine-containing components are combusted completely. The resulting combustion products are swept into a titration cell where the chloride ions are trapped in an electrolyte solution. The electrolyte solution contains silver ions that immediately combine with any chloride ions and drop out of solution as insoluble silver chloride. A silver electrode in the titration cell electrically replaces the used up silver ions until the concentration of silver ions is back to where it was before the titration began. By keeping track of the amount of current needed to generate the required amount of silver, the instrument is capable of determining how much chlorine was present in the original sample. Dividing the total amount of chlorine present by the weight of the sample gives the concentration of chlorine that is actually in the sample.

Microcoulometers can detect chlorine (and bromine) concentrations in used oils from the low ppm range up to percentages if dilutions are performed. A trained analyst is required to operate the instrument and calibrations must be performed regularly. After the microcoulometer is turned on, it takes about an hour to warm up before the first analyses can be run. Microcoulometers cost about \$15,000. Microcoulometry has received an EPA method designation of 9076 in the SW-846 manual.

X-ray Fluorescence

X-ray fluorescence (XRF) instruments also are used primarily in the laboratory although some are portable. The sample to be analyzed is placed in a sample cup which has a transparent bottom. The sample cup is then placed in the analyzer where it is irradiated with X-rays of a specific wavelength. Any chlorine atoms in the sample absorb a portion of the X-rays and then emit radiation back out of the sample cup at a wavelength specific for chlorine. A detector in the instrument then quantifies the amount of radiation coming back from the chlorine atoms and, by knowing the surface area that is exposed, can then calculate the concentration of chlorine in the sample.

The technique requires a trained analyst and is subject to some interference from other elements such as sulfur. A sample which is not homogeneous and is subject to settling in layers may give incorrect results because the instrument only reads the bottom layer of the sample. XRF analyzers range from about \$30,000 for single element analyzers to hundreds of thousands for sophisticated multi-element instruments. XRF analysis of waste oil has been assigned EPA SW-846 method number 9075.

Gas Chromatography

Gas chromatography (GC) is a laboratory method, and is the only method discussed here that can actually quantify specific halogenated compounds. It is not generally used to test used oils for total halogens because it cannot detect inorganic halogen contamination. GC is often misinterpreted as being an exhaustive test for halogen contamination but cannot be used for classifying whether used oils contain less than or more than 1,000 ppm total halogens. It is the only one of these methods that can be used, however, when looking for a specific halogenated organic compound.

Beilstein Test

The Beilstein, or copper wire, test is the simplest of the methods discussed here. When a compound containing chlorine is burned on a copper surface it emits a green flame that easily can be detected by eye when the chlorine is in sufficient concentration. Copper wire or copper "wool" provides enough surface area to perform the test. The Beilstein test only gives a qualitative reading and is only useful in the percentage range, not at ppm levels. It will not detect chlorine as low as the regulated limits, but will give an indication of gross contamination. Because the sample must be ignited, the test never should be run in the vicinity of flammable materials. This method is very inexpensive, but it is not quantitative, is not approved, and is dangerous. It should only be used when other methods are not available.

Halogen Sniffers

The small, hand-held devices most often referred to as "sniffers" have some applications with used oils, but the user must be careful not to read more into the result than what is actually found. These instruments use a variety of detection techniques, but all of them rely on detecting the presence of halogenated compounds in the headspace above the used oil being analyzed. They easily find volatile compounds that are not halogenated. The instruments are not quantitative because they can only measure what is in the air space above the oil, not what is in the oil itself. The sniffers are inexpensive, costing a few thousand dollars, and are easily portable. Because they are not specific and not quantitative, the sniffers are not EPA-approved, and therefore should not be used to verify compliance with the regulations.

Chemical Test Kits

The portable chemical test kits are designed to test for all sources of chlorine in a sample of used oil, and are easy to use. A sample of oil is taken with a polypropylene syringe and introduced into a plastic test tube. Glass ampules in the test tube contain a diluent and a small amount of metallic sodium. The sodium reacts with any compounds that contain halogens and removes the halogens from their organic backbones. The resulting chloride ions are then extracted into an aqueous buffer solution where they can be easily measured by the use of a calorimetric indicating

reagent. Kits are available to provide either a "go, no-go" answer at the 1,000 ppm level or to give a quantitative result over the range of 200 to 4,000 ppm.

The kits are inexpensive, at about \$5.00 per test, and are designed to be run by anyone. However, as with any analytical test care must be taken to ensure that the test kits are used correctly. The test kits have recently been assigned EPA SW-846 Method number 9077. The kits are applicable for most types of used oil, however oils that contain more than three or four percent sulfur may give false positive (high bias) results.

CONCLUSION

All of the methods discussed above have applications where they are most appropriate. When choosing a method for everyday routine analysis of used oil, make sure to weight all the important variables such as cost, time required, training necessary, reliability, and whether or not the technique has been recognized by EPA. If there is ever a discrepancy between test methods, it is always to the tester's advantage to have used a test method, which is recognized by EPA. Keep in mind that EPA methods do not in themselves guarantee good data--the tests must be run properly, samples must be taken and stored correctly, and results must be recorded accurately. If the proper time and care is invested early in developing a complete testing policy, the testing procedures will pay for themselves many times over.