Technical note

Process monitoring

Comparing on-line gas chromatography and mass spectrometry

Fast, comprehensive on-line gas composition analytics

Keywords
Process monitoring, on-line gas analysis, process analyzers, gas chromatography, mass spectrometry, magnetic sector technology

Introduction

On-line analyzers have become increasingly important for process monitoring, optimization, and control of many large-scale applications that span the petrochemical, refining, metals, power generation, and biotechnology industries. Instruments need to deliver fast, accurate, and comprehensive real-time gas measurements within an industrial process, so that operational conditions can be regularly checked and rapidly corrected if they drift away from the required parameters.[1] Reliable on-line analytical data is also essential for safe and efficient operation of production plants, and to meet the stringent legislative requirements that are increasingly being set by health and safety, emissions control, and energy conservation protocols. Choosing the appropriate technology and system is, of course, crucial, and the selection process must consider factors such as long-term cost, footprint, ease of maintenance, sample time, precision, and sensitivity. Historically, on-line monitoring has relied on gas chromatography (GC) and, although technicians are confident and familiar with this robust industry standard, mass spectrometry (MS) is becoming the rising star for these applications. This technical note compares GC and MS analyzers for on-line monitoring of industrial processes, and outlines clear arguments for plants to upgrade to scanning magnetic sector MS instruments for faster, more precise, and more comprehensive gas analysis with greater long-term affordability.

The need for accurate real-time monitoring

On-line analyzers perform continuous measurements of gas streams to improve control, provide details on the product, and detect impurities. Industrial plants depend on reliable gas stream data to optimize their processes, and fine tune the reaction mixture to maximize product yields, improve the quality of finished products, and ensure safety within the production plant. Many large-scale operations require meticulously balanced conditions and fast decisions on any process parameter changes, as delays of even a minute can result in colossal losses.

Gas chromatography—the industry standard

GC is the most widespread method for on-line monitoring of gases within production lines, mainly due to relatively low cost per instrument, familiarity with the technique, ease of automation, and the ability to measure many components simultaneously. GC separates and analyzes hundreds of individual species even in complex mixtures, and measures the composition both qualitatively and quantitively. Gaseous samples are distributed between a stationary and mobile phase, while a chemically inert gas carries molecules through a heated column. Results are ready in a few minutes with high precision and very low detection limits.

Challenges of gas chromatography for process monitoring

However, despite GC being a popular technique, it does have its limitations, the first of which is time. A process gas chromatograph delivers result intermittently—at intervals of minutes—and this restricts the method's suitability for on-line analysis and automatic control where a delay between sampling and analytical time does not allow for immediate reaction correction.[2] This is largely because of time-consuming

chromatographic separation of components as the sample passes through the column.[3,4] Speed is a real advantage for on-line protocols, especially as plants will often assess two or three sequential datapoints before taking any action to change a process. The way round this when using GC is to use several instruments or columns in tandem to reduce the measurement interval and circumvent the slow analysis time; facilities tend to install an array of GC units in order to achieve continuous monitoring of multiple components—the longer cycle time of GC means that it is often utilized on a single stream basis. This set-up, though, comes with extra costs and constraints. Large configurations of GC units—with intensive maintenance schedules to guard against retention time drift—are often housed outdoors to save valuable lab space, requiring large, purpose-built, expensive shelters. There are additional consumables costs too for replacement columns, as well as calibration and carrier gases.

Mass spectrometry for faster and more comprehensive analysis

MS is a powerful and sensitive technique that provides a versatile and highly specific tool for the analysis and control of industrial production lines with key advantages in comparison to GC. Mass spectrometers can characterize many aspects of a chemical reaction, including the formation of products and impurities, and the consumption of reactants. They essentially ionize neutral sample gas molecules to charged particle components which are then separated according to their molecular weight. The analytical power of MS comes primarily from its speed, sensitivity, dynamic range, and capacity for multiplexing and multicomponent analysis.[5] MS detectors make it possible to simultaneously determine compounds of the most diverse elemental composition and establish the structural features of components.[4]

Advantages of process mass spectrometry

Although process MS analyzers are relatively more complex and initially more expensive to implement than GC, they offer unmatched speed and precision—usually several orders of magnitude higher—with more favorable long-term cost-effectiveness.[3] MS instruments based on scanning magnetic sector technology—where charged particles are separated in a variable magnetic field—provide flat-topped peak profiles that tolerate mass scale drift with no effect on measurement results, leading to high stability, reduced maintenance times, and maximum availability for plant productivity (Figure 1).[5] These analyzers are able to measure very small concentrations immediately adjacent to high concentrations as a result of the clean baseline between peaks, offering excellent reproducibility and linearity. This powerful and flexible technology is ideal for exceptionally stable and rapid analysis of gases with unparalleled precision, accuracy, resistance to contamination, and long intervals between recalibration. Process MS analyzers are able to perform direct analysis on multiple sample streams, and a single instrument can replace multiple GC units, resulting in a lower total footprint and reducing overall capital costs.

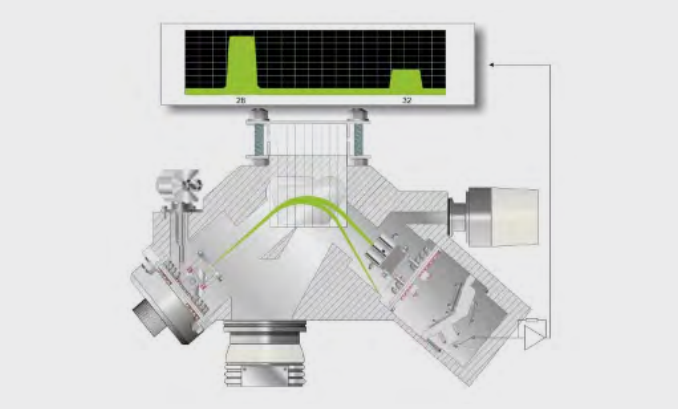

Figure 1. Schematic of a magnetic sector process mass spectrometer.

Instruments that use scanning magnetic sector MS, such as the compact and rugged Thermo Scientific™ Prima PRO (Figure 2), are ideal for the challenging applications in process monitoring. The Prima PRO magnet is laminated to allow scanning at high speeds for rapid analysis while maintaining excellent stability, and is equipped with the unique rapid multi-stream sampler (RMS) to provide fast and reliable sample selection from up to 64 streams (Figure 3). It can precisely measure gas component concentrations in the range of 10 parts per million (ppm) to 100% with a single Faraday detector. Thermo Scientific GasWorks Software is integrated into the analyzer to guide operations and provide a secure, stable platform for process analytics (Figure 4). Service and support options with promised response rates have also been designed by Thermo Fisher Scientific to ensure timely instrument optimization.

Figure 2: Prima PRO Process Mass Spectrometer.

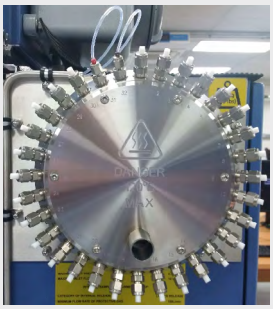

Figure 3: The Prima PRO's 32-port rapid multi-stream sampler (RMS).

Figure 4. GasWorks Software sample display.

Feature	Standard process GC	Prima PRO process MS
Sample time		
• **Simple**	3–4 minutes	10 seconds
• **Complex**	7–15 minutes	20 seconds
Multicomponent analysis	Requires an array of multiple units	Analysis of up to 64 sample streams performed by a single instrument.
Precision	0.1 %	0.01 % on most components and with better linearity.
Footprint	Single instrument is more compact, overall footprint of a bank of multiple instruments is larger.	Less compact, with a smaller overall footprint as fewer instruments are required.
Shelter	Array of units often requires large, expensive outdoor shelter.	• A smaller shelter is required if the instrument is housed outdoors.
Maintenance, calibration, and lifetime	• Prone to retention time drift, lower stability. • Higher maintenance with a standard process. • GC requiring, for example, a six-week preventative maintenance schedule for valves, alongside quarterly maintenance on other instrument parts, with common applications needing daily calibrations.	• Minimal drift due to inherent stability of magnetic sector analyzer. • Minimal maintenance. • Automatic calibration (30-day or 30- to 90-day intervals).
Approximate analyzer cost (USD)	$50–75k	$175k
Associated costs	High cost of consumables, including carrier gases and replacement columns.	• Low lifetime cost of consumables (no carrier gases or column replacement). • Long replacement intervals (one year or more).

Table 1: Comparing the features of a standard process GC with the Prima PRO process MS.

Direct comparison of a standard process GC with the Prima PRO

Reduced sample times

The Prima PRO offers analysis in 10 to 20 seconds if the analyzer inlet remains on a single sample stream, rather than the 3 to 15 minutes usually seen on standard process GC analyzers, with actual analysis time depending on target gas complexity. A single Prima PRO can measure multiple sample points with very short cycle times by plumbing several streams into the same instrument's RMS, reading datapoints on these multiple sample streams every 30 seconds, including the 10 seconds to flush out the previous gas.

Unmatched precision and linearity

Analysis of fuel gas components is around five times more precise on the Prima PRO compared to a standard process GC. Performance assessments have shown that the Prima PRO gives significantly better linearity than a thermal conductivity detector fitted to a gas chromatograph when analyzing complex gas mixtures (Figure 5).[6,7]

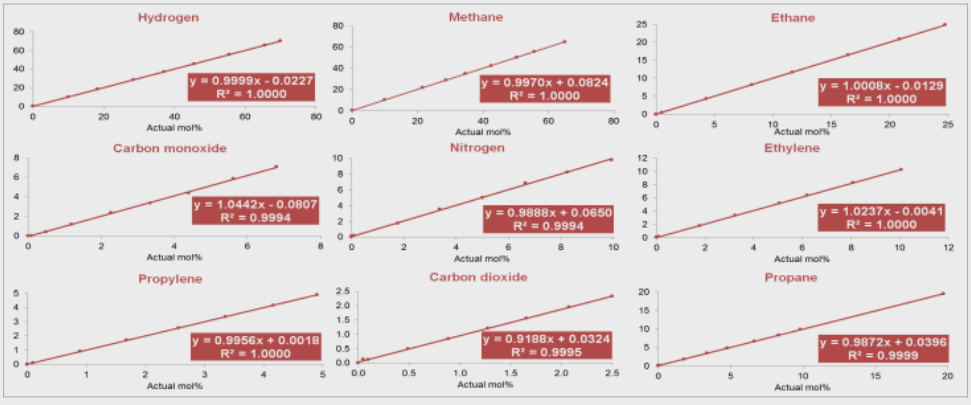

Figure 5. Prima PRO linearity data generated by EffecTech.

Exceptional availability for simplified maintenance and calibration

The rugged, fault-tolerant design of the Prima PRO leads to exceptional availability that exceeds 99.7 %, reaching 100 % with redundant installation. This reliability significantly lowers the Prima PRO's maintenance requirements to further reduce operating costs, freeing up a maintenance manager's time for other tasks, especially compared with the maintenance that multiple legacy GC units would need. The Prima PRO's typical calibration interval is between one month and 90 days, and normally takes place automatically. A standard process GC might require, for example, a six-week preventative maintenance schedule for valves, alongside quarterly maintenance on other instrument parts, with common applications requiring daily calibrations.

Reduced overall long-term costs

Although the capital outlay for the Prima PRO (approximately US $175k) is greater than that for a standard process GC (approximately US $50 to 75k), a single system performs the job of multiple GC units, lowering the total cost of ownership, shelter size and maintenance. Unlike a process GC analyzer, the Prima PRO does not require separation of the sample via a column, avoiding consumables costs on replacement columns, as well as calibration and carrier gases.

Table 2 outlines a 10-year customer case study that analyzed the total cost differential associated with replacing two legacy process GCs with one Prima PRO for flare gas monitoring. The Prima PRO offers fast, accurate and multicomponent analysis for a plant stack, lending itself ideally to this demanding application that requires analysis of extremely complex gas streams. At the close of the decade, total operating costs were reduced by almost a half, largely due to lower utility costs, and significantly reduced consumables expenses.

Flare gas monitoring	1x Prima PRO MS	2 x process GC
Analyzer cost (USD)	$155,400	$155,000
Utilities (USD)	$39,000	$278,000
Consumables	$67,257	$100,000
Total operating costs for 10 years	**$261,691**	**$533,000**

Table 2: Customer case study cost analysis over 10 years comparing one process MS (Prima PRO) with two legacy process GCs.

Conclusion

The demands of manufacturing processes and associated legislative requirements have led to a need for rapid, accurate, and reliable process analyzers at affordable costs. The choice of on-line analyzer has largely been driven by familiarity but it is clear that the highly versatile magnetic sector MS can provide faster analysis at higher levels of precision—with a reduced number of analyzers—and these systems are becoming increasingly popular as a result. The Thermo Scientific Prima PRO is an ideal example of this; it is optimally suited to industrial process monitoring and, although MS is relatively more complex and expensive to implement, a single instrument can perform the work of multiple GC units to reduce sample time, simplify maintenance, and lower overall costs. The Prima PRO MS delivers fast, precise, and comprehensive on-line gas composition analytics that is unmatched, as well as extremely favorable flexibility compared to a standard process GC, ensuring a strong return of investment. It is built to meet the application-specific needs of today, already the system of choice in refineries and plants across the globe to monitor emissions and optimize a diverse range of production processes, and is set to be the industry standard in future.

References

1. Valcárcel M, Luque de Castro MD, eds. 16 Process analysers. In: *Techniques and Instrumentation in Analytical Chemistry.* Vol 9. Elsevier; 1988:524-556. doi:https://doi.org/10.1016/S0167-9244(08)70028-3
2. Frauendorfer E, Wolf A, Hergeth WD. Polymerization Online Monitoring. *Chem Eng Technol.* 2010;33(11):1767-1778. doi:10.1002/CEAT.201000265
3. Cheng Z, Mozammel T, Patel J, et al. A method for the quantitative analysis of gaseous mixtures by online mass spectrometry. *Int J Mass Spectrom.* 2018;434:23-28. doi:10.1016/J.IJMS.2018.09.002
4. Borisov R, Kulikova L, Zaikin V. Mass Spectrometry in Petroleum Chemistry (Petroleomics) (Review). *Petroleum Chemistry.* 2019;59:1055-1076. doi:10.1134/S0965544119100025
5. Cook KD, Bennett KH, Haddix ML. On-Line Mass Spectrometry: A Faster Route to Process Monitoring and Control. *Ind Eng Chem Res.* 1999;38(4):1192-1204. doi:10.1021/IE9707984
6. EffecTech UK | Global Leaders in Gas Measurement. Accessed February 24, 2023. https://www.effectech.co.uk/
7. ISO - ISO 10723:2012 - Natural gas — Performance evaluation for analytical systems. Accessed February 24, 2023. https://www.iso.org/standard/55712.html

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