

TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM  
PRODUCTS BY X-RAY FLUORESCENCE SPECTROMETRY (XRF)

1.0 SCOPE AND APPLICATION

1.1 This test method covers the determination of total chlorine in new and used oils, fuels, and related materials, including crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene. The chlorine content of petroleum products is often required prior to their use as a fuel.

1.2 The applicable range of this method is from 200  $\mu\text{g/g}$  to percent levels.

1.3 Method 9075 is restricted to use by, or under the supervision of, analysts experienced in the operation of an X-ray fluorescence spectrometer and in the interpretation of the results.

2.0 SUMMARY OF METHOD

2.1 A well-mixed sample, contained in a disposable plastic sample cup, is loaded into an X-ray fluorescence (XRF) spectrometer. The intensities of the chlorine K $\alpha$  and sulfur K $\alpha$  lines are measured, as are the intensities of appropriate background lines. After background correction, the net intensities are used with a calibration equation to determine the chlorine content. The sulfur intensity is used to correct for absorption by sulfur.

3.0 INTERFERENCES

3.1 Possible interferences include metals, water, and sediment in the oil. Results of spike recovery measurements and measurements on diluted samples can be used to check for interferences.

Each sample, or one sample from a group of closely related samples, should be spiked to confirm that matrix effects are not significant. Dilution of samples that may contain water or sediment can produce incorrect results, so dilution should be undertaken with caution and checked by spiking. Sulfur interferes with the chlorine determination, but a correction is made.

Spike recovery measurements of used crankcase oil showed that diluting samples five to one allowed accurate measurements on approximately 80% of the samples. The other 20% of the samples were not accurately analyzed by XRF.

3.2 Water in samples absorbs X-rays emitted by chlorine. For this interference, use of as short an X-ray counting time as possible is beneficial. This appears to be related to stratification of samples into aqueous and nonaqueous layers while in the analyzer.

Although a correction for water may be possible, none is currently available. In general, the presence of any free water as a separate phase or a water content greater than 25% will reduce the chlorine signal by 50 to 90%. See Sec. 6.4.

#### 4.0 APPARATUS AND MATERIALS

4.1 XRF spectrometer, either energy dispersive or wavelength dispersive. The instrument must be able to accurately resolve and measure the intensity of the chlorine and sulfur lines with acceptable precision.

4.2 Disposable sample cups with suitable plastic film such as Mylar®.

#### 5.0 REAGENTS

5.1 Purity of reagents. Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Mineral oil, mineral spirits or paraffin oil (sulfur- and chlorine-free), for preparing standards and dilutions.

5.3 1-Chlorodecane (Aldrich Chemical Co.), 20.1% chlorine, or similar chlorine compound.

5.4 Di-n-butyl sulfide (Aldrich Chemical Co.), 21.9% sulfur by weight.

5.5 Quality control standards such as the standard reference materials NBS 1620, 1621, 1622, 1623, and 1624 for sulfur in oil standards; and NBS 1818 for chlorine in oil standards.

#### 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 The collected sample should be kept headspace free prior to preparation and analysis to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

6.3 Laboratory sampling of the sample should be performed on a well-mixed sample of oil. The mixing should be kept to a minimum and carried out as nearly headspace free as possible to minimize volatilization losses of organic halogens.

6.4 Free water, as a separate phase, should be removed and cannot be analyzed by this method.

## 7.0 PROCEDURE

### 7.1 Calibration and standardization.

7.1.1 Prepare primary calibration standards by diluting the chlorodecane and n-butyl sulfide with mineral spirits or similar material.

7.1.2 Prepare working calibration standards that contain sulfur, chlorine, or both according to the following table:

Cl: 500, 1,000, 2,000, 4,000, and 6,000  $\mu\text{g/g}$   
S: 0.5, 1.0, and 1.5% sulfur

1.	0.5% S, 1,000 $\mu\text{g/g}$ Cl	5.	1.0% S, 6,000 $\mu\text{g/g}$ Cl
2.	0.5% S, 4,000 $\mu\text{g/g}$ Cl	6.	1.5% S, 1,000 $\mu\text{g/g}$ Cl
3.	1.0% S, 500 $\mu\text{g/g}$ Cl	7.	1.5% S, 4,000 $\mu\text{g/g}$ Cl
4.	1.0% S, 2,000 $\mu\text{g/g}$ Cl	8.	1.5% S, 6,000 $\mu\text{g/g}$ Cl

Once the correction factor for sulfur interference with chlorine is determined, fewer standards may be required.

7.1.3 Measure the intensity of the chlorine K $\alpha$  line and the sulfur K $\alpha$  line as well as the intensity of a suitably chosen background. Based on counting statistics, the relative standard deviation of each peak measurement should be 1% or less.

7.1.4 Determine the net chlorine and sulfur intensities by correcting each peak for background. Do this for all of the calibration standards as well as for a paraffin blank.

7.1.5 Obtain a linear calibration curve for sulfur by performing a least squares fit of the net sulfur intensity to the standard concentrations, including the blank. The chlorine content of a standard should have little effect on the net sulfur intensity.

7.1.6 The calibration equation for chlorine must include a correction term for the sulfur concentration. A suitable equation follows:

$$Cl = (mI + b) (1 + k^*S) \quad (1)$$

where:

I = net chlorine intensity  
m, b, k\* = adjustable parameters  
S = sulfur concentration

Using a least squares procedure, the above equation or a suitable substitute should be fitted to the data. Many XRF instruments are equipped with suitable computer programs to perform this fit. In any case, the resulting equation should be shown to be accurate by analysis of suitable standard materials.

## 7.2 Analysis.

7.2.1 Prepare a calibration curve as described in Sec. 7.1. By periodically measuring a very stable sample containing both sulfur and chlorine, it may be possible to use the calibration equations for more than 1 day. During each day, the suitability of the calibration curve should be checked by analyzing standards.

7.2.2 Determine the net chlorine and sulfur intensities for a sample in the same manner as done for the standards.

7.2.3 Determine the chlorine and sulfur concentrations of the samples from the calibration equations. If the sample concentration for either element is beyond the range of the standards, the sample should be diluted with mineral oil and reanalyzed.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 One sample in ten should be analyzed in triplicate and the relative standard deviation reported. For each triplicate, a separate preparation should be made, starting from the original sample.

8.3 Each sample, or one sample in ten from a group of similar samples, should be spiked with the elements of interest by adding a known amount of chlorine or sulfur to the sample. The spiked amount should be between 50% and 200% of the sample concentration, but the minimum addition should be at least five times the limit of detection. The percent recovery should be reported and should be between 80% and 120%. Any sample suspected of containing >25% water should also be spiked with organic chlorine.

8.4 Quality control standard check samples should be analyzed every day and should agree within 10% of the expected value of the standard.

## 9.0 METHOD PERFORMANCE

9.1 These data are based on 47 data points obtained by seven laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. Two data points were determined to be outliers and are not included in these results.

9.2 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 1):

$$\text{Repeatability} = 5.72 \sqrt{x^*}$$

\*where x is the average of two results in  $\mu\text{g/g}$ .

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$\text{Reproducibility} = 9.83 \sqrt{x^*}$$

\*where x is the average value of two results in  $\mu\text{g/g}$ .

9.3 Bias. The bias of this test method varies with concentration, as shown in Table 2:

$$\text{Bias} = \text{Amount found} - \text{Amount expected.}$$

## 10.0 REFERENCE

1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1. REPEATABILITY AND REPRODUCIBILITY  
FOR CHLORINE IN USED OILS BY  
X-RAY FLUORESCENCE SPECTROMETRY

Average value, μg/g	Repeatability, μg/g	Reproducibility, μg/g
500	128	220
1,000	181	311
1,500	222	381
2,000	256	440
2,500	286	492
3,000	313	538

TABLE 2. RECOVERY AND BIAS DATA FOR CHLORINE IN  
USED OILS BY X-RAY FLUORESCENCE SPECTROMETRY

Amount expected, μg/g	Amount found, μg/g	Bias, μg/g	Percent bias
320	278	-42	-13
480	461	-19	-4
920	879	-41	-4
1,498	1,414	-84	-6
1,527	1,299	-228	-15
3,029	2,806	-223	-7
3,045	2,811	-234	-8

METHOD 9075  
 TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED  
 PETROLEUM PRODUCTS BY X-RAY FLUORESCENCE SPECTROMETRY (XRF)

