



Determination of Mercury in Crude Oil

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Besides other heavy metal, crude oil also contains mercury in varying mass fractions. When refining the crude oil, the mercury must be removed to prevent contamination of the resulting products. A precise knowledge of the heavy metal content is decisive for the control of the refinement processes. In addition to the crude oil, the waste products of oil refinement, such as sludge, also contain mercury. Prior to disposing the refinement waste, it must also be examined for mercury.

The mercury concentration in crude oil is usually in the lower mg/kg range or below, therefore a highly sensitive measuring method is required. Refinement waste, on the other hand, can contain several percentage points of mercury, making a flexible analysis system necessary, which can analyse both very small and clearly increased concentrations, without significant carry-over effects. Usually cold vapor AAS or AFS is used, with atomic fluorescence (AFS) being characterised by lower detection limits and a clearly larger dynamic range. Both methods can be combined with an enrichment of the mercury by amalgamation in a gold net to further increase the measuring sensitivity. Due to the wider analysable concentration range, cold vapor AFS is the preferred method.

Common methods of heavy metal determination, such as AAS, AFS and ICP OES, usually process samples as aqueous solutions, oil samples must be mineralized prior to analysis. A simple dilution of the samples in a low viscosity solvent is usually not possible because of the heterogeneous nature of the samples. The particle-bonded element parts would be lost by sedimentation. Various standardized methods are available for mineralising oil samples; e.g., by ASTM. These are usually dry or wet incineration methods carried out in open crucibles. They are either carried out on a heating plate or in the muffle furnace. Alternatively, the samples can be mineralised in a microwave-assisted pressure digestion.

Whilst open digestion methods provide satisfactory results for numerous elements, they are unsuitable for volatile mercury. There is also the danger that the sample is contaminated by dust and thus distorts the measurements. Therefore, digestion in a sealed pressure vessel is the most reliable method of sample preparation.

Sample Preparation

Both the loss of volatile species and the contamination of the sample are largely precluded when using sealed pressure vessels. This is evident in table 1 where the recovery rates for mercury in certified reference



Figure 1: Microwave digestion system TOPwave

Table 1: Recovery rate (WFR) for mercury using different digestion methods

	ASTM D 5863-00a (muffle furnace) WFR [%]	Open wet incineration (heating plate) WFR [%]	Microwave pressure digestion WFR [%]
Kerosene (approx. 10 mg/kg)	2,0	-	98
Paraffin-base oil (approx. 10 mg/kg)	2,2	-	91
Refined oil 20 cSt (approx. 10 mg/kg)	2,1	-	99
Conostan standard (100 mg/kg)	-	54	-
Naphtha 1	-	-	88
Naphtha 2	-	-	91
Naphtha 3	-	-	92
Heavy oil 1	-	-	94
Heavy oil 2	-	-	98

materials or spiked real samples are compared by various digestion methods. Both open methods apparently lead to significant analyte losses. Only in the pressure vessel can the samples be digested without significant losses.

Microwave-heated pressure digestion also allows a precise reaction control through power output, controlled by temperature and pressure. Oil samples can contain very reactive components that can already react exothermically at a low temperature. To keep such reactions under control, a precise monitoring of the individual digestion vessels is useful to adjust the heating output in accordance with the progression of the reaction. The digestion duration is also reduced significantly compared to open methods.

These and other samples were digested in the microwave system TOPwave (figure 1), equipped with the high performance vessels CX 100 (100 mL, max. 300°C, max. 100 bar). For this a mixture of 6 mL nitric acid, 2 mL hydrochloric acid and 2 mL hydrogen peroxide was used together with the temperature program shown in table 2. The program contains two steps at low temperature to digest reactive sample components. The stable components are then mineralised at high temperature. The sample weight was 100 - 200 mg in each case.

Step	1	2	3
Temperature [°C]	130	160	230
Max. pressure [bar]	80	80	100
Max. output [%]	70	70	100
Heat ramp [min]	10	10	10
Hold time [min]	10	10	30

The system features a contact-free temperature and



Figure 2:

Cold vapor atomic fluorescence spectrometer mercur

pressure measurement individually for each digestion vessel. Because every sample can be monitored separately, comprehensive reaction control is possible. Because the measuring methods work using optical methods and without sensors in the digestion vessel, handling the vessels is very easy and due to the use of optical measuring principles there are also not wearing parts.

When using digestion vessels from PTFE there is the occasional risk of adsorption of mercury in the pores of the material. The use of quartz vessels is therefore recommended. This is not necessary for digestion vessels of Analytik Jena, because the PTFE-TFM material is processed using a patented method drastically reducing the porosity and related analyte adsorption. This is evidenced by the very good recovery rates for mercury.

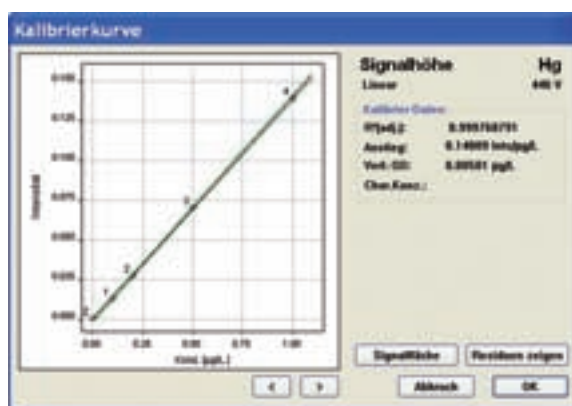


Figure 3: Calibration used for AFS determination

Analysis

The analysis of mineralised samples is carried out using the cold vapor atomic fluorescence spectrometer mercur (figure 2). The device operates using the principle of time-controlled flow injection. By means of a valve switchover the hydrochloric acid sample solution is introduced to the flow of a carrier solution and then fed to the reaction with tin(II) chloride. During the time when the sample valve remains open the sample volume can be defined with great precision. Thus a larger sample volume can be introduced for determination in the lower trace range in order to increase the measuring sensitivity, whereas a smaller sample volume is fed to the reaction for samples with higher concentration. The system can thus be adjusted

flexibly to the respective task via software control without requiring hardware modifications such as changing an injection loop. Depending on the measuring conditions only a 5-10 mL sample is required, leaving sufficient sample solution for determining other elements. If necessary, the measuring sensitivity can be further increased by adding a simple or double enrichment on the integrated amalgamation unit until a detection limit in the sub-ng/L range is reached. However, higher mercury concentrations up to the mg/L range can also be detected without carry-over effect.

The materials used and the gas and liquid tubes were optimised purposefully for minimum carry-over effect and low dead volumes. In addition, the control and analysis software features comprehensive routines for flushing the device and control functions, ensuring that the analyser is free from contamination. The system can be coupled with an automatic sampler with integrated dilution function and thus also process large sample series automatically. Standard series can be automatically prepared from a stock solution; the intelligent automatic sample dilution dilutes samples exceeding the calibration range automatically by the correct factor. This technology makes mercury analysis child's play both in the routine and the research lab and copes with all analysis tasks (See Figure 3).

Summary

Microwave digestion is currently the most reliable method for preparing crude oil and similar samples. It provides the necessary reaction control for the reliable digestion even of reactive samples and ensures at the

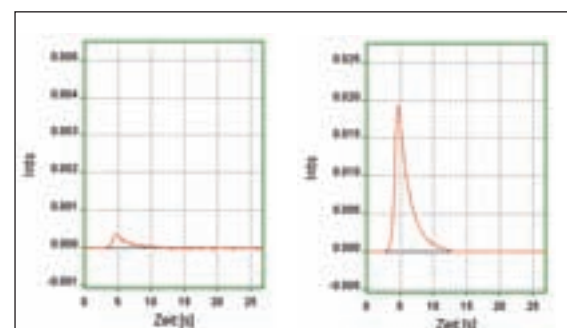


Figure 4 a and b:

- a) Original sample Naphta 1 after microwave digestion
b) sample Naphta 1 spiked with 0.2µg/L Hg

same time that all samples reach the necessary temperature for the mineralisation of stable components. The use of sealed vessels prevents the risk of the loss of volatile element species such as organic metal compounds or elementary mercury. The risk of contamination from dust entering or between samples is also almost precluded unlike in classic open digestion. The fast heating and cooling allows many samples to be processed in a short time with an unsurpassed quality of the digestion solutions. Combined with flexible analysis systems such as mercur and HR-CS AAS (High-Resolution Continuum Source AAS) all tasks required in the crude oil refining industry can be carried out with great reliability.

A New Era of Density and Refractive Index Meters to the Petrochemical Industry

Mettler Toledo (Switzerland) is delighted to announce the new LiquiPhysics™ Excellence instruments for density and refractive index determinations within the petrochemical industry. The new LiquiPhysics™ Excellence density- and refractometers are simple to operate and very robust, making them the ideal tools to easily deal with the high demands of the petrochemical industry environment. The One Click™ user interface allows quick, simple and direct access to all routine tasks, and provides clear user information utilizing shortcut buttons to start routine tasks immediately. Every operator has a personalized home screen, shortcuts and operation language. Bubble Check™ and other error recognition possibilities eliminate measuring errors, whilst barcodes automatically ensure the right measuring method is always chosen.

Operators needing to wear heavy-duty protective gloves, due to exposure to dangerous chemicals, can start a measurement by simply waving their hand over ErgoSense™, a special hands-free sensor. No need to touch anything. Powerful sampling and automation units enhance the automated analysis of even the most demanding samples, such as bunker oils and, thanks to automated cleaning procedures, operator contact with poisonous solvents is prevented. LiquiPhysics™ provides these benefits and much, much more. Full modularity protects investments and allows the combination of density with refracto-, color- and/or pH-meters. This supports the simple expansion of measuring systems as and when additional needs arise, enabling the simultaneous determination of multiple parameters. Complete and secure traceability is only a click away with LabX™ PC software, making it easy to fully comply with the many regulatory demands facing the petrochemical industry. Sophisticated barcode functions quickly and conveniently input sample data, and automatically ensure the right measurement method is always chosen. Comprehensive testing and error detection functions, along with automatic adjustment verifications, offer tight security to ensure the instruments consistently provide precise results.



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Application for Optimised Determination of Sulphur in Fuels

Due to the increasing shortage of valuable raw materials such as mineral oil and natural gas, alternative fuels and the synthesis of substitute fuels from biomass (biodiesel, bioethanol etc.) are rapidly gaining in importance. On one hand, the basic materials which often contain extremely high levels of sulphur and, on the other hand, virtually sulphur-free end products with traces of sulphur of < 100 ppb have to be properly controlled. This requires the analysis technology itself to be just as varied as the new challenges facing sulphur analysers in fuel analysis, in order to meet requirements.

The multi EA® 5000 by Analytik Jena (Germany) is a multi-matrix analyser which has been especially developed for determining sulphur contents in a uniquely wide concentration range for all fuel types, whether in a gaseous, solid, or liquid state. The fully-automatic, matrix optimised dosing technique guarantees highest precision during sample preparation, while eliminating potential operator errors. This combined with the highest safety standards is especially important during the analysis of complicated matrices such as liquefied gases under pressure (CNG, LPG etc.). Just as modern fuels are varied, so are the demands they place on the combustion process. Failure to take this into account in the selection of the process parameters may quickly lead to incomplete combustion, thereby significantly impairing analysis accuracy and operational safety. Conventional systems require a special method for each sample to be analysed. The multi EA® 5000, in contrast, only works with one method. Optimisation of the process parameters to the respective samples is achieved here fully automatically, using flame sensor technology during combustion.

The use of the intelligent wide-range principle of the UV fluorescence detector facilitates reliable determination of sulphur contents in the range of ultra traces up to mass percent in a single analysis cycle. It has a fully automatic sample preparation to ensure maximum precision and safety as well as a flame sensor and double furnace technology for matrix-optimised sample digestion. In addition, it provides a reliable coverage of the relevant concentration range from ultra traces up to mass percent and includes an integrated safety system (Self Check System) and automatic system tightness tests (high-performance gasbox); to ensure maximum operational safety even during the analysis of critical sample matrices such as liquefied gases. It is ideally suited for shift operation with minimal maintenance requirements and can be extended at any time for C/N/Cl analysis and determination of important environmental parameters TOC/AOX/EOX.

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Software for Comprehensive Chromatography Offers In-depth Insights at any Point in the Process

Shimadzu (Germany), has introduced its brand-new ChromSquare software, designed for analysis of data from Comprehensive Chromatography. At any point in the process, ChromSquare is capable of delivering in-depth insights on the sample. ChromSquare has been launched at the 34th ISCC event (International Symposium on Capillary Chromatography) in Riva del Garda, Italy. At the same event, the new quadrupole series also had its world premiere with the introduction of the GCMS-QP-2010 Ultra and GCMS-QP-2010 SE systems. The new series is by far the fastest and most sensitive system worldwide.

In both LC and GC product ranges, Shimadzu offers equipment with unique capabilities for fast data acquisition. This is extremely important for the method of Comprehensive Chromatography, where all compounds of a sample are analyzed by two columns of different separation mechanisms. In this way, the separation capacity of a chromatographic system is highly increased. Developed from analysts for analysts in the laboratory of Prof. Luigi Mondello at the University of Messina / Italy, ChromSquare provides all means for quantitative and qualitative analysis of data from Comprehensive LC or GC, with and without MS detection.

Even more, it makes data handling very easy. Simultaneous display of raw data chromatogram and contour plot in one window gives users an overview of their data at any time. Based on data generated with GCMS-QP2010 Ultra, it enables searching with Linear Retention Indices in various commercial MS libraries as well as user-generated databases. A simple click on a data point in the contour plot starts the library search for GCMS data. ChromSquare uses up to five libraries at the same time, including users' libraries. In GCMS analysis, SIM and Scan measurements in one run in Comprehensive mode lead to high quality results never seen before. For example: the minimum dwell time for SIM has been reduced to 1 ms. Now for the first time it is possible with Comprehensive GC to quantitate a set of target compounds and at the same time identify other compounds present in the sample. All of this data can be handled easily using ChromSquare software.

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