

**Challenge**
Fast and reliable analysis of sulfur contents in the ultra-trace range in different types of liquid aliphatic and aromatic hydrocarbons and their mixtures.

**Solution**
Optimized vertical combustion combined with HiPerSens UV fluorescence detection for concentration-independent TS determination.

**Intended audience**
Laboratories and users in the refinery, petrochemical, chemical industries, producers and QC labs working with aromatic hydrocarbons and polymer intermediates.

# Determination of total sulfur in aromatic hydrocarbons and related chemicals by UV fluorescence according to ASTM D7183

## Introduction

Liquid aliphatic and aromatic hydrocarbons play an important role in refinery processes, the petrochemical, chemical and polymer industry, either as raw materials, process intermediates, or as end products. Regardless of their source or their further use, they all have in common that they need to be ultra-pure. This means that they have to be free of undesired compounds, as these could affect the production process and the quality of the final products.

Impurities such as sulfur-containing compounds not only affect the performance and economic life of the used catalysts (catalyst poisoning), but also form unwanted by-products and thereby decrease the quality of the end product. Therefore their content has to be kept as low as possible, preferably below 100 ppb. To make this possible, the exact knowledge of the present sulfur (TS) is required. Combustion-based elemental analysis coupled with a UV fluorescence detector is the only method that has proven to be suitable for this challenging task.

The compEAct S is an analysis system which has been specifically optimized for the fast and trouble-free determination of sulfur contents in the ultra-trace range. Combining catalyst-free high-temperature combustion and highly sensitive HiPerSens detection, it allows the determination of sulfur at concentrations ranging from 5 µg/l up to 10,000 mg/l with one and the same device.

analytikjena
An Endress+Hauser Company

# Materials and methods

## Samples and reagents

- Different aliphatic and aromatic hydrocarbons and their mixes (e.g. toluene, isooctane, naphtha)
- Isooctane ($C_8H_{18}$), Suprasolv®, GR for gas chromatography (Merck Art.-No.: 1.15440.1000)
- Dibenzothiophene ($C_{12}H_8S$), GR for synthesis (Merck Art.-No.: 8.20409.0025)
- Extended calibration standard kit Sulfur (0–10 mg/L) (Analytik Jena, Art.-No.: 402-889.061)

## Sample preparation

The samples are light volatile, have a low viscosity, and contain TS in the ultra-trace level. This made a pretreatment step redundant. The samples were analyzed directly.

## Calibration

Prior to the actual determination, the system was calibrated using sulfur standard solutions based on dibenzothiophene (S) in isooctane in the range of 0 to 200 ng S. Figure 1 and 2 depict typical calibration curves and performance parameters for ultra-trace applications. The calibration was checked with different concentrated standards

| calibration range | 1 |
|---|---|
| measurement range [µg] | 0 - 0.2 |
| measurement range [AU] | 91 - 79,514 |
| $k_0$ | -40.38 |
| $k_1$ | 397,642.5 |
| coefficient of determination, $R^2$ | 0.99999 |
| calculation volume, $V_{Cal}$ [µl] | 20 |
| calculation density, $\rho_{Cal}$ [-] | - |
| detection limit [µg/l] | 20.7 |
| quantification limit [µg/l] | 80.55 |
| method standard deviation [µg/l] | 13.57 |
| method coefficient of variation [%] | 0.49 |
| linearity | linear |

Figure 1: TS calibration for ultra-trace range

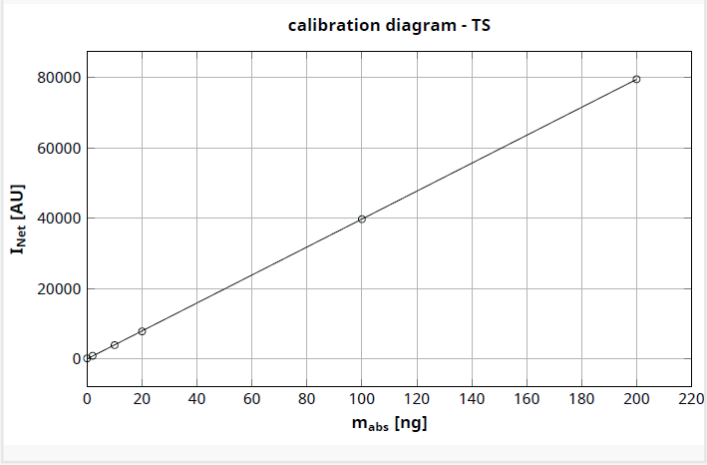



Figure 2: Wide-range calibration curve of the HiPerSens UVF detector

## Instrumentation

The measurements were performed using a compEAct S, equipped with HiPerSens UV fluorescence detection for the determination of sulfur. Sample introduction was carried out fully automatically using the LS 2 liquids sampler to ensure a high sample throughput.

The analyses have been run in vertical operation mode. The samples were dosed directly into the evaporation zone of the quartz glass combustion tube. This process took place fully automatically by means of the LS 2 high-throughput autosampler. The catalyst-free, bi-phasic combustion process is carried out at temperatures of up to 1050 °C. In the first process phase, evaporation of volatile sample components in an inert gas stream takes place, followed by the combustion of the formed gaseous products in an oxygen-rich atmosphere. In the second phase the heavier, nonvolatile sample components and formed pyrolysis products are quantitatively oxidized in pure oxygen. Thereby the quartz pyrolyzer ensures a uniform evaporation, modulates the combustion process, and prevents incomplete combustion. This establishes the best conditions for a reproducible and fast ultra-trace analysis. The implemented Auto-Protection System (particle and aerosol trap) guarantees highest operational safety and a complete transfer of the formed $SO_2$ into the UVFD, after a sufficient drying of the reaction gases. The compEAct S enables a detection limit of as low as 5 µg/L S

### Method parameters

The standard method ASTM D7183 from the method library of compEAct's EAvolution software was used for all analyses. The following table summarizes the parameter settings for the combustion process.

Table 1: Process parameters compEAct S

| Parameter | Specification |
|---|---|
| Furnace temperature | 1050 °C |
| Second combustion | 60 s |
| Ar flow (first phase) | 150 mL/min |
| $O_2$ main flow | 200 mL/min |
| $O_2$ flow (second phase) | 150 mL/min |
| Draw up | 2 µL/s |
| Injection volume | 40 µL |
| Injection | 0.5 µL/s |

### Evaluation parameters

Standard method settings were applied. The parameter settings are summarized in the following table.

Table 2: Detection parameters UVFD

| Parameter | Specification |
|---|---|
| Max. integration time | 300 s |
| Start | 1 cts |
| Stop | 1 cts |

## Results and discussion

The examined samples are a representative spectrum of hydrocarbons from refinery applications, the petrochemical and chemical industry as well as in polymer production. The results given in Table 3 are averages of three replicate analyses of samples and test standards. For all samples and standards an injection volume of 40 µL was used. Figures 3–6 show typical measuring curves for selected samples resp. standards.

Table 3: Results of the TS analysis

| Measurement | TS | SD |
|---|---|---|
| Isooctane | 48.9 ppb | ± 1.22 ppb |
| Xylene (mix of isomers) | 272 ppb | ± 2.02 ppb |
| n-Hexane | 36.3 ppb | ± 1.42 ppb |
| Toluene | 51.1 ppb | < 1 ppb |
| Acetone | 42.7 ppb | < 1 ppb |
| Naphtha (light) | 632 ppb | ± 3.27 ppb |
| TS Standard (c = 725 ppb) | 724 ppb | < 1 ppb |
| TS Standard (c = 74.8 ppb) | 72.7ppb | ± 2.14 ppb |

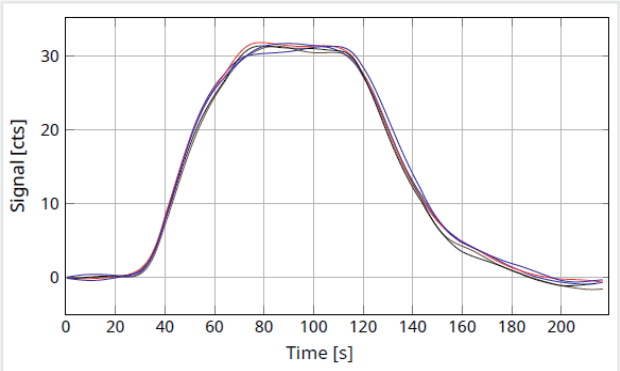



Figure 3: TS analysis curve for sample "Naphtha"

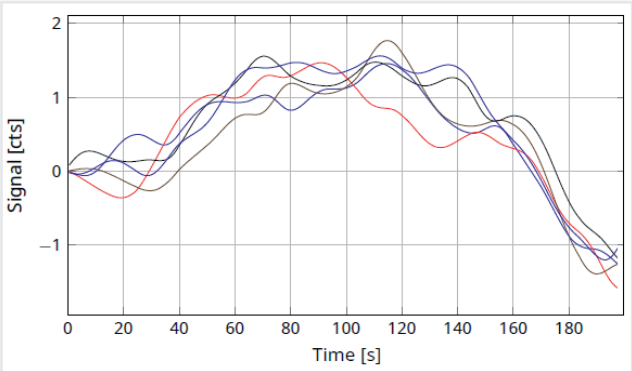



Figure 4: TS analysis curve for sample "Xylene"

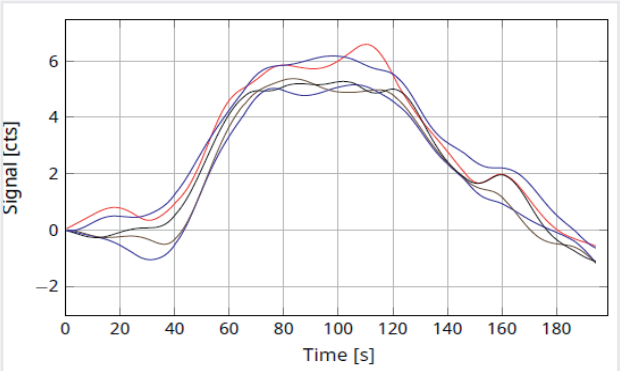



Figure 5: TS analysis curve for TS standard "74.8 ppb S"

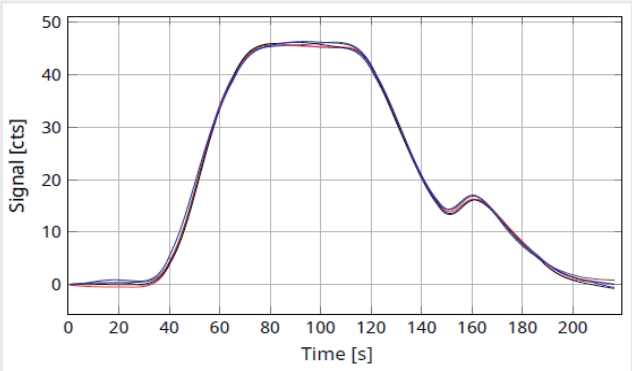



Figure 6: TS analysis curve for TS standard "725 ppb S"

Due to the optimal process conditions a three- to fivefold determination, with injection volumes between 20 and 40 µL per replicate analysis, is generally sufficient to reach satisfying results for ultra-trace applications. This significantly affects the sample processing time and thereby generates a higher sample throughput. Utilization of large injection volumes and time-consuming strategies like trap and release are redundant. The obtained analysis results and their reproducibility depict the high quality of the sample combustion. The proper performance of the analysis system was confirmed by analyzing standard materials with known sulfur contents (see Table 3).

## Summary

The compEAct S is extremely well suited for the measurement of ultra-trace sulfur concentrations in versatile aliphatic and aromatic hydrocarbons and their mixes (e.g., naphtha, toluene, xylene, acetone). The detector, with its unique HiPerSens technology, achieves a measuring range of up to 10,000 mg/l starting at a limit of detection as low as 5 µg/L of sulfur.

The optimal sample digestion and the efficient Auto-Protection system, including a high-capacity membrane dryer, enable excellent reproducibility, independent of the TS concentration or digestion characteristics and composition of the sample matrix analyzed. A high sample throughput is easily achieved by using the LS 2 liquids sampler. For lower throughput demands the LS 1 liquids sampler resp. the AI auto injector can be used alternatively.

If required, the analyzer can be extended to include the analysis of gaseous and liquefied pressurized hydrocarbons at any time by adding a matrix-optimized sample supply system.




Figure 2: compEAct S with LS sampler

### Recommended device configuration

Table 3: Overview of devices, accessories, and consumables

| Article | Article number | Description |
|---|---|---|
| compEAct S | 450-300.001 | Analyzer for the determination of sulfur in liquids and gases |
| LS 2 | 450-900.451 | Autosampler for liquids |
| EAvolution software | 450-011.300 | Control and evaluation software |

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**Headquarters**
Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

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