Hydrocarbon Processing Industry

Dear Readers,

Shuzo Maruyama

General Manager,
Analytical & Measurement Instruments Division

As COVID-19 maintains its grip on the world, Shimadzu Corporation would like to express our greatest sympathies to those affected by COVID-19. We would also like to offer our deepest condolences to the loved ones of those who lost their lives to this disease.

We believe in the power of science, and that it will get us through this pandemic. We have been engaging in various activities to support everyone who fights against COVID-19. On April 20, 2020, we released the "2019 Novel Coronavirus Detection Kit" in Japan. (This kit is Research Use Only and only available in Japan.) On September 8, 2020, we obtained approval from the Japanese Ministry of Health, Labor and Welfare for the marketing of the "Ampdirect 2019-nCoV Detection Kit" for in vitro diagnostics in Japan. In addition, we released the Automated PCR test system, on November 2020 in Japan. We will continue to make every effort to combat this crisis, applying the full capabilities of the Shimadzu Group.

Despite the issues caused by COVID-19, we have continued to develop new applications to support activities in a range of markets. In this issue, we highlight recent trends, the utilization of Shimadzu products, and new applications in the Hydrocarbon Processing Industry (HPI).

We start with two interviews in which users introduce the GC-SCD and their relationship with Shimadzu. The first is with Dr. Pan Yi, the deputy director of the Chemistry Research Division, National Institute of Measurement and Testing Technology. He discusses his relationship with Shimadzu and the reason why Shimadzu was chosen as their partner. In the second one, Dr. Pierre Giusti, the co-founder and scientific coordinator of the International Joint Laboratory i-C2MC (Complex Matrices Molecular Characterization), and Dr. Marco Piparo, the GC lab manager at Total, discuss their research and partnership with Shimadzu. An application report from this project, "Reliable Sulphur Detection in Petrochemistry", follows the interview.

In addition to the interviews, we highlight three applications. The first one introduces a new analytical method for analysis of fuel as an alternative to the FIA method. The second showcases an analysis of sulfur in fuels by Energy-Dispersive X-ray Fluorescence Spectrometry. Lastly, we introduce the use of Frequency-Modulation Atomic Force Microscopes for analysis of lubricants.

The HPI market, encompassing petroleum refining, gas processing, petrochemicals and chemicals, is a foundational field. With a wide range of products, from GC and elemental analyzers to an on-line water quality analyzer, Shimadzu offers total support for all customers in the HPI market. We hope that this journal will be a great help for all of you. Your generous feedback is always appreciated.

Yours Sincerely,

Hydrocarbon Processing Industry Issue 2

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"We all share the same working concept and goals"

Main research content of NIMTT

The National Institute of Measurement and Testing Technology (NIMTT), as a comprehensive national research institute integrating legal metrological technology institution, third-party calibration and inspection agency, testing technology and standard research institution, mainly carries out the research of national metrological primary standards, metrological verification and calibration, product inspection and testing as well as engineering testing and evaluation. NIMTT has established and

secondary legal entity directly under NIMTT, specializes in the research of chemical testing technologies and metrological standards (reference materials), metrological verification/calibration and product inspection, and undertakes the quantity value transmission of instruments, metrology testing arbitration, product prototype testing and type evaluation in the national chemical field. As a secretariat unit, NIMTT has established the National Technical Committee for Standardization
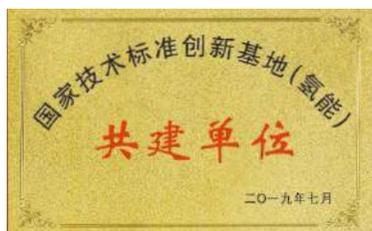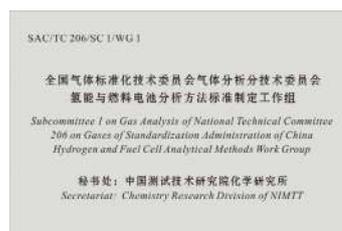
NIMTT is a research institute representing China which develops and supplies standard substances, and it has a laboratory which cooperates with Shimadzu.

preserved 38 national primary standard devices, 286 national metrology standards and more than 200 national reference materials involving chemical component measurement. It is the main technical institution participating in the construction of the national important physical quantity and national standard substance resource sharing service platforms, an important part of national quantity value transmission and traceability system, and a key contributor to ensuring the accuracy and uniformity of national quantity values.

The Institute of Chemistry, National Institute of Measurement and Testing Technology (Institute of Chemistry, NIMTT), as the

of Testing Equipment for Operation Safety Technology of Power-Driven Vehicles (SAC/TC364), National Technical Committee for Standardization of Biochemical Detection (SAC/TC387) as well as Hydrogen Energy and Fuel Cell Analytical Method Work Group of Subcommittee 1 on National Technical Committee 206 on Gases (SAC/TC206/SC1/WG1), been committed to the standardization in the field of gas analysis and testing, presided over and participated in drafting a number of national standards on gas analysis and related national standards on the environmental field and natural gas field, and participated in the technology transfer of ISO/TC158 Analysis of gases and the drafting of international standards.

Dr. Pan

The Institute of Chemistry, NIMTT, relying on the strong scientific research ability and excellent scientific research team, has made fruitful achievements in scientific research on "national chemical reference materials" close to the technical issues of testing and standards urgently needed by the industry. In particularly, its research achievements in trace multi-component VOCs and sulfide gas reference materials have reached the international advanced level and the products are fully self-made, ensuring the quality safety and traceability of the testing data of relevant components. Meanwhile, NIMTT also provides professional customized technology services according

Nexis GC-2030 and SCD-2030 installed in the Hydrogen Energy and Fuel Cell Analytical Method Work Group lab

to the requirements of the enterprises and public institutions in the fields of environmental monitoring, petrochemical engineering, public security, fair trade and instrument R&D. NIMTT has established the key laboratory for natural gas quality control and energy measurement of CNPC jointly with China National Petroleum Research Institute to prompt the natural gas quality control and energy measurement in China; closely cooperated with CRAES and CNEMC to provide technical support of analysis and testing for environmental monitoring in China.

Application of Shimadzu instruments in your work

At present, the analytical instruments of Shimadzu are mainly used in the daily work of NIMTT in the following aspects:

(1) Quality control of reference materials and development of analytical methods for scientific research projects.

(2) Validation of national standards for gas analysis (provide validation and application demonstration for the development and revision of the national standards for gas analytical methods in the industries of industrial gas, ambient air, hydrogen energy, natural gas and coal chemical);

(3) Development and revision of national or local

analytical instrument verification regulations or calibration specifications in urgent need.

Reasons for NIMTT to choose Shimadzu as the partner

First, we all share the same working concept and goals. Shimadzu, since its establishment in 1875, has always adhered to the corporate philosophy "Contributing to Society through Science and Technology", continued study the science and technology leading the times and meeting social needs, developed and produced products with high added value for the society. NIMTT, as a comprehensive national institute of testing technology, is also committed to the development and establishment of the most of chromatography, mass spectrometry and spectroscopy of Shimadzu. It may establish the world's advanced integrated solutions of gas sample analysis for the industries such as environmental monitoring and petroleum gas chemical industry in China to solve the key testing technological problems urgently needed for the development of these industries.

Contributions of Shimadzu GC-SCD to NIMTT

GC-SCD method is widely used in industrial gas, hydrogen energy, coal chemical industry, natural gas and other related industries. It is mainly used for the analysis of trace sulfur forms and total sulfur content

Dr. Pan

in gas. NIMTT led the formulation of the national standard GB/T 33318-2016 Gas Analysis—Determination of Sulfide—Gas Chromatography with Sulfur Chemiluminescence in 2016, solving the long lasting problem of lacking standards in the industry. The standard is also about to be revised. The new-generation NexisSCD-2030 sulfur chemiluminescence detector of Shimadzu was released this year, and after its release in China. We conducted a series of tests on the performance of the instrument and obtained satisfactory results.

In this period, we participated in the verification test for the formulation and revision of the national standard for natural gas *Natural Gas—Determination of Sulfur Compounds—Part 10: Determination of Sulfur Compounds Using Gas Chromatography Method* and the petrochemical industry standard *Determination of Sulfur Compounds in Middle Distillate-Gas Chromatography and Sulfur Chemiluminescence Detector* and obtained satisfactory experimental data.

In terms of national standards for quality analysis methods of the hydrogen for fuel cell, we are researching and developing the preconcentration-GC-SCD method, which is expected for the analysis of the total sulfur in the hydrogen (total sulfur content not exceeding 0.004ppm). At present, we have preliminarily obtained the relatively ideal data. After further verification,

we hope to develop this method into a national standard to solve the world-class problem of trace sulfide measurement in hydrogen for the fuel cell industry.

Characteristics compared with competitive products

Through our experiments, Shimadzu GC-SCD has certain advantages over similar products in sulfide detection limit, repeatability, instrument operation, maintenance and software use. With our sulfide gas standard substance, trace gas analysis pipeline and valve injection analysis system, the repeatability of direct injection analysis for 1 μmol·mol-1 H2S/N2 gas standard substance is within 1%. The maintenance of the instrument ceramic tube is simpler and more convenient. The analysis software workstation is more in line with the operating habits of our laboratory staff.

Future expectations for Shimadzu

We established the "Gas analysis standardization and solution demonstration application laboratory" with Shimadzu this time based on our good cooperation with Shimadzu in the

Dr. **Pan**
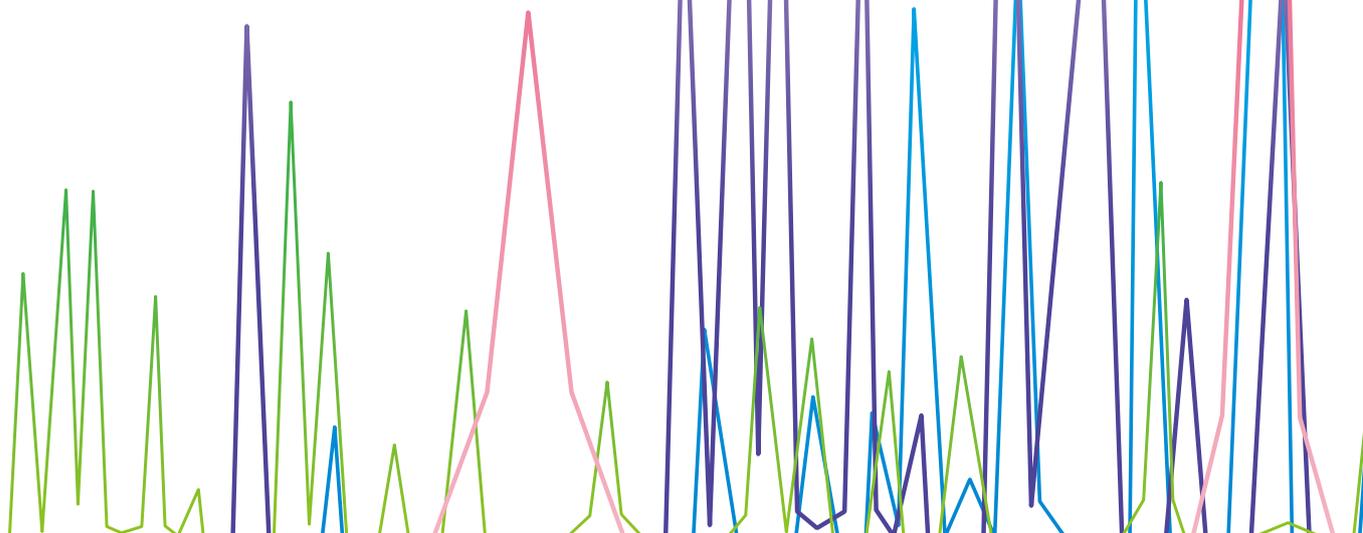
early stage. With the opportunity of the establishment of the united laboratory, NIMTT will, through the joint efforts, build the laboratory into a R&D base for tackling problems in key technologies in the field of gas analysis and testing, into a demonstration application base for incubation and transformation of gas analysis and testing results and into a public technology service platform for technology integration and technology radiation in this field to make newer and greater contributions to promoting the scientific and technological progress and career development in the field of gas analysis. Meanwhile, the research results of the united laboratory can be directly applied to the ambient air monitoring and chemical production, which will help improve the quality of environmental monitoring data and the production technology level of gas chemical industry in China and promote industry transformation and upgrading. The united laboratory will focus on the gas analysis technology of frontier industries, such as hydrogen fuel quality analysis. Relevant research results will strongly support the rapid development of hydrogen energy industry in China, which may help improve the quality level of hydrogen energy products and occupy the upper reaches of the industrial chain.

We hope that Shimadzu can cooperate closely with us, actively participate in the research work of the laboratory, and jointly develop more excellent analysis and testing solutions in line with the urgent need for industrial development.

About the author (in particular, papers or academic publications)

Pan Yi, master and associate researcher, is the deputy director of Chemistry Research Division, National Institute of Measurement and Testing Technology, deputy secretary general of Subcommittee 1 on National Technical Committee 206 on Gas of Standardization Administration of China Gas Analysis Technical (SAC/TC206/SC1), Head of Hydrogen Energy and Fuel Cell Analytical Method Work Group of National Technical Committee 206 on Gas of Standardization Administration of China
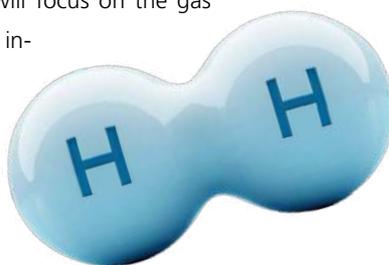
Gas Analysis Technical Committee (SAC/TC206/SC1/WG1), deputy director of Sichuan Analysis and Testing Society Spectral Analysis Committee, and the accreditation assessor of China National Accreditation Service for Conformity Assessment. Having been engaged in the research of chemical reference materials preparation technology and gas analysis methods; He has been responsible for the preparation of more than 20 national reference materials (including 6 kinds of national first-class gas reference materials) and participated in the development of more than 100 national reference materials. He presided over and participated in the preparation and revision of more than 10 gas analysis-related national standards, such as GB/T 38677-2020 "Gas Analysis-Measurement Process and Results-Technical Requirements for Calibration" and GB/T 33318-2016 "Gas Analysis-Determination of Sulfide-Gas Chromatography with Sulfur Chemiluminescence". His related research has been funded by more than 10 national, provincial and ministerial-level scientific research projects. He presided over the 2018 Sichuan Major Scientific Instruments and Equipment special project "Development and Application of Online Chromatograph on Natural Gas Energy Measurement"; The project "Research and Application of New Technology for Micro-trace Multi-component Gas Reference Materials Preparation" won the first prize of 2019 Chinese Society for Measurement Science and Technology Progress Award, and the main projects such as "Key Technology for Detection and Traceability of Environmental Micro-Trace Odor Sulfide Gas" and "The Development of Hydrogen Sulfide in Nitrogen Gas Reference Material at 1 μmol·mol-1 Level" won first prize and third prizes respectively; In the past 5 years, he has published more than 10 academic papers, including 5 SCI retrieval papers, and obtained 3 state-authorized patents.

Dr. Pan

In recent 5 years, he has been dedicated to the research of traceability system of hydrogen fuel quality inspection in the field of hydrogen energy and fuel cells, and the corresponding analysis method standardization system.

Representative Papers in Recent Five Years:

(1) 2017, In series connection of flame ionization detector and sulfur chemiluminescence detector for interference free determination of total sulfur in natural gas. Chinese Chemical Letters (SCI, first author)

(2) 2018, A study on preparation technology of 9-component volatile organic compounds solution reference materials. Chemical Reagent. Correspondence author. (SCI, second author)

(3) 2019, Determination of ultratrace tellurium in water by hydride generation atomic absorption spectrometry using online separation and pre-concentration with nano-TiO2 microcolumn. Microchemical journal (SCI, second author).

(4) 2019, Application of Sulfur Chemiluminescence Gas Chromatography in Gas Analysis. Second author.

(5) 2019, Cerium-based UiO-66 Metal-organic Frameworks Explored as Efficient Redox Catalyst: Titanium Incorporation and Generation of Abundant Oxygen Vacancies. Chemical Communications (SCI, second author, cover article).

(6) A selective cataluminescence sensor with a homemade gaseous sample introduction system for accurate and sensitive determination of H2S using catalytic g-C3N4@Fe. Microchemical Journal (SCI, first author).

(7) Recent advances in ratiometric luminescence sensors. Applied Spectroscopy Reviews (SCI, second author).

Joint laboratory with Shimadzu at NIMTT

Interview 2 | Interview with **Dr. Giusti** and **Dr. Piparo**

"Listen to our needs and problems, and constantly look to progress in the development of new instruments and concepts"

Dr. Giusti, thank you very much for spending some time on this interview. First, can you outline your research and let us know what discovery and achievements have been made so far?

Thank you for giving us the opportunity, with Dr. Piparo, to share our goals. The biggest part of the work in our R&D Analytical Department is to provide the tools needed by our industry, and eventually to support our businesses. One mission within that overarching goal is seeking out and evaluating new technology that could be potentially useful. When it comes to utility, there is a real demand for (analytical) information at the point of need – for us, that means considering ways of shifting robust analysis out of research laboratories and into control labs. It is within this context that we also provide analytical support to all other departments of our research direction in order to get a deep molecular understanding of our complex mixtures (crude oil fractions, pyrolysis oils, polymers). We are now looking at new challenges. In particular, the development and use of bio-based fuels and the recycling of plastics, whether mechanically or chemically after a pyrolysis step.

Why are you interested in this research? What is the goal?

Energy markets are changing, driven by climate change, technology and societal expectations. Our goals as analysts are to adapt and improve the methods historically developed for petroleum matrices, in order to establish molecular-level fingerprints of oil, new feedstocks and polymers. The ability to access molecular-level descriptions is a game changer. It enables us to better optimize the use of new feedstock, such as pyrolysis oils from plastic, and understand the fate of bio-based molecules in the refining scheme.

Could you tell us why you chose Shimadzu as your partner for this project?

To realize solutions for all these multiple projects, we need external collaborations that bring innovations and ideas. Our academic and instrument manufacturer

Meeting with Shimadzu Scientists

Dr. **Giusti** / Dr. **Piparo**

partners need to be willing to listen to our needs and problems, and constantly look to progress in the development of new instruments and concepts. Shimadzu fulfills all these characteristics.

In fact, it is in this context that we started a collaboration, based on a patent, for the development of a new kind of detector for oxygen speciation.

How are our instruments helping you?

For many years, Shimadzu has been providing several instruments that are important to our daily laboratory work. These include specific sulfur detectors (SCD), with completely new technology that allows us to determine and quantify potential sulfur compounds present in trace amounts, and mass spectrometers that allow high-speed scanning without loss of sensitivity or spectral distortion. But above all, the main feature is that they provide incredible robustness and stability over the years, ensuring stable measurements.

At the entrance of Shimadzu European Innovation Center.

Finally, could you share any requests that you have concerning analytical and measuring instrument vendors? How can we help you?

The implementation of a platform for regular discussion where we could, within our joint lab iC2MC, organize specific brainstorming sessions with Shimadzu experts in various techniques (elemental analysis, mass spectrometry, chromatographic separations) in order to better define our actual expectations.

About iC2MC
https://ic2mc.cnrs.fr/

▶ Dr. Pierre Giusti is specialized in Analytical Chemistry from proteomics to petroleomics. Focused on molecular analytical strategies for complex matrices/samples such as heavy crudes fractions, new bio-feedstocks and polymers, taking advantage of state of the art molecular separation techniques and mass spectrometry. Interested in instrumental developments with manufacturers. Co-founder and Scientific Coordinator of the International Joint Laboratory iC2MC (Complex Matrices Molecular Characterization) TOTAL - CNRS - Rouen University - Pau University - Florida State University. ~35 scientists involved.

▶ Dr. Marco Piparo is the GC lab manager in the Molecular Separation & Identification team in TOTAL RAFFINAGE CHIMIE. He has deep knowledge and experience researching high separation technologies such as multidimensional gas chromatography (GCxGC) for the detailed qualitative and quantitative characterization of complex matrices and the injection technique for high boiling point samples.

Reliable Sulphur Detection in Petrochemistry

An investigation using gas chromatography with sulphur chemiluminescence detection

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International Joint Laboratory — iC2MC: Complex Matrices Molecular Characterization, Harfleur, France

Abstract ▸ Sulphur compounds, even at low concentrations, are of high importance in petrochemical products as they can act as catalyst poisons in the refining process. This poses the need for sensitive, yet selective detectors providing reliable detection and quantitation of potential sulphur compounds. Using the example of diesel matrix, an investigation of petrochemical samples via gas chromatography (GC) combined with sulphur chemiluminescence detection (SCD) is presented. Selectivity, reproducibility, equimolarity and recovery of the setup are examined to judge reliability of the sulphur content determination.

sulphur amount in the fuels is steadily decreasing to the higher level of 10 ppm for diesel and gasoline. Since even low sulphur concentrations are harmful, already trace-level identification of potential poisons is essential. This creates the demand for a highly sensitive detector, which can also cope with the high matrix interference seen when analysing petrochemical samples. Universal detectors do not fulfil this condition, therefore sulphur selective detectors are the key to success.

Sulphur in petrochemistry

Sulphur compounds are of high importance in petrochemical products. Crude oils are even classified to be sweet or sour depending on their sulphur content: Sweet crude oils contain less than 0.5% sulphur, whereas sour ones hold more than 0.5% sulphur, part of it as H_2S[1]. Yet, compounds containing sulphur are non-favoured substances in petrochemistry. Besides the health risk H_2S poses by itself, sulphur compounds generate several problems because they are responsible of atmospheric pollutions (SO_2 and SO_3) and are proven to be poison for catalysts used in refining processes[2]. The

Sulphur chemiluminescence detection

Selective sulphur detection is particularly essential for high matrix load samples, as in these cases the hydrocarbon background cannot be separated chromatographically from the sulphur compounds, typically present in low concentrations down to trace levels. Flame photometric detection (FPD) is widely used for selective sulphur detection e.g. in food chemistry, but it suffers from hydrocarbon quenching and non-linearity of calibration curves[2]. Consequently, this detector is not an ideal choice for petrochemical samples where

the goal is to analyse the undiluted sample wherever possible. The detection method of choice is sulphur chemiluminescence detection (SCD), which is a technique both sensitive and selective and therefore common in petrochemistry to study the sulphur content of e.g. diesel or gasoline. Sulphur chemiluminescence detection offers increased selectivity and linearity when compared with flame photometric detection. Additionally, it shows the benefit of equimolar response, which facilitates quantitation of especially complex mixtures as it erases the need for an individual calibration of each target compound[2].

The reason for the advantages of sulphur chemiluminescence detection over FPD technique lies in its detection principle: The use of an oxidation-reduction sequence followed by a reaction with ozone creates excited SO_2^* molecules from sulphur containing compounds eluting from the column. These SO_2^* molecules can then be detected based on their chemiluminescence at a given wavelength range. The matrix entering the detection system mainly consists of hydrocarbon compounds, which in contrast create CO_2, that is not seen by the detector, making sulphur chemiluminescence detection a highly selective technique.

From a petrochemical perspective the second most important point is the equimolarity of the detection principle. Especially with a huge amount of different sulphur compounds being potential targets, an individual calibration for each target substance is not practical or even not possible. Due to the generality of the detection process, all sulphur containing compounds produce SO_2^* molecules, their number being dependent solely on the number of sulphur atoms in the molecule. Consequently, a disulfide produces two SO_2^* molecules leading to twice the response of a monosulfide. The response of different monosulfides is the same provided that the same amount of sulphur (in moles) is present. Therefore, when working with SCD technique concentrations of the target substances are typically given as concentrations sulphur (e.g. mg/L S), not as compound concentrations.

Samples and reagents

To investigate selectivity, reproducibility and equimolarity of the sulphur chemiluminescence detector for petrochemical samples, a matrix of desulphurized diesel with a remaining sulphur content below 10 mg/L was chosen as blank matrix. This was spiked with a mix of seven different sulphur compounds belonging to different sulphur substance groups relevant for diesel samples: sulfides, mercaptans and thiophenes. The investigation range was chosen as 10, 100 and 500 mg/L per target substance since higher levels of a single compound are highly unlikely to occur in diesel samples.

This resulted in concentrations sulphur of 1 to 4 mg/L S for the lowest level (level 1), 16 to 40 mg/L S for the medium level (level 2) and 82 to 200 mg/L S for the highest level (level 3) investigated, respectively (Table 1).

To investigate possibly occurring matrix effects, the target sulphur mix was spiked into hexane at the same three concentration levels to prepare pure solvent matrix solutions. By comparing the response in diesel and hexane matrix, the recovery of the system could be investigated.

Table 1. Standard mix of seven sulphur compounds, concentrations given as sulphur

#	Compound	Level 1 concentration (mg/L S)	Level 2 concentration (mg/L S)	Level 3 concentration (mg/L S)
1	Thiophene	4.02	40.18	200.89
2	Butyl mercaptan	3.62	36.25	181.23
3	2-Methylthiophene	3.39	33.87	169.34
4	tert-Butyl disulfide	3.97	39.72	198.61
5	Benzothiophene	2.56	25.59	127.97
6	Ethyl phenyl sulfide	2.29	22.95	114.74
7	Dibenzothiophene	1.65	16.54	82.69

Instrumentation

The sulphur samples were analysed using a Shimadzu Nexis GC-2030 system equipped with SCD-2030 sulphur chemiluminescence detector (fig. 1). A high split ratio of 1:100 was chosen since 1 µL of the undiluted diesel samples was injected into the GC using an AOC-20i Plus autosampler. Compound separation was realized using a Shimadzu SH-Rtx-1 column, with dimensions of 30 m length, 0.32 mm ID, 0.1 µm df. The temperature program was chosen to provide a typical screening method, not only ensuring good separation of the seven target sulphur compounds, but also allowing a closer investigation of the remaining sulphur content from the blank diesel matrix. This led to a chromatographic runtime of 63 min.

Fig. 1. Gas chromatograph GC-2030 with sulphur chemiluminescence detector SCD-2030

Selectivity and reproducibility

The desulphurized diesel matrix blank used for this study contained trace sulphur compounds in an overall content below 10 mg/L. It showed residues of benzothiophenes and dibenzothiophenes, but no considerable amounts of sulfides, disulfides, mercaptans and thiophenes, which would elute within the first minutes of the chromatogram (fig. 2). This allowed the usage for spiking with the sulphur standard mix, as the matrix does not provide significant signal for the target compounds. The spiked components elute in the early chromatogram range within 10 min, except for dibenzothiophene, which elutes later at 22.3 min. Yet, also this target component is nicely separated from the benzothiophenes and dibenzothiophenes present in the blank diesel matrix (fig. 3).

Nevertheless, background subtraction with the blank diesel matrix was performed for all analyses to consider even minimum matrix interference.

Comparing the desulphurized diesel matrix sample with hexane solvent matrix sample, no negative matrix effects were observed. The signals in the diesel sample are not shifted significantly as against the hexane sample (fig. 3). Similar base widths for the signals in both matrices were found, indicating no severe peak broadening due to the diesel matrix. This not only allows for convenient comparison of diesel and hexane samples with just one processing method, but also ensures detection limits to be as good in the diesel as in pure solvent, enabling sensitive, yet selective detection of the target compounds down to trace levels despite the high matrix load in the diesel sample.
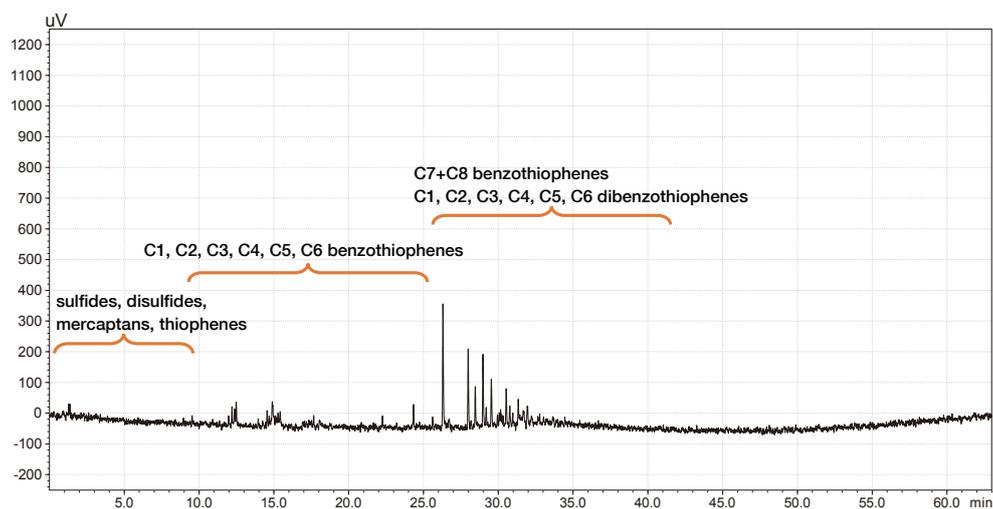

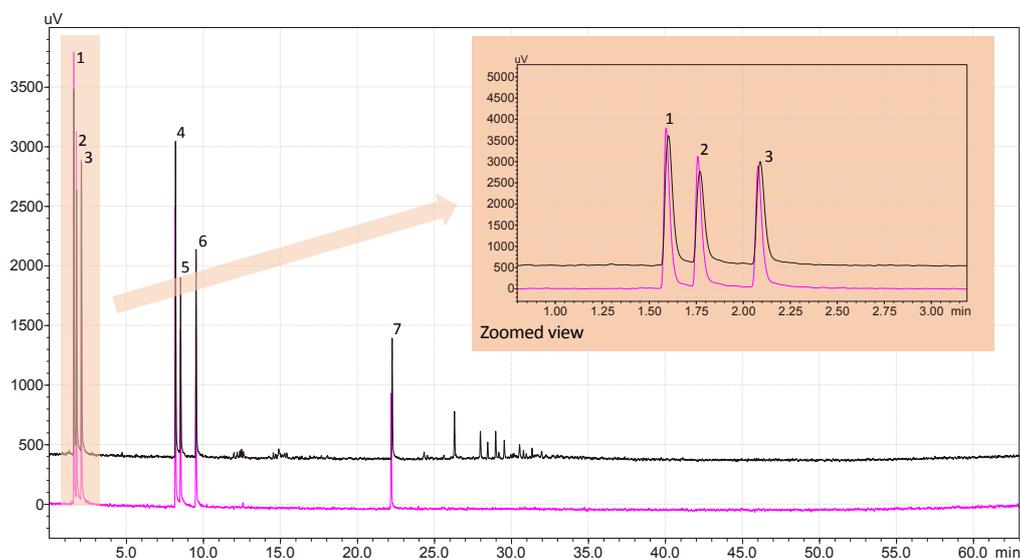Fig. 2. Chromatogram of the desulphurized diesel sample used as blank matrix

Fig. 3. Comparison view of the chromatograms for level 1 sulphur standard in desulphurized diesel matrix (black) and hexane solvent matrix (pink), chromatograms are base shifted for better visibility

To reveal reliability of the setup, consecutive measurements of the lowest level concentration (level 1) were performed, calculating the relative standard deviation (RSD) for retention times and peak areas (Table 2). Retention times were found to be highly stable with a reproducibility below 0.05% for all target compounds. Area reproducibility was below 4% for all spiked components, ensuring reliable detection and quantitation of the sulphur targets even at low concentrations.

Table 2. Relative standard deviations at
level 1 for n = 6 consecutive measurements

#	Compound	Retention Time (min)	%RSD Retention Time	%RSD Area
1	Thiophene	1.61	0.02	1.33
2	Butyl mercaptan	1.78	0.03	1.90
3	2-Methylthiophene	2.10	0.04	2.99
4	tert-Butyl disulfide	8.21	0.04	2.75
5	Benzothiophene	8.54	0.04	2.78
6	Ethyl phenyl sulfide	9.55	0.03	1.17
7	Dibenzothiophene	22.28	0.01	3.93

Equimolarity and recovery

Equimolarity of sulphur compound detection facilitates target substance calibration by providing a response for different compounds solely dependent on the amount of sulphur (in moles) being present. To provide a measure for this, relative response factors (RRF) can be used. The response factors (RF) calculated from area and concentration S for each compound are averaged over all compounds to determine values for the single response factors relative to the average value (RRF). In a perfectly equimolar detection, the response factors for all components are the same, resulting in an RRF value of 100 for every compound. The relative response factors determined for the hexane solvent samples and the desulphurized diesel matrix samples of all three levels investigated are summarized in Table 3 and 4. For the samples diluted in hexane, RRF values were between 90 and 115 for all compounds at all concentration levels; in the diesel matrix samples, RRF values were between 75 and 120. This demonstrates good equimolarity for not only the monosulphur compounds belonging to different substance groups, but also for the disulfide, independent of the chosen concentration level.

Recovery of the sulphur compounds in diesel matrix was

investigated by comparing the response in the desulphurized diesel matrix with the response in a hexane solvent matrix for all three concentration levels. The resulting recovery values were in the range 0.8 to 1.1 for all compounds at all levels (Table 5), ensuring reliable recovery regardless the target component concentration.

Table 3. Relative response factors (RRF) determined for
the hexane solvent samples at level 1, 2 and 3

#	Compound	Level 1	Level 2	Level 3
1	Thiophene	103.5	98.4	106.3
2	Butyl mercaptan	104.5	93.5	100.2
3	2-Methylthiophene	105.5	95.1	103.0
4	tert-Butyl disulfide	94.3	97.8	94.7
5	Benzothiophene	89.7	99.2	90.8
6	Ethyl phenyl sulfide	109.1	114.7	106.7
7	Dibenzothiophene	93.3	101.3	98.3

Table 4. Relative response factors (RRF) determined for
the desulphurized diesel matrix samples at level 1, 2 and 3

#	Compound	Level 1	Level 2	Level 3
1	Thiophene	103.7	98.3	104.8
2	Butyl mercaptan	93.7	74.8	81.4
3	2-Methylthiophene	107.9	99.5	104.5
4	tert-Butyl disulfide	100.6	100.9	98.1
5	Benzothiophene	90.5	98.5	92.9
6	Ethyl phenyl sulfide	107.4	120.2	113.1
7	Dibenzothiophene	96.2	108.0	105.1

Table 5. Recovery determined at level 1, 2 and 3

#	Compound	Level 1	Level 2	Level 3
1	Thiophene	1.03	1.01	1.01
2	Butyl mercaptan	0.92	0.81	0.83
3	2-Methylthiophene	1.05	1.06	1.04
4	tert-Butyl disulfide	1.09	1.04	1.06
5	Benzothiophene	1.03	1.00	1.05
6	Ethyl phenyl sulfide	1.01	1.06	1.08
7	Dibenzothiophene	1.06	1.08	1.09

Conclusion

Sulphur chemiluminescence detection using SCD-2030 enables selective detection of sulphur compounds in high matrix load petrochemical samples down to low concentration levels. Excellent selectivity and reproducibility ensure reliable results, while equimolarity for different sulphur target species facilitates the analysis of unknown sulphur compounds. Additionally, providing good recovery independent of the sulphur component concentration, SCD-2030 allows to accurately determine sulphur target substances both in lower and higher concentrations relevant for petrochemical samples.

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Analytical method for determining aromatics and olefins in fuel as an alternative to FIA method

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Fuels such as gasoline, diesel, and jet fuels used in automobiles and aircraft have various quality control parameters to ensure their performance and to comply with environmental regulations. Fuels consist of hundreds of different hydrocarbon molecules such as paraffins, olefins, and aromatics. Because aromatics and olefins affect combustion characteristics and can cause air pollution, their concentration in fuels is restricted by fuel quality and environmental regulations.

Aromatics and olefins in fuels are known to cause air pollution and generate harmful compounds in exhaust gases. For example, aromatics in diesel fuel can affect combustion and the formation of particulate and polycyclic aromatic hydrocarbons (PAH) and NOx emissions. Combustion of olefins in gasoline can lead to the formation of ozone whereas aromatics can cause the formation of carcinogens such as benzene in exhaust gas[1]. Aromatic compounds are also known to affect elastomeric seals and o-rings in engines and need to be maintained at a proper concentration. Therefore, quality standards in each country and Worldwide Fuel Charter (WWFC) show the specification of upper limit concentration of aromatics and olefins in diesel and gasoline[2], and the United States Environmental Protection Agency (U.S. EPA) regulates the content of these components[3]. In jet fuels, aromatic compounds can cause excess smoke and particulate emissions and, at high concentrations, can negatively affect the durability of engine components. The upper concentration limit for aromatics is specified in ASTM D1655 for jet fuel and the U.S. Federal Aviation Administration (FAA) requires fuels to conform with this standard.[4]

The Fluorescent Indicator Adsorption (FIA) method is the conventional method to measure the volume-percentage of aromatics, olefins and paraffins in fuel, with the technique having first been introduced in 1940s. The FIA method is a rudimentary chromatography technique and works by adding a fuel sample to a long, glass column packed with activated silica gel (Fig. 1). A small amount of silica gel is mixed with a specially-formulated UV-fluorescent dye and added onto the top of the packing and is then dye is desorbed with the addition of alcohol. Air or another gas is used to pressurize the top of the column, forcing the sample and the dye to elute. The fuel components have different affinities for the silica packing, with saturates eluting furthest on the column and aromatics showing the least elution, with olefins in between. The different dye components adsorb uniquely to the individual fuel components (e.g., aromatics, olefins, and saturates). After a length of time, the column is exposed to UV light and distinct fluorescent bands of color indicate the start

and end of the different fuel components that have been separated within the column. Quantification of components is based on the distance travelled within the column and is measured by hand. A typical analysis takes ≥60 minutes and requires manual placement of samples, close attention, and quick and decisive measurement of moving fluorescent color changes.
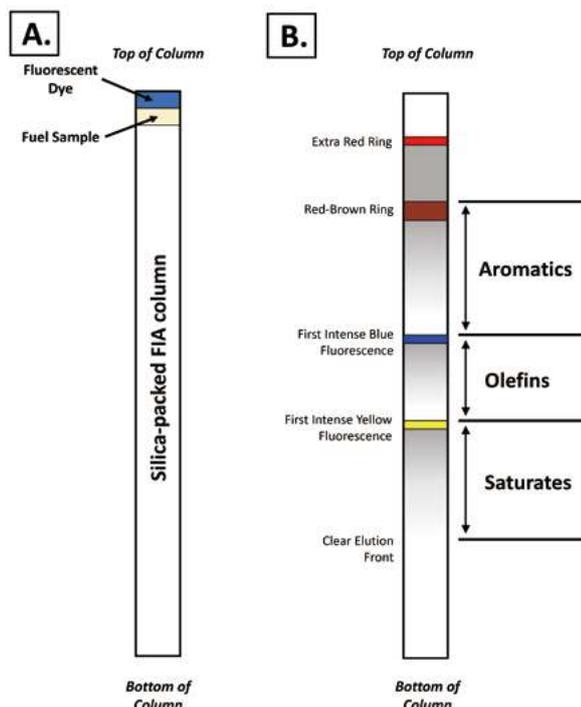

Figure 1. Diagrammatic depiction of a FIA column before (A) and after (B) separation of fuel components. Note that this depiction greatly simplifies the color changes, which are more gradational within the column in practice.

Because of its longevity and relative simplicity, the FIA method has been widely used for the analysis of aromatics and olefins in fuels since and is stipulated several international analytical standard methods such as ASTM D1319, ISO 3837, IP 156, and JIS K2536[5]. Due to the widespread adoption of the technique, the sudden lack of fluorescent indicator dye gel required for the FIA method since 2018 has had a significant impact on fuel producers, refiners, and testing laboratories. These companies have had to adapt rapidly to alternative methods for analysis to ensure that their fuels and products meet international specification and are safe for use.

In early 2018, a new formulation of the fluorescent indicator dye gel reagent required for the FIA method produced unreliable results, increasing the demand for analytical alternatives to the FIA method. Shimadzu offers High-Performance Liquid Chromatograph (HPLC) and Gas Chromatograph (GC) systems based on analytical standards that replace the FIA method. We describe here methods for analysis of aromatics in jet and diesel fuels based on ASTM D6379 and D6591 by HPLC, and analysis by GC with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV) which is a novel analytical method with several ASTM standard methods approved or in progress.

Table 1 shows alternative methods to the FIA method (ASTM D1319) for various fuel types. Efforts are ongoing with ASTM International committee D02 is revising these standards to add a correlation equation between relevant standards and ASTM D1319[6]. The standard specification for jet fuel, ASTM D1655, is being revised to include alternative methods to ASTM D1319[4], and there has been an industry-wide transition away from ASTM D1319 to alternative methods during the past two years.

Table 1. Alternative methods to ASTM D1319 [6]

Target components		No.	Title
Jet Fuel	Aromatics	ASTM D6379	Standard Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection
		ASTM D8267	Standard Test Method for Determination of Total Aromatic, Monoaromatic and Diaromatic Content of Aviation Turbine Fuels Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV)
		ASTM D8305	Standard Test Method for The Determination of Total Aromatic Hydrocarbons and Total Polynuclear Aromatic Hydrocarbons in Aviation Turbine Fuels and other Kerosene Range Fuels by Supercritical Fluid Chromatography
Diesel	Aromatics	ASTM D6591	Standard Test Method for Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection
		ASTM D5186	Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography
Gasoline	Aromatics	ASTM D5769	Standard Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry
		ASTM D5580	Standard Test Method for Determination of Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-Xylene, C9 and Heavier Aromatics, and Total Aromatics in Finished Gasoline by Gas Chromatography
	Olefins	ASTM D6550	Standard Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography
	Hydrocarbon Group Types	ASTM D8071	Standard Test Method for Determination of Hydrocarbon Group Types and Select Hydrocarbon and Oxygenate Compounds in Automotive Spark-Ignition Engine Fuel Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV)

Aromatic analysis in fuels using HPLC with Refractive Index Detector (LC-RID) is an alternative to the FIA method for which analytical standards were approved in the early 2000s[7, 8]. ASTM D6379 for aromatics analysis in jet fuel and ASTM D6591 for aromatics analysis in diesel have been published. ASTM D6379 is similar to British standard IP 436. The FIA method requires manual operation, requires a long analysis time (>60 minutes per sample), and quantification ultimately relies on human measurement in the column, modern chromatographic products can be automated, provide shorter analysis time, and yield more precise quantification than the FIA method. The Nexera series with high productivity and automated support functions utilizing digital technology and the integrated LC system i-Series Plus can meet these analytical methods. In addition, a single HPLC platform can be easily configured to jet fuel analysis and diesel analysis.

GC with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV) is a relatively new analytical technique. Since the VUV spectra are specific to the chemical structure of the component, it can easily analyze for each hydrocarbon type, and hydrocarbon species can be determined without baseline resolution of each component and coeluting peaks can be easily deconvoluted[9]. ASTM D8071 for the analysis of hydrocarbon group types in gasoline was published in 2017, and ASTM D8267 for aromatic analysis in jet fuel was published in 2019. VUV Analytics, Inc. continues to be aggressive in pursuing the development of standard test methods for all types of samples. GC-VUV improves laboratory productivity and reduces costs by enabling multiple analysis methods on a single platform[10]. Shimadzu has a **Global Solutions Distribution agreement** with VUV Analytics Inc. to provide GC-VUV instrumentation worldwide.

* For information on VUV sales support, please contact the Shimadzu sales office in your region.

In late 2019 and early 2020, a reformulated FIA dye gel was produced and sent through ASTM D02 subcommittees for an interlaboratory study (ILS) to prove statistical equivalence to the previous formulation. As of publication of this article, the new dye gel seems to be suitable for analysis and final balloting for the revised D1319 method is moving through the ASTM D02 committee. Despite the newly-available, functional dye gel, many laboratories are finding that HPLC and GC-VUV analytical methodologies are faster, quantitatively more accurate, and more easily automated than the FIA dye gel method. Therefore, it is likely that we will continue to see development of alternative methods for analysis of hydrocarbon types in common fuels.

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Dark, particulate-laden exhaust from a seagoing vessel.

Hydrocarbon Processing Industry

Analysis of Sulfur in Fuels by Energy-Dispersive X-ray Fluorescence (EDXRF)
—Compliance with New International Standards

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Abstract The sulfur content of hydrocarbon fuels is regulated to limit atmospheric emission of sulfur oxides (SOx), which can cause negative health and environmental impacts. In 2020, new regulations from the International Maritime Organization (IMO) went into effect that restrict the acceptable sulfur concentration in marine fuel oil to a maximum of 0.5% (m/m). A Shimadzu EDX-7000 Energy dispersive X-ray fluorescence spectroscopy (EDXRF) was used to establish compliance with common standard test methods, ASTM D4294 and ISO 8754, and to analyze a sample of marine fuel oil. The successful evaluation of the EDX-7000 demonstrates its functionality for assessing the sulfur content of heavy hydrocarbon distillates and compliance with the new IMO 2020 regulations.

Introduction

The sulfur content of fuels is regulated to reduce atmospheric emissions of sulfur dioxide (SO_2) and other sulfur oxides, collectively referred to as SOx, during combustion of the fuel[1]. Atmospheric SOx and related particulate matter (PM) have wide-ranging negative health effects, particularly impacting the respiratory system as well as contributing to the formation of acid rain and smog (e.g., refs. 2 & 3). The primary sources of SOx in the atmosphere is from sulfur contained in fossil fuels that are burned for power generation and transportation, bacterial reduction of sulfate to H_2S during decomposition, aerosolization of seawater sulfate, and as gases emitted during natural volcanic processes[4]. To limit anthropogenic SOx discharge into the atmosphere, various organizations and governments have imposed increasingly strict limits on the sulfur content of fuels.

Although many developed nations have set stringent sulfur content regulations for common motor fuels such as gasoline and diesel[1], fuel used for commercial shipping has historically allowed comparatively high sulfur concentration. The fuel used in seagoing ships, commonly called fuel oil, residual fuel oil, or bunker fuel, is comprised of residual hydrocarbons that remain after the distillation of lighter gasoline and diesel fractions. Fuel oils are commonly dark black in color, very viscous, and can contain up to C70 hydrocarbons[6]. These properties make its use difficult in conventional internal combustion engines. Though the use of these fuels is cost-effective for maritime shipping, their environmental and health impacts have not gone unnoticed. Corbett et al. (2007) estimate 60,000 annual global deaths can be attributed to excess atmospheric particulate matter associated with shipping activity[5].

Beginning on January 1st, 2020, the International Maritime Organization's (IMO) has established a new regulation limiting the content of sulfur in fuel oil at 0.50% (m/m) (5000 ppm), reduced from the previous 3.50% (m/m) limit[7]. There are even stricter limits

of 0.10% sulfur (m/m) in so-called emission control areas (ECAS). The primary stated goal of this new regulation is to improve environmental air quality in and around port cities and areas with high shipping traffic by minimizing SOx emissions.

There are two ways in which fuel producers or ship owners can comply with the new regulations. First, refiners and producers of fuel oils may process those fuels so that they are stripped of their sulfur compounds. Alternatively, ship owners have the option to retrofit their fleet with SOx scrubbers on their exhaust stacks to minimize emissions to make them equivalent to using compliant fuels. Either approach puts a significant financial burden on the responsible party, whether they be refiners or ship owners.

Due to these new regulations from the IMO, refiners and fuel producers must now assess fuel oil for its sulfur content to ensure compliance. Because of its ease of use and minimal sample preparation, energy dispersive X-ray fluorescence, (EDXRF) is a preferred method for the analysis of sulfur. At concentrations of 0.50% and higher, EDXRF is sufficiently sensitive for sulfur detection and avoids the challenges associated with other analytical methods, such as atomic absorption, gas chromatography, or combustion methods. In this paper, we describe the use of Shimadzu's EDX-7000 for compliance with the new IMO standards for marine fuels as well as ASTM D4294[8] and ISO 8754[9].

Analytical Instrumentation and Considerations

The instruments used in this study were Shimadzu EDX-7000 series, energy-dispersive X-ray fluorescence (EDXRF) spectrometers.

Details on the theory and fundamentals of EDXRF as an analytical technique are provided in Grieken and Markowicz (2001) and are presented briefly here[10].

As a technique, EDXRF has many advantages when used for analysis of fuels and oils. Namely, the technique is sufficiently sensitive and can be adapted for multiple element analysis. Also, EDXRF instruments tend to be small, requiring minimal benchspace and laboratory infrastructure. The analyses carried out in this study can be performed in a laboratory equipped with electricity and helium gas. A brief comparison of advantages and drawbacks of common analytical techniques for sulfur in petrochemicals is provided in Table 1.

The EDX-7000 operates under the principles of X-ray fluorescence that takes advantage of the fact that the elements that comprise a sample each have a unique atomic structure which is conceptually diagrammed in Figure 1. An X-ray source is used to bombard a sample with X-ray radiation which excites inner-shell electrons to an elevated state. Subsequently, an outer-shell electron relaxes into the hole left by the ejected electron and, in that process, emits energy in the form of an X-ray. The X-ray emission line (e.g., Kα, Kβ, Lα) depends on the shell from which the relaxing electron originates and that which it ends up in. The emitted X-ray photon energy for each element for each element are unique and can be used to identify each element, whereas the abundance of X-rays produced correlate to the concentration of that element. The resulting spectra consists of the photon energy of X-rays generated from the sample (in kiloelectronvolts, keV) and the abundance of those X-rays (in counts per second per microampere, cps/µA) and is typically processed by software to interpret elemental composition and concentration.

Table 1. General comparison table of common analytical techniques for sulfur. Note that this list is not exhaustive and other techniques are available.

Technique	Advantages	Drawbacks
EDXRF	• Easy to operate • Minimal sample preparation • Minimal laboratory requirements • Multi-element analysis	• High detection limits (~10s of ppm) • No speciation information • Solids or liquids only
ICP-OES	• Quick sample throughput • Robust for complex matrices • Simultaneous multi-element analysis	• No speciation information without LC or GC front end • Low sensitivity at common sulfur emission lines • Higher cost of ownership
ICP-MS	• Quick sample throughput • Low detection limits • Nearly simultaneous multi-element analysis	• No speciation information without LC or GC front end • Interferences on predominant sulfur isotope 32S • Higher cost of ownership
GC-FPD	• Highly sensitive (ppb levels) • GC separations enable speciation analysis	• Non-specific to sulfur • Matrix signal quenching
GC-SCD	• Highly sensitive (ppb levels) and specific for sulfur • GC separations enable speciation analysis	• Historically complex • Only analyzes for sulfurs, other detectors required for other compounds

There are three primary variables that determine the elemental selectivity and sensitivity of an EDXRF instrument when analyzing liquid samples such as fuels and oils: analytical measurement time, use of special X-ray filters, and modification of the atmosphere within the analytical chamber. All of these variables can affect the ability to detect low concentrations of sulfur within a sample.

Analysis Time

Often, detection limits will decrease with an increase in analytical integration time. By increasing the time during which the sample is irradiated, the detector has more time to average the signal from the element of interest thereby increasing the signal-to-noise ratio. Figure 2 shows the effect of increasing integration time between 5 seconds and 300 seconds. It is visually apparent that signal to noise ratios improve with increasing integration time, allowing for better quantification.
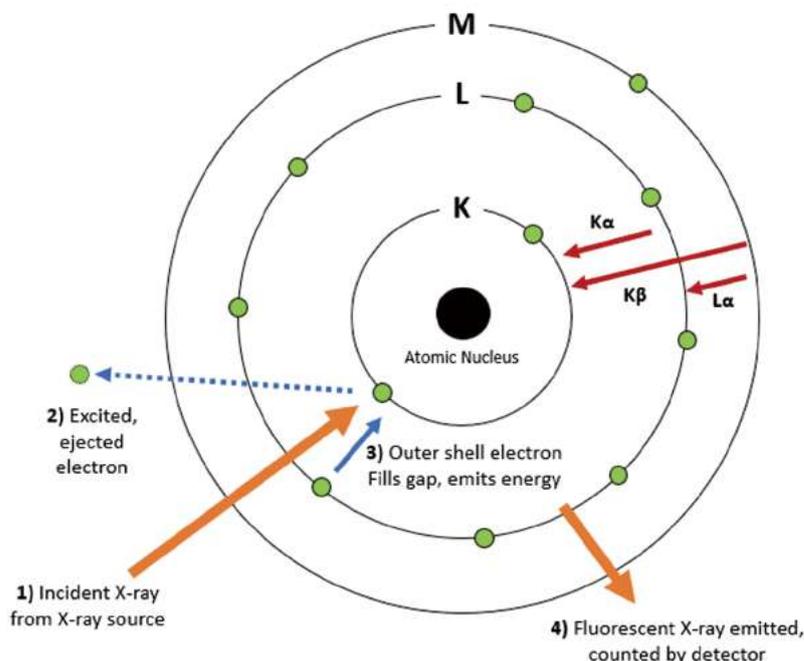

Figure 1. Simplified, conceptual diagram of EDXRF excitation and emission principles. Electrons denoted as green circles, incident and fluorescent X-rays as orange arrows, and characteristic emission lines (e.g., Kα, Kβ, Lα) shown as red arrows.

However, the improvement in signal-to-noise ratio diminishes along a curve approximated by the square root of the integration time. Therefore, the improvement in quantification will be greatest during increases at low total integration times, for example, from 5 s to 10 s, and lower at greater integration times, e.g., from 100 s to 300 s.

X-ray Filters

Fluorescent X-rays can be subject to particle scattering phenomena, such as Compton scattering and Rayleigh scattering, in which their energy levels or directions can be changed. This can give rise to interfering signals and peaks on a spectrum and decrease

sensitivity for elements of interest. The example in Figure 2 shows two spectra of the same sample with and without the use of filter. The spectrum generated without a filter shows a large signal at ~2.6 keV, corresponding to a scattering effect of X-rays emitted from the rhodium-based X-ray source. This peak interferes with quantification of sulfur, with a peak at ~2.3 keV.

On the spectrum generated using the filter, the errant peaks for rhodium are removed and the sulfur peak shows better signal-to-noise ratio. Although the overall intensity of the fluorescent X-rays is diminished when using filters, the increase in the signal-to-noise ratio of elements of interest can yield better quantitative results.
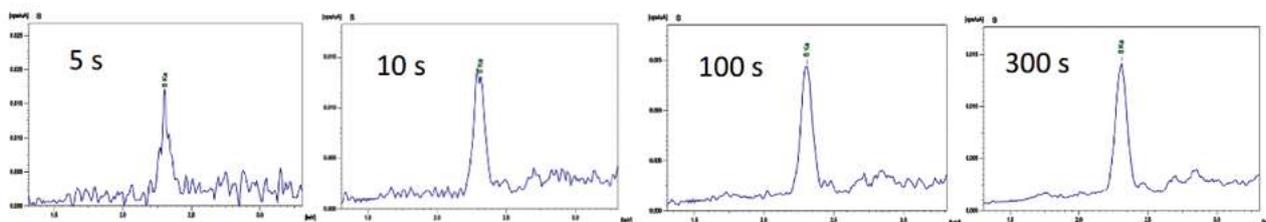

Figure 2. Spectra of sulfur Kα at different integration times demonstrating increased signal-to-noise ratio with increased integration time.
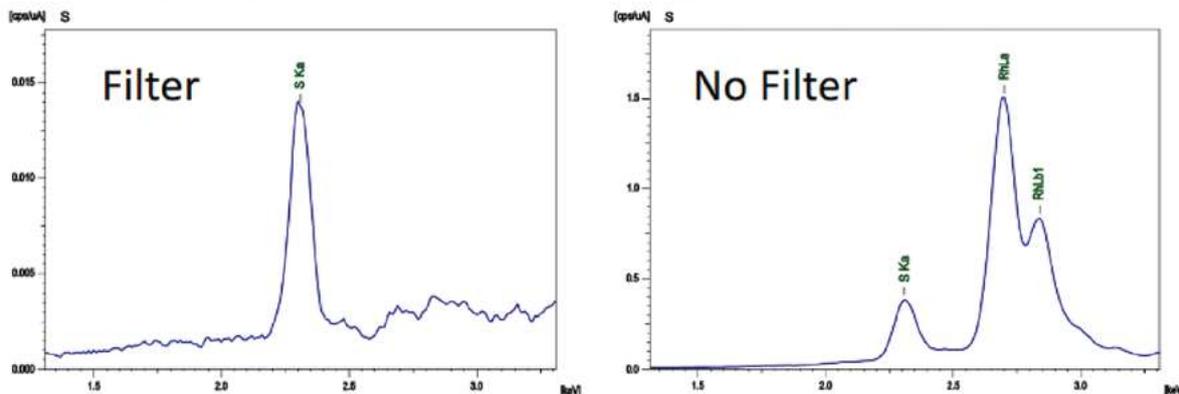
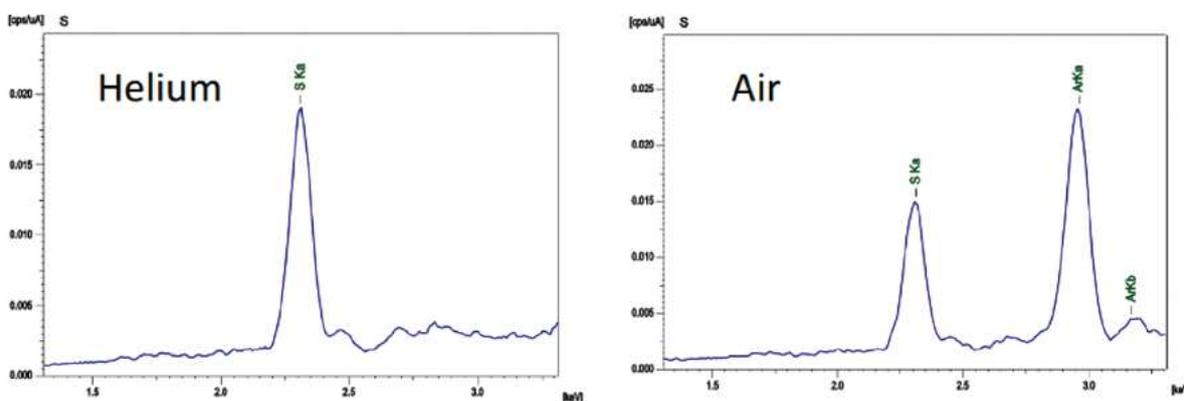Figure 3. Spectra of sulfur Kα showing the effect of the use of X-ray filters to minimize detection of scattered X-rays.

Figure 4. Spectra of sulfur Kα showing the effect of purging the analytical chamber with helium to minimize errant peaks and increasing the absolute intensity of the sulfur Kα line.

Atmospheric Control

Controlling the atmosphere in the analytical chamber is another approach by which the analyst can optimize their analysis. Major components of atmospheric air, including N_2, O_2, and H_2O absorb X-ray energy around the same energy that sulfur and other light elements fluoresce X-rays. Therefore, the intensity of fluorescent X-rays will be attenuated prior to detection. The two common approaches to minimizing atmospheric interference during analysis include purging the analytical chamber with helium, which does not absorb X-rays to the same extent that atmospheric air does, or pulling a rough vacuum on the analytical chamber. Both methods are effective, however, the vacuum method is not recommended for liquid samples as it may cause splattering, evaporation, or boiling of samples.

The effects of using a helium purge in the analytical chamber during analysis of sulfur is demonstrated in Figure 3. Without the use of helium, two large argon peaks are seen at energy levels near that of the sulfur Kα emission line. By purging the analytical chamber with helium, these argon emissions are eliminated and the absolute intensity of the sulfur emission Kα emission line increases. The overall increase in signal is attributed to both more X-ray flux getting to the sample and more S photons reaching the detector, both of which are increased when helium is used as an atmosphere.

Application towards Standard Test Methods

The method employed for this study adheres to the methodologies described in ASTM D4294, *Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-ray Fluorescence Spectrometry,* and ISO 5784, *Petroleum Products−Determination of Sulfur Content−Energy Dispersive X-ray Fluorescence.*

The measurement conditions for each standard method as well as the actual parameters used in this study are outlined in Table 2.

Table 2. Method specifications and actual operating parameters for analysis.

Specification	ASTM D4294 Requirement	ISO 8754 Requirement	Actual Measurement Parameters
Temperature	*Not Specified*	*Not Specified*	Room temperature (25°C)
Humidity	*Not Specified*	*Not Specified*	Normal Ambient Condition (~50% RH)
Atmospheric Pressure	*Not Specified*	*Not Specified*	Normal Ambient Condition
Warm-up Time	"whenever possible the instrument is left on…"	"Continuously Switched On"	≥15 minutes
Sample Film	Polyester, Polypropylene, Polycarbonate, Polyimide films, "usually <10 μm"	"Normally 6 μm polyester, polypropylene, or polycarbonate"	5 μm Polypropylene
Atmosphere	Air and Helium	*Not Specified*	Ambient Air and Helium (99.999% purity)
Analysis Time	100 to 300 seconds, concentration dependent	*Not Specified*	100 to 200 seconds, concentration dependent

Several factors were assessed for method compliance, including repeatability (r), reproducibility (R), blank measurement, and a lower limit of detection (LLD).

For both test methods, calibration curves were generated using oil-based standards of known concentration. An example concentration curve is provided in Fig. 5
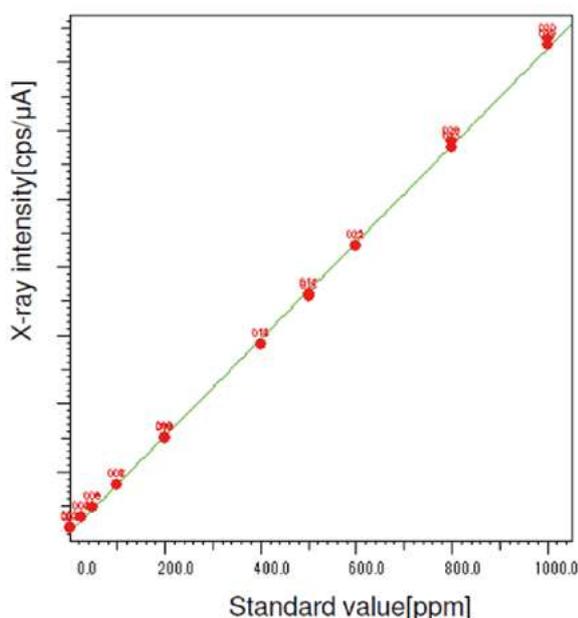

Figure 5. Example calibration curve of known samples using a helium-purged sample chamber.

For ASTM D4294, repeatability was assessed by analyzing one sample 20 times on the same instrument and performed by the same operator. Reproducibility was assessed by analyzing one sample 20 times on one instrument in one laboratory, and then the same sample was analyzed a further 20 times on a different instrument (of the same model) and in a different laboratory by a different operator. The result is the magnitude of the range of results for the 20 replicated about the true value and the results were then compared to the calculated, statistical limit as per the method specifications, calculated based on equations 1 and 2. The blank was assessed by analyzing a blank sample 20 times. The blank measurement must be below 2 ppm. When analyte concentrations were ≥500 ppm, analysis was conducted with the analytical chamber purged with He and under standard atmospheric conditions. At concentrations <500 ppm, analysis was conducted only with the chamber purged with He.

a) $r = 0.4347 \times S^{0.6446}$

b) $r = 1.6658 \times S^{0.3300}$

Equation 1: Repeatability (r), in ppm, according to ASTM D4294 for base oil (a) and diesel fuel (b). The target concentration is represented as S.

a) $R = 1.9182 \times S^{0.6446}$

b) $R = 1.6658 \times S^{0.3300}$

Equation 2: Reproducibility (R), in ppm, according to ASTM D4294 for base oil (a) and diesel fuel (b). The target concentration is represented as S.

a) $r = 0.045 \times (S + 0.05)$

b) $r = 0.0215 \times (S + 0.15)$

Equation 3: Repeatability (r) in weight percent (wt. %) according to ISO 8754 for sulfur in concentration range of 0.03 to 0.05 wt. % (a) and greater than 0.05 wt. % (b). The target concentration is represented as S.

a) $R = 0.1781 \times (S + 0.05)$

b) $R = 0.0812 \times (S + 0.15)$

Equation 4: Reproducibility (R) in weight percent (wt. %) according to ISO 8754 for sulfur in concentration range of 0.03 to 0.05 wt. % (a) and greater than 0.05 wt. % (b). The target concentration is represented as S.

$$LLD = 3 \times \frac{C}{NET} \sqrt{\frac{BG}{T \times A}}$$

Equation 5: Equation to calculate the Lower Limit of Detection (LLD). C is the concentration of S in ppm, NET is the fluorescent X-ray intensity of S (cps/µA), BG is the background intensity of S (cps/µA), T is the integration time (sec), and A is the current (µA).

For ISO 8754, repeatability was assessed by performing two sets of 20 analyses (40 total analyses) of the same sample on the same instrument in the same laboratory by the same operator. Reproducibility was assessed in the same manner as that for ASTM D4294. The results were then compared to the calculated, statistical limit as per the method specifications, calculated based on equations 3 and 4. The analytical chamber was operated under ambient atmospheric conditions for all analyses.

The lower limit of detection (LLD) was calculated using equation 5.

Results for Standard Test Method Compliance

A summary of results of this study are presented in Tables 3 and 4 for ASTM D4294 and Tables 5 and 6 for ISO 8754.

Table 3. Results for repeatability (r) testing based on ASTM D4294 criteria.

Test	Sample	Conc.	Count Time (sec)	Method Criterion (ppm)	Result in Air (ppm)	% RSD	Result in He (ppm)	% RSD
Repeatability	Base Oil	50 ppm	300	5.4	-	-	5.0	2.89
Repeatability	Base Oil	100 ppm	200	8.5	-	-	7.1	2.08
Repeatability	Base Oil	500 ppm	200	24	16	0.89	12	0.71
Repeatability	Base Oil	0.5 wt. %	100	105	64	0.29	44	0.26
Repeatability	Base Oil	4.0 wt. %	100	405	257	0.17	159	0.12
Repeatability	Diesel	100 ppm	200	7.6	-	-	5.2	1.29
Repeatability	Base Oil	500 ppm	100*	24	23	1.26	13.5	0.72
Repeatability	Base Oil	0.5 wt. %	50*	105	80	0.35	41	0.22
Repeatability	Base Oil	4.0 wt. %	50*	402	220	0.19	91	0.12

*Analysis performed more rapidly than specified in method for given concentration.
Note: Samples represented by dashes (-) are more amenable to analysis with helium atmosphere.

Table 4. Results for reproducibility (R) testing based on ASTM D4294 criteria.

Test	Sample	Conc.	Count Time (sec)	Method Criterion (ppm)	Result in Air (ppm)	% RSD	Result in He (ppm)	% RSD
Repeatability	Base Oil	50 ppm	300	24	-	-	5.4	2.44
Repeatability	Base Oil	500 ppm	200	105	31	1.00	12	0.43
Repeatability	Base Oil	4.0 wt. %	200	1776	388	0.25	667	0.09
Repeatability	Diesel	100 ppm	200	41	-	-	17	1.85

Note: Samples represented by dashes (-) are more amenable to analysis with helium atmosphere.

Table 5. Results for repeatability (r) testing based on ISO 8754 criteria.

Test	Sample	Conc.	Count Time (sec)	Method Criterion (ppm)	Result in Air (ppm)	% RSD
Repeatability	Base Oil	0.03 wt. %	200	36	19	1.12
Repeatability	Base Oil	0.05 wt. %	200	45	23	1.23
Repeatability	Base Oil	0.2 wt. %	100	75	35	0.28
Repeatability	Base Oil	1.0 wt. %	100	247	100	0.15
Repeatability	Base Oil	4.0 wt. %	100	892	315	0.18

Table 6. Results for reproducibility (R) testing based on ISO 8754 criteria.

Test	Sample	Conc.	Count Time (sec)	Method Criterion (ppm)	Result in Air (ppm)	% RSD
Repeatability	Base Oil	0.03 wt. %	200	143	38	0.99
Repeatability	Base Oil	4.0 wt. %	100	3370	464	0.10

In addition to the above results, the results of measurement of 20 analyses of the blank sample yielded a maximum result of 1.9 ppm. Lower limits of detection (LLD) calculated using a 200 second integration time yield results of 5.61 ppm with a non-purged sample chamber, and 2.49 ppm with a helium-purged chamber.

Application towards Marine Fuel Oil

This methodology was assessed on an actual marine bunker fuel sample obtained from a local shipyard in Baltimore, MD, USA. The fuel was produced by BP Marine and the sample was bottled as a grab sample in 2005 and therefore predates the new IMO 2020 regulations. The EDX-7000 was calibrated for sulfur in the range of 5000 to 50000 ppm (0.50 to 5%) using sulfur in residual oil standards from Conostan® to ensure appropriate matrix matching. The sample was analyzed using the same analytical conditions as described above for 300 seconds and repeated 5 times.

The resulting calibration curve had excellent linearity (Fig. 6) enabling accurate quantification of sulfur in the unknown samples.

The sulfur content of the analyzed fuel is 2.96%, based on analysis using the EDX-7000.
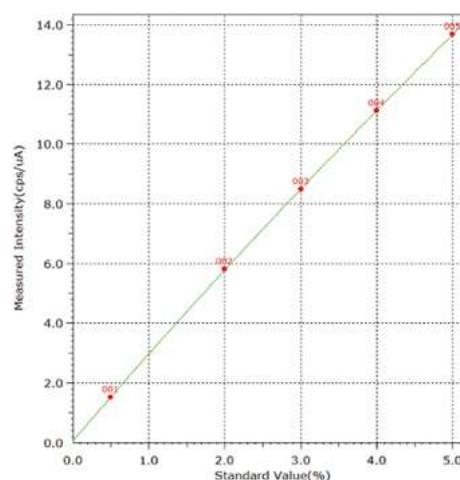

Figure 6. Calibration curve of sulfur in residual oil.

Table 7. Results from five analyses of marine fuel oil.

Run Number	Intensity (cps/μA)	Sulfur Conc. (m/m %)
1	8.2798	2.920
2	8.2967	2.925
3	8.2670	2.915
4	8.2745	2.918
5	8.2757	2.918
Average	8.2787	2.919
Std. Dev.	0.0111	0.004
% RSD	0.1335	0.127

Discussion

Calibration of the EDX-7000 with known standards yielded a linear and steep calibration curve, critical to effective quantification (e.g., Figs. 5 and 6). Such a predictable response on the instrument results in accurate and precise quantification of unknown samples.

Repeatability results per ASTM D4294 for base oil show that the EDX-7000 can comply with the method at sulfur concentrations of ≥500 ppm using a non-purged analytical chamber and ≥50 ppm when purging the chamber with helium (e.g., Fig. 7). Furthermore, for sulfur concentrations of ≥500 ppm, the analytical time can be reduced by 50%, more stringent than the scope of the method, and still comply with repeatability requirements. For diesel fuel, repeatability complied with ASTM D4294 at sulfur concentrations of ≥100 ppm.
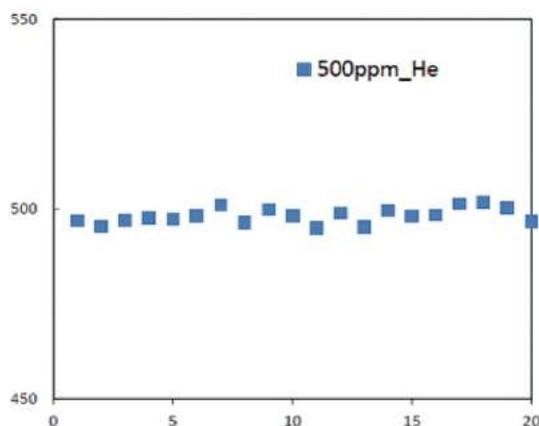
Figure 7. Repeatability of 500 ppm sulfur sample
using helium-purged sample chamber.

Reproducibility results per ASTM D4294 for base oil show that the EDX-7000 can comply with the method at sulfur concentrations of ≥500 ppm using both a non-purged and a helium purged chamber. For diesel fuel, the concentration range is lower at ≥100 ppm sulfur using a helium purge.

For both repeatability and reproducibility as per ISO 8754, the EDX-7000 complied across the entire concentration range of 0.03 to 4 weight percent sulfur using ambient (non-purged) conditions.

Calculations of the LLD demonstrate sensitivity of the EDX-7000 for sulfur as low as 2.49 ppm. This concentration is far lower than the new IMO requirements of <0.50% (m/m). Even when operating the instrument without the use of the helium-purged chamber, sensitivity was only diminished slightly, to 5.61 ppm. Again, this value is well within the scope of new IMO regulations.

The marine fuel sample tested contained 2.96% sulfur, which was not unexpected due to its age predating the new IMO 2020 regulations. A fuel such as this could still be used in seagoing vessels provided that they have appropriate scrubbers in their exhaust stacks to minimize SOx emissions. Nonetheless, this demonstrates appropriate quantification abilities for the EDX-7000 and EDXRF, in general, for sulfur in heavy fuels.

Conclusions

Regulations on the chemistry of fuels continue to become more stringent in efforts to minimize their environmental impact. The reduction of sulfur content in fuels minimizes SOx emissions, thereby decreasing their potential to generate acid rain, smog, and negatively affect human health. Strict regulations on the sulfur content of on-highway fuels, such as gasoline and diesel, have been in place for years, whereas those for fuel oils and marine fuels have existed but have historically allowed for higher total sulfur content. New regulations from the IMO enacted in 2020 limit the sulfur content of marine fuel oil to 0.50% (m/m) or to equip ships with emission-reducing scrubbers.

Due to these new regulations, refiners that produce fuel oil for marine use must expand analytical testing for compliance purposes. Analysis of fuels by EDXRF instruments has gained traction due to their ease of use, minimal requirements in terms of laboratory infrastructure, and their sensitivity appropriate for sulfur at new regulatory limits. Shimadzu's EDX-7000 provides a simple way for analysis of sulfur, and other elements, in petroleum products. This methodology allows for fast analysis with limited sample preparation and a minimum of conventional laboratory infrastructure.

The method and data outlined above demonstrate the applicability of Shimadzu's EDX-7000 towards ASTM D4294 and ISO 8754 for measuring total sulfur in petroleum products in addition to compliance with the 2020 IMO standards. Furthermore, successful analysis of a pre-regulation fuel demonstrates the applicability of the EDX-7000 for such analyses.

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Applications of Frequency-Modulation Atomic Force Microscopes (FM-AFM) to Lubricant

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and Global Application Development Center, Analytical & Measuring Instruments Division, Shimadzu Corporation

Tribology (technology related to lubrication, friction, and wear) is fundamental for a wide variety of mechanical instruments and related markets are widespread. Lubricant improvements and research into the material properties of solid surfaces are conventionally performed experientially. However, there is a pressing need to systematically assess lubrication interfaces through microscopic observations, based on the ever growing interest in reducing loss and saving energy.

For example, with automotive oil, the need for reduced fuel consumption in environmentally friendly automobiles is accelerating the reduction of base oil viscosity, with an aim to reduce resistance to stirring. At the same time however, the oil film on sliding parts becomes thinner as the viscosity of the base oil is reduced, which leads to concerns about reductions in seizure and wear resistance. Many cases have been reported of improvements from additives used as countermeasures. Though additives are known to form an adsorption layer on metal surface, it is difficult to analyze this adsorption layer with high resolution within lubricant. As a result, many uncertainties remain regarding this formation process and the mechanism of its action.

In recent years, due to advances in analytical techniques, analyses have become possible that would have been conventionally unthinkable. In this context, frequency-modulation atomic force microscopes (FM-AFM) can capture the shape (XY) of solid surfaces in liquids and cross sectional images (Z-X) of solid-liquid interfaces with high resolution. These instruments have become a focus of attention as a new method for clarifying the structure of lubricant at solid-liquid interfaces at the molecular level (Fig. 1).

FM-AFM is commercially available from Shimadzu as the SPM-8100FM model. Here, we will briefly describe two examples of applications of this instrument to lubricant.

(1) In this example, an adsorption film of a phosphate ester (C18AP) added to a base oil (Poly-α-Olefine: PAO) as an anti friction agent was analyzed with respect to its formation on an iron oxide surface. At the lubricant-iron oxide interface, when PAO on its own was applied, a layered structure was observed due to the orientation of the PAO molecules. Next, when C18AP was added to PAO, it was found that as the concentration of C18AP was increased, the layered structure disappeared. The disappearance of the layered structure implied that the C18AP adsorption film was coating the iron oxide surface and was disrupting the orientation of the PAO molecules. Macroscopic wear tests were performed on a similar lubricant and a correlation was obtained between the

kinetic coefficient of friction and the existence of the adsorption layer.

(2) In this example, the adsorption film formed on an iron oxide surface by carboxylic acid, which is widely used as an oiliness agent, was analyzed. When the iron oxide surface was subjected to a simulated sliding motion using the probe of the FM-AFM in lubricant to which carboxylic acid was added, it was confirmed that an adsorption film originating from the carboxylic acid had formed on the sliding part. Further, cross sectional imaging was performed at the lubricant-iron oxide interface,

enabling capture of the flexible tail part of the carboxylic acid molecules. From this data, an adsorption layer molecular model of the additive was estimated.

FM-AFM can perform high-resolution analyses of the lubricant-iron oxide interface from as little as 500 µL of lubricant. Lubricant performance can be evaluated by laboratory scale material tests, so this shows promise as a new evaluation method that will substantially reduce the cost of lubricant development.
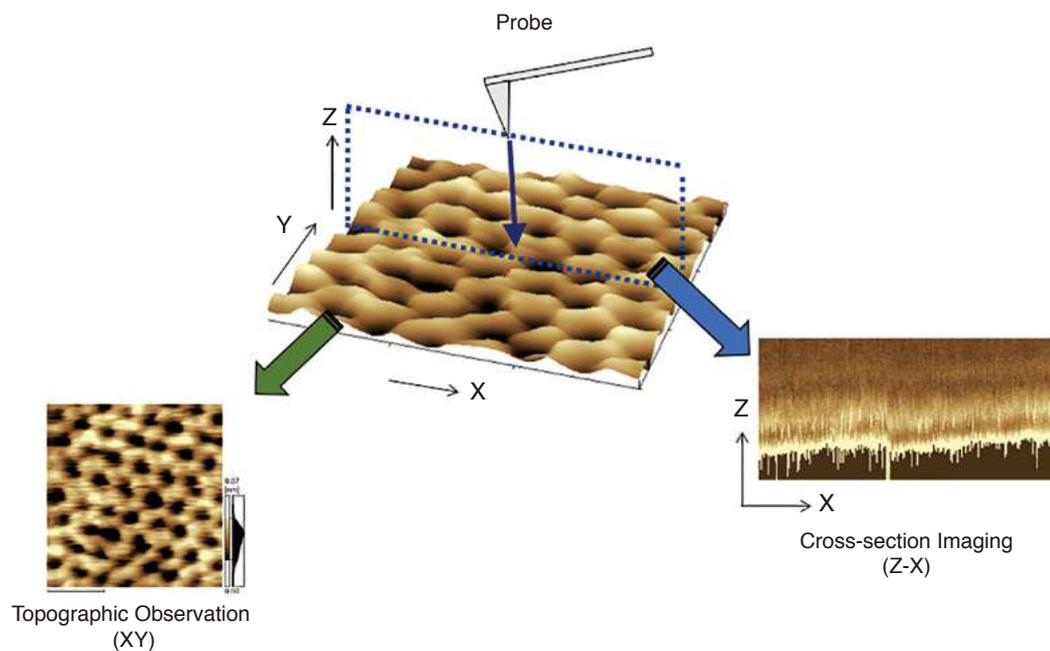

Fig. 1. Topographic Observation (XY) and Cross-section Imaging (Z-X) by FM-AFM

Shimadzu Selection

These article were selected by Shimadzu. Relating HPI analysis and development, they are from posters presented at Gulf Coast Conference 2019, ASMS 2020 and from application notes. They feature a variety of instruments we produce and include cutting-edge technologies. Please obtain the articles of your interest through the links on the titles.

From Crude to Fuels – Trace Metals Analysis by ICP-OES for ASTM D7691 and D7111

Understanding the metals content of crude oil and refined fuels are critical to assessing their value, determining refining workflows, and ensuring appropriate functionality during combustion. To accomplish testing for trace metals in crude oils and fuels derived from them, laboratories typically adhere to standard test methods from organizations such as ASTM or UOP, among others. Here, we present trace metals data acquired using a Shimadzu ICPE-9820 in compliance with ASTM D7111 for middle distillates. The ICPE-9820 is ideally suited for oil and fuels analysis.

Evaluation of Long-term Stability of Analysis of Fuel Dilution for Engine Oils using a Backflush GC System

Fuel contamination such as gasoline/diesel in engine oil is known to decrease the viscosity of lubricating engine oil. This contamination also known as fuel dilution leads to a shortened lifetime of engine oil. For this reason, the extent to which a fuel is diluted is an important indicator of engine oil conditions. Test methods used to measure the fuel dilution rate are standardized by U.S. ASTM D3524, D3525 and D7593. ASTM D7593 regulates gasoline, diesel oil and biodiesel. In this experiment, a long-term stability of Shimadzu GC was examined in the analysis of diesel fuel dilution in engine oil using a backflush system according to ASTM D7593.

Using a Barrier Ion Discharge Detector for Trace Water Analysis: An Alternative to the Karl Fischer Titration Technique

The determination of water content in a sample is among the most widely used analyses. Water within a sample can provide positive benefits as well as negative impacts on goods depending on its abundance. In polymer and plastics manufacturing, including polysiloxanes, excess water in precursor components can negatively impact the desired structural properties of the final product and be detrimental to its visual properties. Shimadzu's proprietary Barrier Discharge Ionization Detector (BID) coupled with Supelco's WaterCol™ column is a great alternative to the Karl Fischer Titration technique for trace moisture analysis.

Energy Dispersive X-ray Fluorescence Spectroscopy for Analysis of Sulfur and Other Elements in Petroleum Products

In 2017, the Environmental Protection Agency (EPA) enacted Tier 3 regulations on sulfur content in fuels which changed the maximum allowable sulfur content from 30 parts per million on an average annual basis to 10 parts per million. In addition, the International Marine Organization (IMO) will implement on January 2020 a directive to reduce sulfur in marine/bunker fuels to less than 0.5 percent. With these two pieces of legislation, quantifying sulfur in petroleum products is now becoming ever more important. In this poster, we demonstrate how a Shimadzu Energy Dispersive X-ray (EDX) spectrometer can be used for not only sulfur determination in petroleum products, but also for quantification of other elements in addition to sulfur.

Detailed analysis of lubricant deterioration using multiple analyzers

Engine lubricants play an important role in lubrication, cooling, cleaning, and rust prevention for vehicles, construction machinery, ships, airplanes, and other equipment with internal combustion or turbine engines. As the lubricant deteriorates through use, its performance will decline and the inside of the engine can wear, leading to a decrease in service life and potential malfunction. Lubricants deteriorate due to decomposition and chemical changes of oil components and additives caused by physical and thermal stresses, as well as contamination by metal wear particles and incorporated fuel. Therefore, it is recommended to analyze the lubricant throughout its lifespan to assess its quality, utility, and remaining service life. These analyses can be accomplished with a number of instruments, including FTIR, GC, and ICP-AE

Analysis of Aromatic Hydrocarbons in Fuels by ASTM D6379 and D6591 on a Single HPLC Platform

Determining the aromatic content of hydrocarbon fuels is crucial to assessing their combustion characteristics and compliance with environmental regulations. Two methods that are used for quantitation of aromatic components of fuels are ASTM D6379 and D6591, for kerosene and middle distillates (e.g., jet fuel) and diesel fuel, respectively. This poster demonstrates the detection and quantitation of MAH and DAH by ASTM D6379, as well as detection and quantitation of MAH, DAH, and T+AH by ASTM D6591 using a single Prominence HPLC.

Sulfur Analysis by GC-SCD using Shimadzu's SCD-2030 for ASTM D5504, D5623, and D7011

Analysis for and quantification of sulfur in crude oil, natural gas, petro-chemicals, and industrial chemicals is critical to ensuring quality, process control, and safety for refinery, processors, and users. Sulfur is naturally present in raw hydrocarbon materials and often needs to be removed to ensure processing efficiency because sulfur can poison precious-metal catalysts. Furthermore, some sulfur species, such as H2S present safety and health hazards to processors and end users. Finally, some sulfur compounds are intentionally added into finished products, such as odorants in natural gas.

Testing the Dilution Rate of Diesel in Engine Oil in Accordance with ASTM D3524

If gasoline or diesel mixes into the engine oil, it decreases the oil viscosity and prevents achievement of the proper performance as a lubricating oil. Measuring the fuel dilution rate serves as a key indicator during oil replacement, because it can determine the degradation status of the engine oil. The test methods used to measure the fuel dilution rate are specified in standards such as U.S. ASTM D3524, D3525, and D7593. Diesel dilution rate testing methods are specified in ASTM D3524 and JPI-5S-23. This article describes an example of measuring the dilution rate of diesel in engine oil in accordance with ASTM standards.

Testing the Gasoline Dilution Rate of Gasoline in Engine Oil in Accordance with ASTM D3525 and Japan Petroleum Institute Standard JPI-5S-24

If gasoline or diesel mixes into the engine oil, it decreases the oil viscosity and prevents achievement of the proper performance as a lubricating oil. Measuring the fuel dilution rate serves as a key indicator during oil replacement, because it can determine the degradation status of the engine oil. The test methods used to measure the fuel dilution rate are specified in standards such as U.S. ASTM D3524, D3525, and D7593. Diesel dilution rate testing methods are specified in ASTM D3524 and JPI-5S-23. This article describes an example of measuring the dilution rate of diesel in engine oil in accordance with ASTM standards.

Testing the Dilution Rate of Gasoline in Engine Oil in Accordance with ASTM D7593

If gasoline or diesel mixes into engine oil, it decreases the oil viscosity and prevents the oil from achieving its proper performance as a lubricating oil. Measuring the fuel dilution rate serves as a key indicator during oil replacement, because it can determine the degradation status of engine oil. The test methods used to measure the fuel dilution rate are specified in standards such as U.S. ASTM standards D3524, D3525, and D7593. ASTM D7593 governs gasoline, diesel, and biodiesel. This article describes an example of using an ASTM D7593-compliant backflush system to quickly analyze the dilution rate of gasoline in engine oil.


Testing the Dilution Rate of Diesel in Engine Oil in Accordance with ASTM D7593

If gasoline or diesel mixes into engine oil, it decreases the oil viscosity and prevents achieving the proper performance as a lubricating oil. Measuring the fuel dilution rate serves as a key indicator during oil replacement, because it can determine the degradation status of engine oil. The test methods used to measure the fuel dilution rate are specified in standards such as U.S. ASTM standards D3524, D3525, and D7593. ASTM D7593 governs gasoline, diesel, and biodiesel. This article describes an example of using an ASTM D7593-compliant backflush system to quickly analyze the dilution rate of diesel in engine oil.

Analysis of Thiophene in Benzene: Comparison of FPD(S) and SCD Analyses

The detectors chosen for trace analysis of sulfur compounds using gas chromatography are Flame Photometric Detector (FPD(S)) and Sulfur Chemiluminescence Detector (SCD) which offer highly sensitive and selective detection. These detectors have different detection characteristics for sulfur compounds because of their difference in the principles of detection. Therefore, looking at methods for analyzing thiophene in benzene, FPD is used in ASTM D4735 and SCD is used in D7011, but these methods analyze different concentration ranges of thiophene. In this article, we measured results with FPD and SCD, and compared them to Flame Ionization Detector (FID), which is a general-purpose detector, through the analysis of thiophene in benzene as an example and described the differences between FPD and SCD.
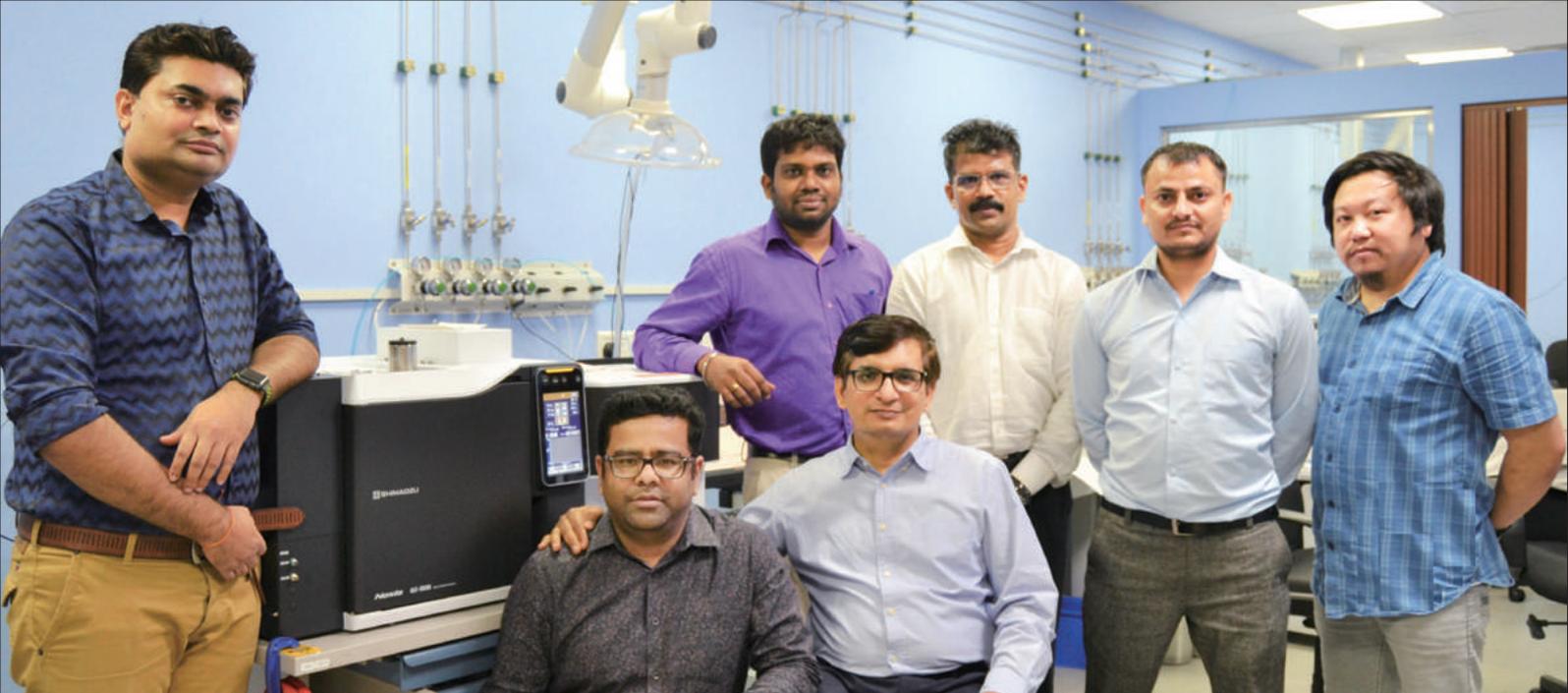
Introducing Refinery Gas Analyzer with trace Sulfur detection

Refinery gas is produced during crude oil refining. Typical composition is C1-C5 Paraffins, C6+ Paraffins, C2-C5 Olefins and non-condensable gases like H2, O2, N2, CO and CO2. This gas is also used as petrochemical feed stock that is used in several catalytic processes. Determining the composition of Refinery gas and measurement of trace sulfur content is very important. Trace amount of sulfurs can poison the catalyst used in processes, which can cost millions of dollars.

Shimadzu recently launched highly sensitive Nexis SCD-2030 used in well-established High-Speed Refinery Gas Analyzer for speciation and quantification of trace sulfur components. This complete system, which uses 4 detectors simultaneously, is very accurate and robust.

This system is in compliance with ASTM D7833, D5504, D5623, D1945, D1946, D2163, UOP 539.

Following are the main features of the system
- Robust system uses 2 TCD, 1 FID and SCD detector
- Simultaneous analysis of Hydrocarbons and Sulfur can be performed
- Highest sensitivity and very low maintenance Nexis SCD-2030
- Faster analysis time

For this analysis, process gas stream having all above components is injected into the system based on Shimadzu Nexis GC- 2030 with 4 detectors - 2 TCDs, FID and SCD. Four sample loops are filled with sample and injected onto the columns. Respective columns do the separation of required components which are then analyzed by the respective detectors.

Shimadzu uses parallel valve configuration with backflush for light gases and light hydrocarbons. This way system becomes very simple and can be maintained easily.

O2, N2, CO, CH4, CO2 and H2S (High Concentrations) are measured with TCD-1 detector with Helium carrier gas. Hydrogen is analyzed on TCD-2 with Nitrogen carrier gas. C1 to C5 Paraffins and Olefins with C6+ or C7+ backflushed, are analyzed with FID detector. Typically trace sulfur components like H2S, COS, Methyl Mercaptan, Ethyl Mercaptan are analyzed with SCD detector.

Typical concentration range for analysis of sample components is as below.

Components	Low	High	Detector
O2, N2, CO, CO2	0.01%	100%	TCD-1
H2S	0.02%	100%	TCD-1
H2	0.01%	100%	TCD-2
Hydrocarbons C1-C6+	0.001%	100%	FID
Sulfurs	0.01ppm	100ppm	SCD

The total analysis time is between 10–15 minutes, depending upon number of sulfur components.

By adding SCD to routine Refinery Gas Analyzer, complete composition of the sample can be analyzed thus saving time for analyzing in different systems and thereby increasing productivity.

Shimadzu Middle East & Africa (SMEA) has been building system GCs since 2012 and until now has produced more than 350 system GCs. The system GC team has been developing various new applications and analyzers such as Capillary TOGA, Trace Oxygenates (LOWOX), Simdist, DHA, Trace CO–CO2, LPG analyzer, Trace Gases with PDHID etc. in addition to accessories such as vaporizers and stream selectors. They have improved overall design of the system so that the space on GC can be optimized and utilized for some complex applications like RGA–SCD and Extended RGA/NGA with 4 Channels.

SMEA provides sales and service trainings to its partners and has been providing support for system GC to all customers. It also has the facility to conduct Factory Acceptance Test (FAT).

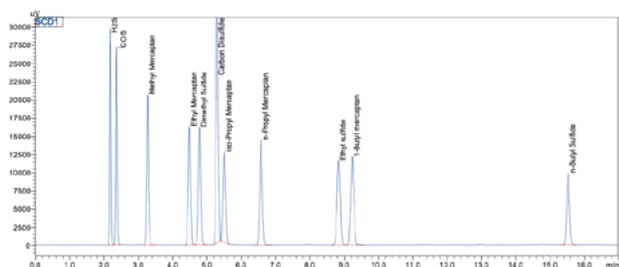Top image: System GC Team, Shimadzu Middle East & Africa FZE

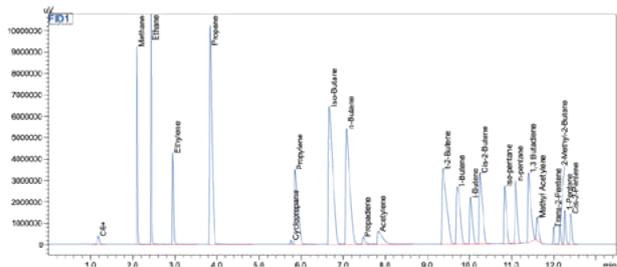Fig. 1. SCD Chromatogram – 5ppm Sulfur Components
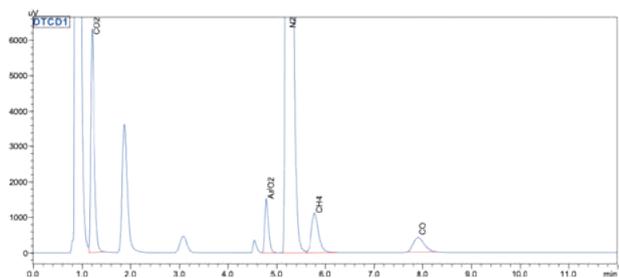

Fig. 2. FID Chromatogram – Hydrocarbons
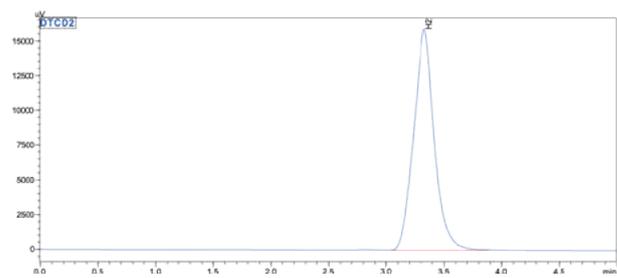

Fig. 3. TCD 1 Chromatogram – Permanent Gases

Fig. 4. TCD 2- Chromatogram – Hydrogen

Tohoku University and Shimadzu Jointly Announce a New Breath Test for Detecting COVID-19

Tohoku University announced the development of a non-invasive breath testing technology for COVID-19 through collaboration with Shimadzu Corporation, the leading provider of analytical instruments and solutions. The technology termed 'breathomics' analyzes viral and host biomolecules contained in breath aerosols that can be collected by freely breathing into the newly-developed device for five minutes. The research team aims to further apply the breathomics technology to other infectious and non-infectious diseases to bring closer the future health monitoring based on breath sampling.

Research Abstract

For minimizing both spread of COVID-19 and health hazard caused, there is an urgent need for an effective test that can simultaneously screen the disease and give other diagnostic indications such as disease severity and prognosis. To this end, Tohoku University Graduate School of Medicine and the Institute of Aging Medicine, in collaboration with Shimadzu Corporation, worked on the development of the breathomics analysis system to combat SARS-Cov-2 pandemic and more.

The system developed here utilizes a technology termed 'breathomics', which means comprehensive analysis of biological components in exhaled aerosol using mass spectrometry. Its major benefits over other testing techniques are non-invasive nature of aerosol sampling and the wealth of information that can be associated with various biological implications.

For aerosol sample collection, Tohoku University developed the high-performance collection device that acquires approximately 1 mL of exhaled breath condensate (EBC) by the subject's own manipulation in five minutes of breathing at rest. Hence the system allows for future point-of-care testing needed for early detection and safe isolation of infected personnel.

The multifaceted analysis data delivered by the system include the levels SARS-Cov-2 proteins, other viral proteins, and the host proteins and metabolites involved in inflammatory responses. In addition to giving direct indication of viral infection, results can be used to evaluate the stage and conditions of the disease, to estimate the risk of disease progression, and to predict prognosis and complications. Further studies with additional input may enable prediction of metabolic diseases such as cardiovascular and pulmonary diseases, lifestyle-related diseases, arteriosclerosis, diabetes, cancer, and health management for preventive medicine. As such, we aim to bring closer the future form of personalized and remote healthcare system which we call 'breath medicine'.

*For Research Use Only. Not for use in diagnostic procedures

Latest topics 3

Research on Alzheimer´s
Early detection of Alzheimer's biomarkers

Shimadzu, one of the world leaders in analytical instrumentation, introduces the collaboration with the Clinical Laboratory and Proteomics Platform of the CHU University Hospital of Montpellier, France. With the team of professors Sylvain Lehmann and Christophe Hirtz, they focus on MS (mass spectrometry) based blood amyloid-beta analysis for early screening of amyloid-positive subjects. The cooperation plans to conduct a joint cohort study from the Memory Resources and Research Center (Professor Audrey Gabelle) to evaluate whether this simple blood analysis method enables early and accurate prediction of amyloid pathology in the brain with an easy-to-acquire blood sample.

Unlike conventional positron emission tomography (PET) imaging and cerebrospinal fluid (CSF) testing methods, Shimadzu's blood amyloid-beta analysis method is minimally invasive and suitable for large-scale deployment. It is a new-approach blood analysis capable of being used for the research of detecting abnormal amyloid-beta concentration which can be a marker for amyloid pathology in the brain.

Opening the door to new advancements in research

These new blood-based biomarkers were discovered in 2014 by Shimadzu and the Japanese National Center for Geriatrics and Gerontology (NCGG). Although the screening analysis is Research Use Only and cannot diagnose Alzheimer's disease, it is ideal for opening the door to new advancements in research, identifying suitable candidates for clinical trials and helping pharmaceutical company to test candidate drugs.

The blood analysis works using a combination of immunoprecipitation and MALDI-TOF mass spectrometry (IP-MS). This technique was first established by a team of scientists including Shimadzu's Koichi Tanaka, who was awarded the Nobel Prize in Chemistry in 2002 for developing a method for mass spectrometric analysis of biological macromolecules.

The CHU of Montpellier is part of Shimadzu's European Innovation Center (EUIC) program. The EUIC merges the cutting-edge analytical technologies of Shimadzu with game-changing topics and expertise in markets and science covered by opinion leaders, strategic thinkers and scientific experts in order to create new solutions for tomorrow.

For more scientific background about Shimadzu's blood amyloid-beta analysis:

Nature: A. Nakamura, N. Kaneko et. al., "High performance plasma amyloid-β biomarkers for Alzheimer's disease" doi: 10.1038/nature 2545

Alzheimer's Drug Discovery Support
https://www.shimadzu.com/advanced-healthcare/case/03.html

New Products

eTOC series
On-Line TOC Analyzer for Pure Water

Demands for highly purified water and its quality control are getting stronger in many industries, such as pharmaceutical, medical device, food/beverage, chemical, precision machinery, and semiconductor. Shimadzu's eTOC has been designed to satisfy this demand. It has very high sensitivity and low detection limits, reaching 0.1 µg/L, making it perfectly suitable for ultra-pure water measurement. Technology, Usability and Reliability: the defining attributes of the ultra-small, high-value eTOC.

Features
- World's first* technology in the world's smallest and lightest* casing
- Easy-to-use and maintain design
- Reliability to support regulations

*According to August 2020 Shimadzu survey

Learn more

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Evaporative Light Scattering Detector for HPLC

ANALYTICAL INTELLIGENCE

The evaporative light scattering detector (ELSD) is a general-purpose universal detector that can even detect components with no UV absorption, such as carbohydrates, lipids, surfactants, and synthetic polymers.* With exceptional sensitivity, a wide dynamic range through Analytical Intelligence features, and easy operability using LabSolutions™ software, the ELSD-LT III contributes to more effective analysis in a wide variety of fields.

*Excluding some volatile compounds

Features
- Unique design achives universal detection
- High sensitivity and a wide dynamic range
- Compact design with excellent usability

Learn more

Nexera MX
Ultra-High Speed LCMS System for Multiplex Analysis

ANALYTICAL INTELLIGENCE

Nexera MX adopts a proprietary Nexera MX Dual Stream Technology (MX-DST) that improves the data collection efficiency of LC/MS by introducing samples into LC-MS using two alternate analysis streams. In combination with the LabSolutions Connect MRM, a series of steps from optimization of MRM to quantitative analysis can be performed seamlessly in a single software package to support easy operations in high-speed analysis.

Features
- Quick and automatic optimization of MRM conditions
- Double sample throughput with the same method
- More efficient, error-free analysis preparation

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