



### Challenge

Is there a fast and accurate alternative to bomb digestion in combination with various detection techniques for total halogen determination in used oil?

### Solution

Combustion with subsequent coulometric detection integrated in one analytical system represents a reliable and automated method for determination of the total halogen content in used oil.

## Determination of Total Halogens in Used Oil

### Introduction

The term "used oil" essentially refers to utilized oils from technical applications. These used oils are of mineral, synthetic, or biogenic nature which, due to changes in their properties during regular use, no longer fulfill their purpose as lubricants or coolants and thus accumulate as waste. Engine oils, for example, need to be renewed regularly because abrasion particles and other pollutants accumulate in them, and the additives contained are used-up. Used oils must not be allowed to enter the environment, as they have a considerable water hazard potential. For this reason, take-back systems for used oil have been established in many countries, and improper disposal is prohibited. Vegetable oils used for cooking and frying are subject to different disposal regulations and are not included under the term used oil. What happens with the used oil? Priority is given to material recycling, i.e. used oil is purified again in refining processes and so-called base oils are produced, which serve as raw materials for new lubricants. In addition to recycling, recovery for the purpose of energy generation is also possible, so-called thermal recycling. The type of

recovery also depends on the pollutant content of the used oils. Here, the contents of PCBs (polychlorinated biphenyls) and total halogens (TX) play a decisive role. In Germany, for example, the German Used Oil Regulation (1) requires all recyclers to test the oils for both pollutant parameters before recycling. If specified limits (20 mg/kg PCB or 2 g/ kg TX) are exceeded, recycling is not possible (unless the limits are met in the product after purification). The Used Oil Regulation also regulates how testing is to be carried out. Various methods are available for determining the total halogen content, which represents the mass fractions of inorganically and organically bound chlorine and bromine in the anhydrous oil phase. After a preliminary test by means of energy-dispersive X-ray fluorescence analysis, the following reference methods are available: wavelength-dispersive XRF, digestion in a calorimetric bomb with subsequent halide determination (usually by means of ion chromatography) or another equivalent method. Combustion in a furnace specially designed for organic samples with subsequent coulometric detection of the halides is ideally suited for this

purpose. AOX/EOX instruments or so-called CNSX elemental analyzers can be used as analytical systems that combine digestion and detection. These systems represent a fast,

cost-effective and automatable alternative to the widely used bomb digestion with subsequent chlorine detection by various methods.

## Materials and Methods

### Reagents

- TX quality control standards: 4-chlorophenol in n-hexane and 2,4,6-trichlorophenol in isooctane
- Hydrochloric acid, 0.01 mol/L for testing the analytical performance of the coulometric cell
- Sulfuric acid, 98%, for drying after combustion
- Used oil samples, free of water

### Sample preparation

The water-free used oil samples were directly analyzed without further sample preparation.

In the case of oil samples containing water, this is separated before analysis with the aid of a separating funnel. The samples are then homogenized and dried by adding anhydrous sodium sulfate, which is then separated by centrifugation.

### Instrumentation

The total halogen content of the oil samples was determined using a multi X 2500 analyzer. The analyzer was configured in horizontal operation mode for this purpose. The horizontal combustion mode was selected because it offers the optimum conditions for quantitative digestion of samples with complex composition and higher viscosity. In this mode, the samples were fed to the furnace using an automatic boat drive (ABD) under control by the flame sensor. Sample dosing was carried out with the autoX 112. Other instrument configurations can also be used to determine the total halogen content (TX) in used oil, see Table 1 for details.

Table 1: Possible instrument configurations for the determination of the TX content in used oil

| Instrument configuration - components | AOX/EOX-Analyzer   | CNSX Elemental Analyzer  |
|---------------------------------------|--|--|
| Basic device                          | multi X 2500 (450-126.430)   | multi EA 5100 (450-300.011)  |
| Detector                              | "Cl-sensitive": already integrated in the basic device                 | Cl Module 5100 (450-300.023)<br>Extension kit "Cl-sensitive" (450-300.025)             |
| Extension for horizontal operation    | Automatic Boat Drive -ABD (450-126.416)<br>Extension kit (450-889.610) | Automatic Boat Drive -ABD (450-300.013)  |
| Sampling/ Automation                  | Universal Sampler - autoX 112 (450-126.690)<br>EOX Rack (450-889.528)  | Multi-Matrix-Sampler - MMS (450-300.030)<br>Liquids Kit (450-300.033)                  |
| Advantage                             | Usable for the determination of AOX and EOX                            | Upgradable for the determination of further elements, e.g. sulfur, nitrogen and carbon |



Figure 1: multi X 2500 and multi EA 5100

All waste oil samples were automatically injected into a quartz boat using a microliter syringe (equipped with a cannula with a large inner diameter). The bottom of the boat was covered with a quartz fleece to achieve a better distribution and evaporation of the sample. The sample boat was placed in the injection port of the automatic boat drive during sample injection. Following the injection, the sample was automatically transported further into the hot zone of the furnace. This process was controlled by a flame sensor, which automatically regulates the speed of introduction based on the intensity of combustion. This ensures safe, controlled sample evaporation and combustion and prevents the formation of soot and other incomplete combustion products.

### Method settings

All used oils were analyzed using a method for liquid samples. The process parameters are summarized in Table 2 and 3.

### Calibration

Calibration of the analysis system is not necessary, since coulometric detection is an absolute detection method. A 0.01 mol/L HCl was used to verify the analytical performance of the coulometer measuring cell. The complete method was checked using control standards 4-chlorophenol in n-hexane (control standard 1) and 2,4,6-trichlorophenol in isooctane (control standard 2).

The combustion of the sample took place in two phases. In the first phase, the sample was heated to 1,050 °C in an argon atmosphere, resulting in the vaporization of the volatile and pyrolysis of the low volatile organic compounds. The gaseous products were completely converted to hydrogen halides (HX) and other reaction products in an oxygen-rich atmosphere. In the second phase of the process, the combustion tube was completely purged with oxygen to ensure that all non-volatile pyrolysis products were converted to the analytes of interest. The combustion gases were dried with concentrated sulfuric acid and finally fed into a microcoulometric titration cell for halide determination.

Table 2: Method parameters

| Parameter                       | Setting    |
|---------------------------------|------------|
| Furnace temperature             | 1,050 °C   |
| 2nd combustion                  | 60 s       |
| Ar flow (1st phase)             | 100 mL/min |
| O <sub>2</sub> main flow        | 200 mL/min |
| O <sub>2</sub> flow (2nd phase) | 2 µL/s     |
| Draw up speed                   | 2 µL/s     |
| Injection speed                 | 3 µL/s     |
| Injection volume                | 40 µL      |

Table 3: Detection parameters

| Parameter             | Setting |
|-----------------------|---------|
| Max. integration time | 1,200 s |
| Cell temperature      | 23 °C   |
| Titration delay       | 30s     |

## Results and Discussion

The measurements were performed as triplicate measurements (with outlier elimination two out of three). The measurement results and the standard deviations obtained for the samples and the control standards are shown in Table 4. Representative measurement curves are shown in the following figures.

Table 4: Summarized results of the samples and control standards

| Sample ID                            | Concentration (TX) $\pm$ SD [mg/L] | RSD [%] |
|--------------------------------------|------------------------------------|---------|
| Used Oil 1                           | 705 $\pm$ 3.8                      | 0.5     |
| Used Oil 2                           | 2,011 $\pm$ 15                     | 0.7     |
| Used Oil 3                           | 157 $\pm$ 1.5                      | 1.0     |
| Used Oil 4                           | 269 $\pm$ 5.0                      | 1.9     |
| Used Oil 5                           | 35.8 $\pm$ 0.86                    | 2.4     |
| Control standard 1,<br>1,000 mg/L Cl | 998 $\pm$ 4.1                      | 0.4     |
| Control standard 2,<br>100 mg/L Cl   | 101 $\pm$ 1.5                      | 1.5     |

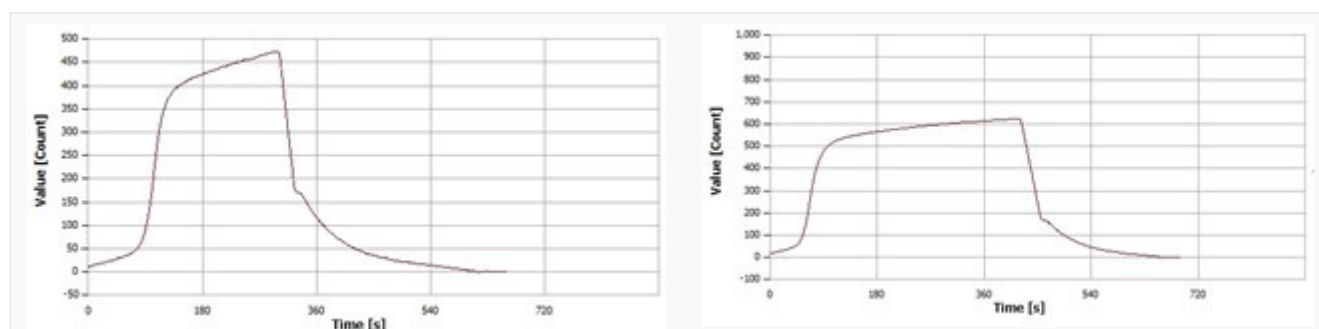


Figure 1: TX measurement curves of samples used oil 1 (left) and used oil 2 (right)

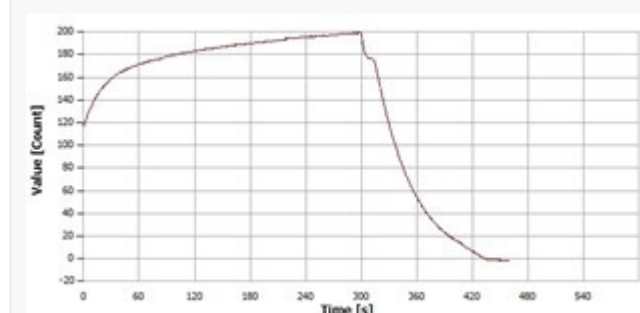


Figure 2: TX measurement curves of control standard 2

The results obtained illustrate that the total halogen content in used oils can be reliably determined using the combustion method followed by coulometric detection. The reproducibility was  $< 2.5$  % RSD for all samples. Dilution of the samples is not necessary even at higher contents, because the measuring range of the coulometer is up to 100  $\mu$ g TX absolute. The average measurement time was about 10 min.

## Conclusion

While two analytical methods and systems are necessary for the digestion in a calorimetric bomb and the subsequent detection of the halogens (e.g. by means of IC), the method presented here has the advantage of combining digestion and detection in only one analytical step in a single system. The combustion, which is controlled by the flame sensor, is always quantitative, and incomplete digestion, e.g. due to splashing of the sample in the bomb, is reliably excluded. Combustion followed by coulometric detection also offers the advantage of a high degree of automation, which

can significantly increase sample throughput for routine laboratories. The large dynamic measuring range of the coulometer allows the determination of both low and high concentrations of total halogen in used oils without prior sample dilution. Other system components such as the Auto-Protection system and the heated transfer line for the analytes ensure a high level of work safety and reliable results. Both systems, the AOX/EOX analyzer multi X 2500 and the CNSX analyzer multi EA 5100, are ideally suited for the automated determination of the TX content in used oils.

## References

- [1] Altölverordnung (AltöIV), BGBl. I 2002, 1375

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