White paper | 003769

Combustion-IC

Enhancing the efficiency and effectiveness of halogen and sulfur monitoring in challenging environmental and industrial samples

Author

Carl Fisher, Thermo Fisher Scientific,
Sunnyvale, CA 94085

Keywords

C-IC, halogens, sulfur, corrosives, contaminants, interference, Cindion, PFAS, AOF, combustion-ion chromatography, sample preparation

Introduction

In industrial processes, the accurate determination of halogens and sulfur is of paramount importance due to their significant impact on product quality, equipment integrity, and environmental compliance. Halogens, such as fluorine, chlorine, bromine, iodine, and sulfur compounds are prevalent in various industries, including consumer product manufacturing, petroleum refining, and chemical manufacturing. These elements and compounds can influence corrosion rates, catalytic efficiency, and the safety of operations, making their monitoring essential for optimal process control.

Additionally, the emerging need to screen for per- and polyfluoroalkyl substances (PFAS) in various environmental and consumer product sources has heightened the importance of halogen determinations. PFAS, a group of fluorinated compounds, is increasingly recognized for their persistence in the environment and potential health risks. Accurate detection and quantification of PFAS in water, soil, and consumer products are critical for assessing the potential exposure to PFAS contaminants.

The objective of this white paper is to provide a comprehensive overview of the methodologies and best approaches for the determination of halogens and sulfur in challenging industrial and environmental samples. It aims to equip analytical lab technicians, lab managers, researchers, and other stakeholders with knowledge to assist them in implementing accurate and reliable analytical techniques. By understanding the principles, applications, and challenges associated with halogen and sulfur determinations, industry professionals can ensure compliance with regulatory standards, improve product quality, and minimize environmental impact.

Determination of halogens and sulfur

Halogens are chemically versatile elements that can form a variety of compounds including salts, acids, and organic halides. They are very good at attracting electrons (i.e. they are highly electronegative) due to their nuclear charge and small size. This is especially true for fluorine, which is the most electronegative element. Their strong tendency to attract electrons makes them highly reactive and allows them to interact with a variety of elements to form ionic bonds, as in salts like NaCl, and covalent bonds, as in organic halides such as chloromethane.[1]

Halogens can be beneficial as disinfectants, as is the case with chlorine, primarily in the form of hypochlorite which is commonly used to kill bacteria and other pathogens,[2] and iodine, which is an often indispensable first aid kit antiseptic.[3] In certain forms and concentrations, halogens can be lifesaving. However, their reactivity also means that they can be highly corrosive. Fluoroantimonic acid (H_2FSbF_6), a combination of hydrogen fluoride (HF) and antimony pentafluoride (SbF_5), is amongst the most corrosive compounds on the planet. Even weaker acids, such as HF or HCl, can cause considerable damage. If left unchecked, they can lead to corrosion that compromises the integrity of critical infrastructure or can be an environmental pollutant in the form of acid rain. These risks make it critical to regularly monitor industrial processes to detect and minimize the impact of halogens by eliminating them whenever possible.

While inorganic halogenated molecules can be highly reactive and corrosive, halogenated organic molecules exhibit major environmental concerns. A prime example of this is Teflon (polytetrafluoroethylene, PTFE), in which fluorine atoms form very strong bonds with carbon atoms to form a highly stable polymer. The C-F bond is one of the strongest in organic chemistry, making PTFE highly resistant to chemical reactions, which means that it is inert to most chemicals and solvents and is also very thermally stable.[1] Other advantageous properties of Teflon include a low coefficient of friction due to the very low intermolecular forces between the polymer chains, making it ideal as a non-stick surface, and its hydrophobicity, which gives it excellent water resistance. Despite its many practical advantages in consumer products, the family of compounds that PTFE is a member of, PFAS, can also have a toxicological effect, such as increased risk of cancers, developmental delays in children, and reduced immune response.[4] An undesirable consequence of the chemical resistance of the PFAS family is its persistence in the environment, earning it the moniker “forever” chemicals. PFAS continues to be an enduring threat, despite its declining use in manufacturing as much less toxic alternatives have been adopted in response to progressively more stringent regulations. In response to evidence of the harmful effects of PFAS, the U.S. Environmental Protection Agency (EPA) introduced regulatory limits in 2024 as part of the National Primary Drinking Water Regulation for six PFAS with the maximum contaminant levels (MCLs) for two of these set at 4 parts per trillion using targeted analysis.[5] These limits are for specific PFAS compounds, but there are more than 10,000 of these compounds potentially in the environment. Thus, it is unlikely that all PFAS in a sample can be represented or identified with such a narrow focus. One method that was also recently approved as a screening tool for PFAS is U.S. EPA Method 1621[6] which uses combustion in combination with ion chromatography.

Perfluorinated compounds (PFCs) are also well-suited as components of flame retardants due to their reactivity, ability to scavenge free radicals, thermal stability, and propensity to interact and retard flames.[7] These can be present in products such as electronics enclosures and in internal components, such as circuit boards. Due to their potential adverse health effects and environmental longevity, there has been a decrease in their use and a switch to non-halogenated alternatives. Products containing these retardants have been banned or restricted for import into many countries (e.g. EU Restriction of Hazardous Substances (RoHS) Directive),[8] making it essential that manufacturers and those dealing with electronic waste be aware of their potential presence and the risk they pose. In addition to consumer products, halogens have also been used in foams as an aid to firefighting (Aqueous Fire Fighting Foam, AFFF). Large quantities were routinely used during training at airports where the foam would then be flushed onto adjacent property and end up in the water supply. These foams are starting to be phased out, with some U.S. states mandating that only fluorine-free foams be used and unused foam recalled.[9] Testing is needed for both the foams themselves, to provide some indication of halogen absence, and as part of land reclamation or other cleanup efforts.

The monitoring of sulfur species in industrial processes is crucial due to their significant impact on both product quality and environmental compliance. Sulfur compounds, such as hydrogen sulfide (H_2S) and sulfur dioxide (SO_2), can cause equipment corrosion, leading to costly maintenance and potential safety hazards.[10] Additionally, sulfur species can act as poisons for catalysts in refining processes, diminishing the efficiency of catalysts and affecting the overall yield and purity of products.[11] From an environmental perspective, the release of sulfur compounds into the atmosphere contributes to acid rain and air pollution, necessitating stringent regulatory compliance.[12] Precise and continuous monitoring of sulfur species is essential for optimizing industrial processes, ensuring product integrity, and maintaining adherence to environmental regulations.

Matrix elimination

To determine the total amount of halogens and sulfur independent of their binding form, we need to make these elements accessible to analytical analyses. This can be a considerable challenge. Many samples are solids or water-insoluble liquids. Hence, we need to transfer the covalently bound halogens and sulfur into water-soluble halides and sulfate. Doing this will also remove potential interferences that could inhibit accurate determinations.

There are several sample preparation options to release the halogens and sulfur:

- **Combustion (oxygen bomb) calorimetry:** This method oxidizes all hydrocarbons to carbon dioxide and water, and converts all sulfur compounds to soluble forms, which are then absorbed in a small amount of water placed in the vessel.[13]
- **Schöniger flask:** In this method, a sample is combusted in pure oxygen, and the combustion products are absorbed by a sodium hydroxide solution.[14]
- **Wickbold apparatus:** This apparatus includes a shell oven, solid-state burner, burning chamber, cooling device, absorption tube, solution tank, rinsing device, and a flask for decomposition solution.[15]
- **Microwave-induced combustion:** Samples are burned in a vessel pressurized by oxygen using microwave energy, which absorbs the analytes in small amounts of liquid. This method can achieve temperatures higher than 1200 °C.[16]
- **Chemical digestion:** This involves using strong acids or bases to break down the sample matrix, converting it into a solution that can be analyzed. Common acids used include nitric acid, sulfuric acid, and hydrochloric acid.[17]
- **Manual tube furnace:** This method involves placing the sample in a quartz or ceramic tube and heating it to high temperatures in the presence of oxygen. The combustion products are then absorbed in a suitable solution for analysis.[18]

These options vary considerably based on cost, extent of oxidation, time, sample volumes, and sample type suitability (Table 1).

Once samples have been adequately prepared, there are several analytical methods available for quantification, including ion selective electrodes (ISE), microcalorimetry, inductively coupled plasma (ICP), X-ray fluorimetry (XRF), and ion chromatography (IC), each having their strengths and weaknesses (Table 2). The available methods may be limited by the solution obtained from the sample preparation. For example, effective microwave-induced combustion requires the use of a solution with a large dipole moment such as ethanol, which has a hydroxyl group that makes it efficient at absorbing microwave energy. Unfortunately, ethanol is a solvent that is not readily compatible with some analytical techniques such as IC.[19]

Table 1. Comparison of sample preparation methods for determining halogens and sulfur in challenging matrices

Parameter	Oxygen bomb	Schöniger flask	Wickbold apparatus	Microwave-induced combustion	Chemical digestion	Manual tube furnace
Cost	$$$	$	$$$	$$$	$	$$
Complete oxidation	√	√	√	√	X	√
Suitable for large samples	X	X	√	√	X	X
Setup time	Time-consuming	Manual and potential for errors	Maintenance-intensive	Rapid and efficient	Time-consuming	Time-consuming
Automation	X	X	X	√	√	X
Flexibility in sample types	Moderate	Moderate	High	Moderate	Wide range	High
Sample processing time	Long	Moderate	Long	Short	Long	Long

√ = Yes **√ = Partially** **X = No**

Table 2. Comparison of analytical techniques for quantifying anions

Parameter	Ion selective electrodes (ISE)	Microcalorimetry	Inductively coupled plasma (ICP)	X-ray fluorimetry (XRF)	Ion chromatography (IC)
Cost of operation	$	$$$	$$$$	$$	$$$
Sensitivity	Moderate	High	Very high	Moderate	High
Skilled operator	Low	High	Very high	Moderate	Moderate
Multiple analyte analysis	X	X	✓	✓	✓
Non-destructive	✓	✓	X	✓	✓
Susceptibility to interference	Moderate	Low	Low	Moderate	Low
Rapid measurement	✓	X	✓	✓	X

✓ = Yes **X = No**

Combustion-ion chromatography (C-IC)

As noted above, there are multiple methods for sample preparation and subsequent analysis, each with its advantages and drawbacks. C-IC is a hyphenated technique that uniquely integrates and automates both processes. This integration ensures consistent, accurate, and sensitive determinations while saving valuable hands-on time and minimizing exposure to hazardous chemicals and pressurized vessels. First utilized in 1980 by two groups using the Dionex Model 10, the first commercially available IC system which had been introduced just five years prior, C-IC was initially applied to analyze sulfur in fuels and halogens in ore samples[24,25] —applications that remain critical in their respective industries today. Since these initial uses, C-IC has been applied to samples ranging from polyethylene,[26] carbonated beverages,[27] and clean room gloves.[28]

C-IC incorporates several key steps (Fig. 1):

1. **Sample introduction:** Samples can be introduced manually, but automation is achieved using a liquid or solid handling autosampler. The rate of sample entry into the oven can be adjusted to ensure controlled combustion, minimizing soot production, an indicator of incomplete combustion that can lead to inaccurate results. Proper rate control also prevents liquid samples from volatilizing too quickly, another source of error.
2. **Pyrohydrolytic combustion:** Pyrohydrolysis involves heating the sample in the presence of water vapor and oxygen to decompose nonvolatile halogens into volatile halide acids.[20] Combustion occurs at temperatures up to approximately 1100 °C, with the specific temperature used varying based on the sample type. Controlling combustion can also be achieved by creating temperature gradients within the oven, progressing from cooler to warmer regions.
3. **Absorption:** The gases produced during combustion are sparged into either water or a hydrogen peroxide solution. The hydrogen peroxide oxidizes sulfur anions to sulfate, facilitating their subsequent analysis.
4. **Ion chromatography:** The absorption solution is injected into an IC system to determine the concentrations of halogens and/or sulfate. This is done by comparing the conductivity intensity of the sample to standard curve measurements.

In comparison to the separate sample preparation and analysis methods noted earlier, C-IC delivers time and labor savings by automating the entire process. Removing manual steps greatly enhances reproducibility, while this method provides sensitivity down to parts per billion, depending on the sample type and specific preparation method used.

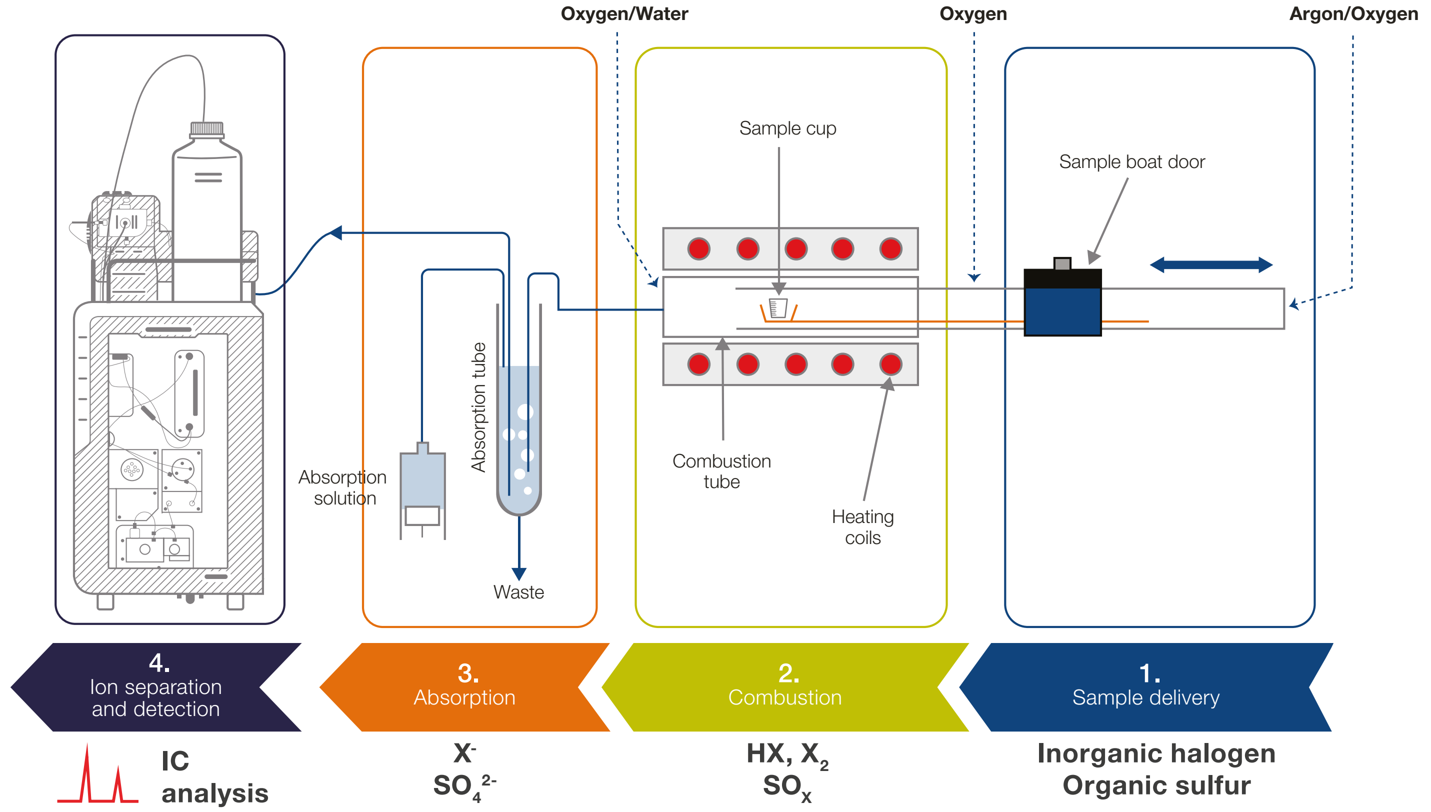

Figure 1. Overview of a C-IC system

C-IC system considerations

When selecting the best option for a C-IC system, several factors should be considered:

- **Sample introduction**
  While manual sample introduction is possible, most systems offer the option of using either a liquid or solid handling autosampler. Ideally, switching between the two should be quick and tool-free, without the need for recalibration. Additionally, a separate module for gas injection and the appropriate connections are necessary for analyzing gas or liquid petroleum gas (LPG) samples.

- **Efficiency and completeness of combustion**
  The system design should optimize combustion efficiency to minimize the time needed for complete combustion, thereby reducing overall analysis time.

- **Presence of potential contaminants in the sample analysis flow path**
  Minimizing contaminants is crucial, especially for analyzing low levels of fluorine in certain analyses such as for PFAS screening. Some systems use PFAS-containing components, such as Teflon-coated parts, which should be avoided.

- **Sample carryover**
  High-concentration samples that are run in sequence adjacent to low-concentration ones can lead to carryover, resulting in erroneously high readings. Shortening the length of the flow path reduces the likelihood of sample adherence to surfaces, significantly minimizing carryover.

- **Sensitivity**

  Sensitivity can be adjusted through several options:

  - **Absorption solution volume:** Smaller volumes can be used for lower concentrations and larger volumes for higher concentration samples.
  - **Injection loop:** The volume can be varied to accommodate differing analyte concentrations although it is constrained by the IC column diameter. For example, for 2 mm columns an injection volume typically ranges from 2.5 – 250 µL.
  - **Sample concentration:** Methods determining adsorbable organic halogens (AOX) or adsorbable organic fluorine (AOF) typically require an adsorption module, where approximately 100 mL of sample is passed over granular activated carbon columns. Post-combustion, a concentrator column can be used on the IC side.

- **Combustion tube lifetime**
  The integrity of the combustion tube is critical to accurate determinations. It should permit complete combustion to occur and ensure the faithful transfer of liberated gases to the absorption solution. High levels of alkali substances can induce quartz devitrification (structural degradation), resulting in decreased accuracy and lower recoveries, necessitating tube replacement. The use of ceramic inserts can reduce quartz tube damage but will also eventually need replacement. Strategies to extend tube life include increasing combustion efficiency to reduce the time needed for combustion, reducing exposure time and restricting the addition of water, a contributor to quartz degradation.

- **Software**
  The software is the control center of the entire system. Ideally, it should be a single application that automates all analysis steps, from sample introduction to report generation. There should not be a need for multiple software programs to control separate components, which can increase the likelihood that parts of the system get out of sync, causing run interruption that impacts productivity.

- **Comprehensive setup and support**
  C-IC systems often consist of components supplied by different manufacturers. This can lead to the sample preparation (combustion/absorption) and IC components being installed and maintained by separate teams, resulting in potential delays and complications. To mitigate these challenges, having a single point of contact for sales, support, and service is highly advantageous.

The Thermo Scientific™ Cindion™ Combustion Ion Chromatography System (Fig. 2) fulfills all the criteria described above. It is an integrated solution that offers numerous benefits:

Compact design: The novel, compact combustion tube design ensures complete combustion over a shorter distance which, when combined with the integration of the autosampler and absorption tube into the same module, greatly reduces the system footprint.

Minimized PFAS contamination: The unique combustion front-end incorporates PFAS-free components whenever possible within the sample pathway, eliminating potential sources of contamination. This results in the lowest achievable background levels (non-detectable PFAS), enabling the most sensitive detection.

Industry-leading IC features: Innovations such as electrolytic suppression and reagent-free ion chromatography (RFIC™) eluent generation enhance consistency and ease of use.

Single-source convenience: Obtain the complete system, all necessary consumables, and a unified software package from a single vendor, ensuring a seamless customer experience.

Complete workflow package: Benefit from a comprehensive range of complementary technologies for analytical determinations, particularly advantageous for PFAS analysis requiring both targeted and non-targeted approaches.

Experience and support: Leverage the extensive library of Thermo Scientific C-IC application notes for numerous sample types and benefit from over 50 years of experience in IC technology.

Figure 2. Cindion C-IC system

Conclusion

C-IC is an innovative analytical technique that combines the processes of sample preparation and analyte determination into a single, automated system. The Cindion C-IC system exemplifies this integration, offering a comprehensive solution for the precise measurement of halogens and sulfur in various matrices. By addressing the challenges of matrix elimination and minimizing contamination risks, particularly from PFAS, the Cindion C-IC system ensures low background levels and, subsequently, high sensitivity.

This system's compact design, industry-leading features, and single-source convenience streamline workflows, reduce hands-on time, and enhance analytical consistency. With robust support, the Cindion C-IC system leverages over 50 years of expertise in ion chromatography to meet the evolving needs of industries that include oil and gas, chemical manufacturing, mining, materials analysis, waste management, and environmental reclamation.

In summary, the Cindion C-IC system not only elevates analytical performance but also provides a seamless and efficient solution for the accurate determination of halogens and sulfur, driving advancements in analytical chemistry and supporting critical environmental and industrial applications.

References

1. Miessler GL, Fischer PJ, Tarr DA (2013) Inorganic Chemistry (5th ed.) Pearson.
2. Chemical Disinfectants: Guideline for Disinfection and Sterilization in Healthcare Facilities, US Centers for Disease Control and Prevention, 2023, Chemical Disinfectants | Infection Control | CDC.
3. Vermeulen H, Westerbos SJ, Ubbink DT (2010) Benefit and harm of iodine in wound care: a systematic review. J. Hosp. Infect. 76(3):191-9.
4. Our Current Understanding of the Human Health and Environmental Risks of PFAS (link). EPA (accessed 2/11/25).
5. Per- and Polyfluoroalkyl Substances (PFAS): Final PFAS National Primary Drinking Water Regulation, U.S. EPA. Per- and Polyfluoroalkyl Substances (PFAS) | US EPA (Accessed 2/14/25).
6. Christison T (Accessed 2/14/25) Why Everyone is Talking About PFAS and EPA Method 1621. AnalyteGuru Why Everyone is Talking About PFAS and EPA Method 1621 - AnalyteGuru.
7. Weil ED, Levchik SV (2009) Flame Retardants for Plastics and Textiles: Practical Applications. Hanser Publishers, Cincinnati, OH.
8. Flame Retardants and Your Health, National Institute of Environmental Health Sciences, 2023. Flame Retardants and Your Health fact sheet.
9. SB-1044 Compliance: Phasing Out PFAS in Class B Firefighting Foam, Cal Fire, 2024. Fire Fighting Equipment and Foam PFAS | OSFM.
10. Speight JG (2014) The Chemistry and Technology of Petroleum. CRC Press, Boca Raton, FL.
11. Meyers RA (2004) Handbook of Petroleum Refining Processes. McGraw-Hill Professional, New York, NY.
12. EPA. Sulfur Dioxide (SO_2) Pollution, 2021. https://www.epa.gov/so2-pollution.
13. Parry SJ (1991) Principles of Analytical Chemistry: A Textbook. Springer.
14. Schoniger W (1955) The Determination of Halogens in Organic Compounds. Microchimica Acta.
15. Wickbold RA (1958) Method for the Determination of Halogens and Sulfur in Organic Compounds. Microchimica Acta.
16. Schmidt L, Bizzi C, Rosa F, et al. (2017) E. Microwave-Induced Combustion: towards a robust and predictable sample preparation method. New J. Chem. 41:6902.
17. Harris DC (2015) Quantitative Chemical Analysis. W.H. Freeman and Company.
18. Vogel AI (1996) Vogel's Textbook of Quantitative Chemical Analysis. Prentice Hall.
19. Weiss J (2004) Handbook of Ion Chromatography. Wiley-VCH.
20. Skoog DA, Holler FJ, Crouch SR (2017) Principles of Instrumental Analysis (7th Edition). Cengage Learning.
21. Grime GW (1991) Microcalorimetry: Methods and Applications. Wiley.
22. Montaser A (1998) Inductively Coupled Plasma Mass Spectrometry. Wiley-VCH.
23. Jenkins R (1999) X-ray Fluorescence Spectrometry. Wiley-Interscience.
24. McCormick MJ (1980). Determination of total sulphur in fuel oils by ion chromatography, Anal Chim Acta 121: 233-238.
25. Evans KL, Moore CB (1980) Combustion-ion chromatographic determination of chlorine in silicate rocks. Anal Chem 52:1908–12.
26. Aggrawal M, Rohrer J (2018) Application Note AN72588: Determination of chlorine, bromine, and sulfur in polyethylene materials using combustion IC with a carbonate/bicarbonate eluent, Thermo Fisher Scientific, Sunnyvale, CA, USA. [Online] Determination of Chlorine, Bromine, and Sulfur in Polyethylene Materials Using Combustion IC with a Carbonate/Bicarbonate Eluent
27. Christison T, Patil S, Rohrer J (2019) Application Note AN72917: Fast determinations of brominated compounds in carbonated beverages using oxidative pyrolytic combustion and ion chromatography, Thermo Fisher Scientific, Sunnyvale, CA, USA. [Online] Fast Determinations of Brominated Compounds in Carbonated Beverages using Oxidative Pyrolytic Combustion and Ion Chromatography
28. Christison T, Rohrer J (2020) Application Note AN73865: Pyrohydrolytic combustion ion chromatography Determination of total chlorine and sulfur in cleanroom gloves, Thermo Fisher Scientific, Sunnyvale, CA, USA. [Online] Determination of total halides in cleanroom gloves using pyrohydrolytic combustion ion chromatography

Learn more at **thermofisher.com/cindion**