



Total Chloride in Liquid Hydrocarbons by Wavelength Dispersive X-Ray Fluorescence

UOP Method 1013-16

Scope

This method is for determining the total chloride content of liquid hydrocarbons by wavelength dispersive X-ray Fluorescence (XRF) spectroscopy. The example given here focuses specifically on gasoline matrix but other hydrocarbon matrices are applicable if calibration standards of similar matrix are used. Highly volatile hydrocarbon species (e.g. LPG) are not applicable. The calibration has been set up for quantitative determination chloride from 5 mass-ppm to 1000 mass-ppm (0.0005 mass-% to 0.1000 mass-%). Matrix effects are not significant over this range so long as routine samples and calibration standards are well matched.

References

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

A liquid hydrocarbon sample is introduced into a wavelength dispersive XRF spectrometer. It is irradiated with x-rays, exciting elements contained in the sample to emit energy in the form of "characteristic x-rays." The emitted x-rays are detected and measured in a helium path at an angle specific to chloride. The intensity of the characteristic Cl x-ray peak is proportional to concentration.

The XRF calibration curve is established using a set of calibration standards prepared from pure chlorobenzene (chloride source) diluted with a chloride-free solvent matrix that matches the composition of the routine samples.

In XRF spectroscopy, the sample matrix composition can strongly affect the accuracy of the method. The applicability of the method should be verified, using matrix-matched standards and references, for sample types other than those described here.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, analytical, capable of weighing samples to 0.0001g

Graduated cylinder, Pyrex, 1000 mL, for preparing 3:1 iso-octane-toluene matrix blank solution, VWR International, Cat. No. 22877-150

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

© COPYRIGHT 2016 UOP LLC. All rights reserved.

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Regulator, counting gas, two-stage, high purity, Matheson Gas Products, Model 3122-350

Regulator, helium, two-stage, high purity, Matheson Gas Products, Model 3122-580

Wavelength Dispersive X-ray Fluorescence Spectrometer (WDXRF), equipped for x-ray detection in the 4.7 Å range, PANalytical. For optimum sensitivity to chlorine, the instrument should be equipped with the following:

Analyzing crystal, suitable for the dispersion of chlorine K α x-rays within the angular range of the spectrometer employed. Germanium or other materials such as pentaerythritol can be used.

Gas proportional detector, designed for the detection of long wavelength x-rays

Optical path, helium

Pulse height analyzer, or other means of energy discrimination

X-ray tube, capable of exciting chlorine K α radiation. Tubes with anodes of rhodium or chromium are preferred although other anodes can be used.

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Bottle, 125 mL (4 oz.) clear glass, case of 24, for preparation of chlorobenzene stock solution, standards, and precision samples, VWR International, Cat. No. 10861-778

Bottle, 1000 mL (32 oz.) clear glass, with PE Cone-lined cap, case of 12, for preparing and storing 3:1 iso-octane-toluene base matrix blank, VWR International, Cat. No. 10861-760

Chlorobenzene, 99.9 % for HPLC, for use in preparing chloride calibration standards, Sigma-Aldrich, Cat No. 270644 CAS No. 108-90-7

Counting gas, for instruments equipped with flow proportional counters, P-10 ionization Gas, 10 vol.-% methane balance argon, Airgas, Cat. No. X02AR90D2000291

Helium, minimum purity 99.9%, local supply

Iso-Octane, HPLC, GC grade, for use in preparing chloride calibration standards, Burdick & Jackson, a Honeywell company, Cat. No. 362

Liquid sample cells, compatible with the sample and the geometry requirements of the spectrometer; disposable cells are recommended, PANalytical, Cat. No. 9430-500-00521

Toluene, ACS/HPLC grade, for use in preparing chloride calibration standards, Burdick & Jackson, a Honeywell company, Cat. No. AH347

Vial, clear borosilicate glass, 30 mL capacity, polycone-lined cap, case of 144, for preparing calibration standards, VWR International, Cat. No. 18087-086

X-ray transparent film, 3.5 μ , any film that resists attack by the sample, is free of chlorine, and is sufficiently x-ray transparent, compatible with the spectrometer. Mylar™ film is recommended, PANalytical, Cat. No. 9200-130-08041

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of x-ray fluorescence spectroscopy, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Preparation of Calibration Standards

The calibration described here uses a base matrix of Iso-Octane - Toluene (3:1) and is suitable for gasoline blends. Other types of liquid hydrocarbon may require calibration standards made from base matrices more similar to them in density and that better match their x-ray absorption properties.

- Using a graduated cylinder, prepare a suitable quantity (about 1000 mL) of blank matrix solvent by combining three parts iso-octane with one part toluene and mix thoroughly. As an example, one liter of matrix blank solution should contain 750 mL iso-octane and 250 mL toluene. Verify ahead of time that these reagents do not contain detectable levels (by XRF or Combustion Ion Chromatography) of chloride.
- Prepare a stock solution of chlorobenzene (C_6H_5Cl) in 3:1 isooctane –toluene - 5000 mass-ppm Chloride. Note: Check the certificate of analysis to ensure chlorobenzene purity $\geq 99.9\%$.
 - Place a clean, dry 125 mL glass bottle on an analytical balance and tare. Dispense 0.794 grams into the bottle and record the mass to nearest 0.0001 gram.
 - Add 3:1 iso-octane–toluene base matrix solution to the bottle to bring the solution mass to 50 grams. Record the mass to the nearest 0.0001 gram.
 - All solutions should be weighed in capped containers to control evaporation induced weight changes.
 - Cap the container and mix the contents vigorously to homogenize
- Calculate the actual concentration **C** of the stock solution using equation 1:

$$C = \text{Chloride, ppm} = \frac{A (31.497) 10^4}{B} \quad (1)$$

where:

31.497 = Cl concentration in Chlorobenzene, mass-%

A = Actual mass of chlorobenzene, grams

B = Total solution mass, grams

C = Chloride concentration of the stock solution, mass-ppm

10^4 = Factor to convert mass-% to mass-ppm

- Prepare a set of calibration standards using the chlorobenzene stock solution and diluting to total solution mass with the 3:1 iso-octane-toluene base matrix solution as outlined below (Table 1). Record the mass of stock solution used and total solution mass for each calibration standard. Calculate the actual concentration **F** of each standard using equation 2:

$$F = \text{Chloride, ppm} = \frac{CD}{E} \quad (2)$$

where:

C = Chloride concentration of the stock solution, mass-ppm (from equation 1)

D = Actual mass of stock solution used, grams

E = Total solution mass after dilution with base matrix, grams

F = Actual concentration of each standard

- This method uses two calibration curves, 5 mass-ppm to 50 mass-ppm (low-range) and 50 mass-ppm to 1000 mass-ppm (high-range).
- For the low concentration range standards at 0, 5, 7.5, 10, 20, 30, and 50 mass-ppm chloride concentration are recommended.
- For the high concentration range standards at 0, 50, 75, 100, 200, 300, 500, 750, and 1000 mass-ppm chloride concentration are recommended.
- Larger quantities (e.g. 100 mL) of test samples may be prepared for later use in the precision analysis. Alternatively, routine samples may also be used for precision analysis if their chloride concentration is within the scope of the method.

Table 1**Guidelines for preparing calibration standards**

Target Concentration (mass-ppm)	Stock Solution (gram)	Total Solution Mass (gram)	Target Concentration (mass-ppm)	Stock Solution (gram)	Total Solution Mass (gram)
1000	4	20	50	0.2	20
750	3	20	30	0.12	20
500	2	20	20	0.08	20
300	1.2	20	10	0.04	20
200	0.8	20	7.5	0.03	20
100	0.4	20	5	0.02	20
75	0.3	20	0	0	20

Measuring Liquid Samples and Standards by XRF

Samples are measured in special liquid cells that include a thin, x-ray-transparent film support. The sample cells are assembled together with the film to form a liquid-tight container that supports the liquid sample over the x-ray tube during the measurement. Various support films are available; Mylar film (3.5 micron thickness) was chosen for this application because it is highly resistant to chemical attack by the gasoline matrix and also has good tensile strength. Standard and routine samples should be prepared as follows.

1. Assemble a disposable sample cell according to the manufacturer's instructions.
 - Ensure that the x-ray transparent film is stretched taut, flat, and is free of wrinkles. Wrinkles in the film will affect the intensity of the x-rays transmitted.
 - Care must be taken to avoid touching the inside of the sample cell or any part of the window film, especially with bare skin. Oil left behind in fingerprints on x-ray support film contains enough chloride to cause an erroneously high measured concentration result when analyzing samples with low levels of chloride.
2. Pour the liquid sample in the assembled disposable sample cell and snap the lid in place. Place the sample cells on clean paper for 5 minutes to check for leaks in the Mylar film. Transfer the contents of any leaking sample cells into a new cell and leak-test again. Samples passing the leak test are ready to analyze.
 - Ensure that the liquid sample cell is filled above a minimum depth, about 1 cm, beyond which additional sample does not significantly affect the measured count rate.
 - Leak testing is important to prevent damage to the x-ray instrument!

Spectrometer Conditions for Chloride Analytical Program

The choice of x-ray spectrometer settings for parameters such as sample excitation, diffraction crystal, x-ray peak angle, detectors, counting times, etc. are instrument dependent. For best results, set up the XRF instrument according to the manufacturer's instructions for measurement of the element chlorine. Assemble the measurement and calculation programs according to the instrument software requirements.

The measurements described in this method were made using a PANalytical Axios Advanced XRF spectrometer operating at 4 kW power. Two separate measurement applications were established, one with a low range calibration (5 - 50 mass-ppm Cl) and the other a high-range calibration (50 – 1000 mass-ppm Cl). The Automatic Program Selection (APS) feature of the PANalytical software was set up to automatically select the calibration most closely-matched (low- or high-range) to each routine sample.

WDXRF spectrometers available from other suppliers may be suitable for this method and may offer a feature similar to the APS discussed above. Follow the recommendations from the manufacturer of that specific instrument.

Establishing the Calibration Curve(s)

1. Prepare each of the chloride calibration standards for measurement as discussed above.
2. Input the identification and chloride concentration information for each standard in the instrument calibration program.
3. Measure the intensity of the emitted chloride radiation from each of the standards.
4. Calculate the regression of the calibration data points (net measured intensity of the chloride peak vs. chloride concentration) according to the manufactures instructions.
 - Use the instrument software to calculate a linear regression model, with the intercept not forced through zero. The RMS for the regression (a measure of the quality of fit) should be less than 0.1.
 - Perform the calibration procedure for each application covering a specific range.

Reference Analysis

Analyze a reference or Quality Control standard to verify the accuracy of the calibration. Determine if the calculated value agrees with the certified value, within the allowable difference shown in *Precision*. If the reference value does not fall within these specified limits, reconfirm the integrity of the calibration standards and check the instrument for proper setup and operation. Then re-establish the calibration curve as described above. Measure the reference sample at the beginning of each day that samples are analyzed and verify that the result lies within specified limits before proceeding to routine samples.

Sample Analysis

Routine samples and standards are prepared in the same way, as discussed above. When a routine sample is measured the calibration model is used to calculate the chloride concentration in the sample using the measured intensity of the chlorine x-ray peak. The calculation is done automatically in all modern XRF spectrometers. Samples whose calculated Cl concentrations are above the scope of this method (>1000 mass-ppm, or 0.1 mass-%) must be diluted with 3:1 iso-octane-toluene matrix blank and measured again. For example, samples containing 1 – 2 mass-% (10,000 – 20,000 mass-ppm) chloride will need to be diluted by a factor of 10 – 20 to bring the chloride concentration within the scope of the calibration. The dilution can be carried out as follows.

1. Place a clean glass sample vial on an analytical balance and tare the balance.
2. Use a clean disposable pipette to transfer some of the sample (e.g. 1.0 mL) into the container. Record mass to the nearest 0.0001 gram.
3. Add 3:1 Iso-Octane–Toluene base matrix to bring the solution to the desired mass, normally 10 grams. Record mass to the nearest 0.0001 gram.
4. Cap the container and mix the contents vigorously to homogenize.
5. Calculate the dilution factor, DF, using Equation 3.

$$DF = Mf / Mi \quad (3)$$

where:

Mi = initial sample mass, grams

Mf = final sample mass after dilution with 3:1 iso-octane-toluene, grams

DF = Dilution Factor

6. Measure the sample and then multiply the measured result times the dilution factor **DF** as calculated in equation 3 above to determine the actual Chloride concentration.

Calculations

Calculations of net corrected intensities, calibration regressions, and measured concentrations of undiluted routine samples are performed by the instrument software. The concentrations of diluted samples must be computed manually by calculating the product of the measured concentration reported automatically by the instrument and the dilution factor.

Reporting

Report results to the nearest mass-ppm. Results below 5 mass-ppm (limit of quantitation, LOQ) should be reported as < 5 mass-ppm.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods."

Repeatability and Site Precision

A nested design was carried out for determining chloride in three naphtha samples with nominal chloride concentrations of 10, 50, and 500 mass-ppm, respectively. Each sample was analyzed by two analysts, with each analyst performing two analyses on two separate days for a total of 24 analyses. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated at the concentration means listed in Table 1. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 1 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 1 with 95% confidence.

Table 2
Repeatability and Site Precision, mass-ppm
Repeatability **Site Precision**

<u>Sample</u>	<u>Mean</u>	<u>Within Day ESD</u>	<u>Allowable Difference</u>	<u>Within Lab ESD</u>	<u>Allowable Difference</u>
Sample A	9.7	0.41	1.6	0.46	1.8
Sample B	49.9	0.75	2.9	1.03	4.0
Sample C	504	0.80	3.0	1.90	11.0

The data in Table 1 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Time for Analysis

The elapsed time and labor requirement for a single chloride analysis is the same, 0.5 hour.

Suggested Suppliers

Airgas, 1601 Nicholas Blvd., Elk Grove IL 60007, USA, 1-847-434-5300, www.airgas.com

Burdick & Jackson a Honeywell company, 1953 S. Harvey Street, Muskegon, MI 49442, Customer Service: 1-800-322-2766

Matheson Tri-Gas, 150 Allen Rd. #302, Basking Ridge, NJ 07920, USA, 1-908-991-9200, www.mathesontrigas.com

PANalytical, 117 Flanders Rd. Westborough, MA 01581 USA, 1-508-647-1100, or, Lelyweg 1, 7600 AA Almelo, The Netherlands, +31 5465 34 444, www.panalytical.com

Sigma-Aldrich, Customer Support, P.O. Box 14508, St. Louis, MO 63178, 1-800-325-3010

VWR International, Radnor Corporate Center, Bldg. 1 Suite 200, P.O. Box 6660, 100 Matsonford Rd., Radnor PA 19087-8660, USA, 1-800-932-5000, www.vwr.com