Agilent ICP-MS Journal

August 2023, Issue 93

ICP-MS Applications from Semiconductor Gases to Li-Ion Battery Electrolyte Solvents.

ICP-MS enables and supports an astonishingly wide range of applications, touching practically every aspect of our lives.

In this issue of the Agilent ICP-MS Journal we report on some of the more unusual types of analyses that Agilent ICP-MS users are performing. Starting with the analysis of impurities and contaminants in high-purity electronic gases, using an Agilent GC-ICP-MS fitted with an appropriate sampling valve. High purity gases are used throughout the semiconductor fabrication process and Agilent GC-ICP-MS systems provide the elemental coverage and detection limits required for the latest generation of advanced semiconductor devices.

ICP-MS is also used by Li-ion battery manufacturers to measure trace element impurities in the solvents used to make the battery electrolytes. And ICP-MS enables researchers to assess occupational exposure by measuring unusual elements using non-specific calibration.

Figure 1. Agilent 8900 ICP-QQQ coupled to Agilent 8890 GC using Agilent fully heated GC-ICP-MS interface.

Configuration and Applications of GC-ICP-MS for Gas Analysis in Semiconductor Manufacturing

Ed McCurdy, Agilent Technologies Inc. and William M. Geiger, CONSCI Ltd, Pasadena, Texas, USA

Semiconductor industry trends

Recent issues with global semiconductor industry supply chains, chip shortages in some sectors, and oversupply in others have been widely reported. Nevertheless, the electronics industry is predicted to grow to more than $1 trillion in annual revenues by 2030, roughly double 2020's figure. The fastest growing sectors are manufacturing, automotive, and servers, data centers, and storage to support the rise in accelerated computing, generative AI, machine learning, and cloud computing.

Advances in integrated circuit (IC) design are mainly derived from reducing device dimensions. Packing more transistors into a smaller space improves performance by creating circuits with faster switching, lower power consumption, and reduced heat generation, useful for applications such as portable and wearable devices.

The latest chips have circuit features measured in single nanometers, where the position of one atom can change the electrical properties, making devices highly susceptible to contamination. Advanced semiconductor manufacturers therefore require the highest level of purity for raw materials, process chemicals, and gases.

Specialty gases in semiconductor fabrication

High purity gases are used extensively in semiconductor manufacturing, for example during purification of the silicon substrate and as precursors for non-silicon wafers such as gallium arsenide (GaAs). Specialty gases are also used to add dopant elements to the substrate, to deposit and etch thin films, and to clean the process chamber between fabrication steps. In a typical semiconductor fabrication plant, high purity gases are the second biggest material cost, after high purity silicon. As with liquid process chemicals such as high purity acids and solvents, gases used in chip fabrication require the lowest possible levels of contaminants.

Figure 1. Many semiconductor gases are toxic, flammable, or pyrophoric, so require specialized GC sample introduction.

Gas chromatography (GC) sample introduction for volatile liquids and flammable gases

Many semiconductor gases and volatile organic liquids are suitable for analysis by GC, but some of these gases are flammable or pyrophoric (ignite on contact with air). Such samples are not compatible with conventional GC sample introduction, as they must be prevented from coming into contact with the air before being introduced into the GC. For example, chlorosilanes are highly volatile liquids that decompose on contact with air, forming HCl and silica, so cannot be introduced using a standard GC injector. Figure 2 illustrates a high-pressure switching valve used at CONSCI for direct injection of chlorosilanes for analysis by Agilent GC-ICP-MS.

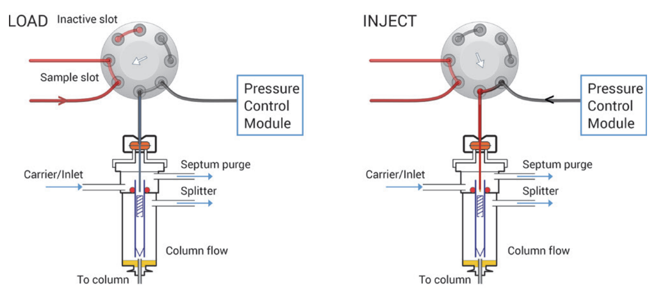


Figure 2. High pressure switching valve for direct injection of volatile liquids such as trichlorosilane (TCS) for analysis by GC-ICP-MS.

GC-ICP-MS analysis of silanes and chlorosilanes

The vast majority of semiconductor chips use a silicon (Si) wafer substrate, the starting material for which is quartzite (sand). The Si is refined to better than 9 nines (9N) purity, which is 99.9999999% pure Si (<1 ppb total impurities). Group III and V elements such as B, P, S, and As alter the electrical properties of the Si crystal, so they must be minimized along with any metallic impurities.

To purify semiconductor Si, metallurgical Si (about 99% pure) is heated in a reaction chamber with gaseous HCl to form TCS, which is purified by fractional distillation. In the Siemens process, pure TCS is deposited on Si threads to form polycrystalline ingots. Alternatively, a fluidized bed reactor (FBR) can be used to form Si beads from TCS or the pyrophoric gas monosilane (SiH_4).

In both processes, the purity of the polycrystalline Si is strongly dependent on the purity of the feedstock. An Agilent GC-ICP-MS can be used to measure impurities and contaminants in Si precursors such as TCS and SiH_4.

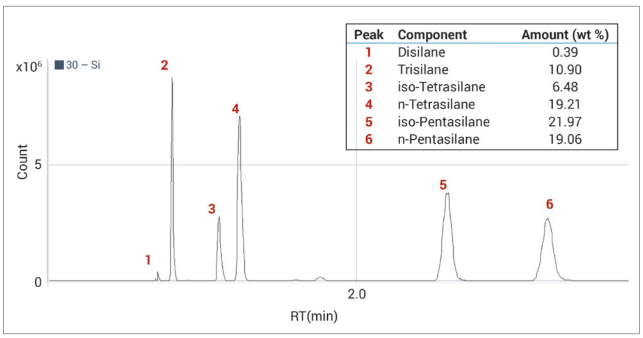


Figure 3. GC-ICP-MS chromatogram of silane compounds in a polysilane mixture. Si measured using minor Si-30 isotope (3.1% abundance).

To optimize the Si purification process, the precursor composition must be tightly controlled. Figure 3 illustrates a GC-ICP-MS chromatogram of a polysilane mixture. The silane compounds were quantified using compound independent calibration (CIC) based on the Si elemental response. The silanes were present at percent levels, so Si was measured using the minor ^{30}Si isotope.

ICP-MS can measure almost every element at low levels, so is an ideal detector for trace contaminants in semiconductor gases. The Agilent 8900 ICP-MS/MS extends ICP-MS capability to include trace analysis of traditionally difficult elements such as Si, P, S, and Cl.

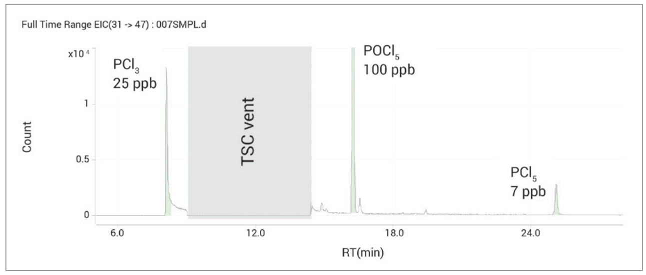


Figure 4. Trace P compounds in TCS measured by GC-ICP-MS/MS.

Figure 4 illustrates the analysis of ppb-level phosphorus-containing compounds, PCl_3, $POCl_5$, and PCl_5, in TCS, quantified using CIC. The low required detection limits were achieved by measuring P as the PO^+ product ion using an Agilent ICP-QQQ operating in MS/MS mode with O_2 cell gas. A Deans Switch was used to vent the TCS matrix to prevent excessive matrix loading to the ICP-MS.

High purity 2-fluorobutane (C_4H_9F) is used as a plasma reaction gas for etching SiN films. Contaminants must be strictly controlled as they can affect the etch rate and contaminate the film and substrate. Figure 5 illustrates GC-ICP-MS analysis of trace contaminants in C_4H_9F.

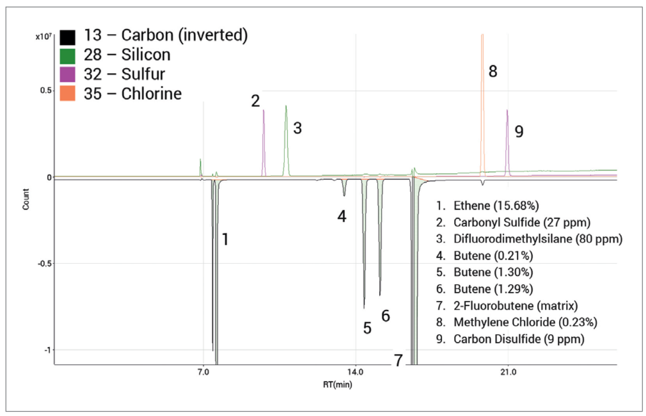


Figure 5. Trace contaminants in 2-fluorobutane by GC-ICP-MS.

Conclusion

High purity semiconductor gases and volatile liquids can be analyzed using GC with direct injection. ICP-MS is a versatile and sensitive detector for GC, giving accurate determination of trace level contaminants.

Reference

1. Trace Analysis of Specialty and Electronic Gases, W. M. Geiger and M. W. Raynor (eds.), Wiley and Sons, 2013.

Direct Analysis of Elemental Impurities in Solvents Used for Lithium-Ion Battery Electrolytes

Aimei Zou, Shuping Li, Chun Hiong Ang, and Ed McCurdy, Agilent Technologies Inc.

Li-ion battery (LIB) electrolytes

Demand for LIBs continues to rise steeply for mobile applications such as electric vehicles (EVs) and consumer electronics, and for static grid storage. In an article in Journal issue 91, we showed how a LIB is made up of four main components: anode, cathode, electrolyte, and separator. Each of these components is itself made up of a carefully formulated mix of raw materials. For manufacturers to develop batteries with smaller size, higher capacity, and improved safety, the specifications for these component materials must become stricter.

Commercial LIBs currently use either a liquid electrolyte (LE) or gel polymer electrolyte (GPE). Both types of electrolytes deliver high ionic conductivity and good permeation into and contact with the electrodes. LEs are cheaper and easier to manufacture, as they can simply be injected into the battery case, while GPEs improve safety by reducing the risk of leaks and fires caused by battery failure due to Li dendrite growth.

In LE batteries, the electrolyte typically consists of the Li electrolytic salt $LiPF_6$ (the charge carrier) and a high-purity organic solvent. The solvent contains a mix of cyclic and chain carbonates, such as ethylene carbonate (EC)/dimethyl carbonate (DMC) (*1*). Other solvents including propylene carbonate (PC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF) are also used.

The battery's integrity, performance, and lifetime depend on electrochemical reactions that may be adversely affected by elemental contaminants. Demand for higher performance batteries leads to more attention on the quality and purity of the materials used. Advanced battery manufacturers are using ICP-MS to analyze trace element contaminants for quality control of battery components including electrolyte solvents.

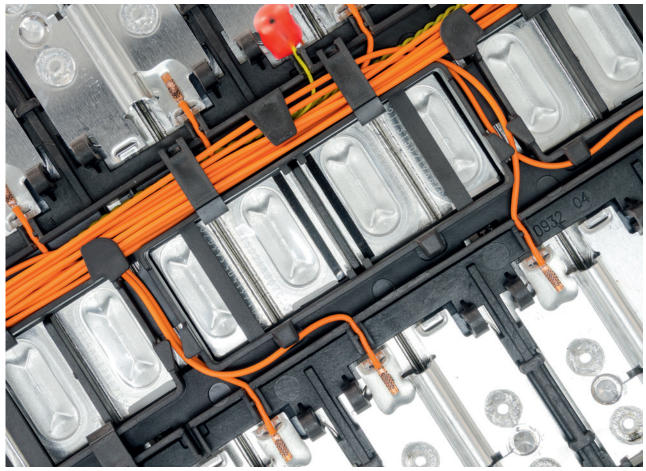


Figure 1. Li-ion battery pack of the type typically installed in EVs.

Organic solvent analysis using ICP-MS

Many ICP-MS users assume that analyzing organic solvents will be challenging. But Agilent ICP-MS systems have a robust, solid-state, 27 MHz variable frequency impedance-matching RF generator that can easily cope with the demands of organic solvent analysis (*2*).

Organic sample analysis applications can be performed routinely on Agilent ICP-MS systems, with a few changes to the instrument configuration and settings:

- Use the optional 5th gas controller to add oxygen (as 20% O_2 in Ar) to the plasma to prevent deposition of undissociated carbon (soot) on the interface cones.
- Set the spray chamber to low temperature, e.g., -5 °C, to reduce the solvent vapor pressure.
- Use a plasma torch with a narrow internal diameter (ID) injector. The 1.5 mm ID injector torch is used for most solvents, and a 1.0 mm ID injector torch is available for more volatile solvents, such as acetone.
- Fit Pt-tipped interface cones.
- Use solvent resistant uptake and drain tubing.

Quantitative analysis of LIB solvent mixtures

In this work, two samples were prepared to represent the solvents used in LIB electrolytes: 70:30 vv DMC:EMC and 70:30 vv DMC:EC. The samples were analyzed using an Agilent 7900 configured for organic solvent analysis. Each sample was calibrated separately by spiking with a 21-element organic standard to give standard additions between 1 ppb and 500 ppb. For each matrix, the unspiked sample was used as the calibration blank. Examples of the calibration plots for the DMC-EMC solvent mix are shown in Figure 2. The near-identical plots (and results) for Cr-52 in H_2 and HEHe cell gas modes shows the effectiveness of the Agilent He mode to resolve the intense $^{40}Ar^{12}C^+$ overlap at mass 52.

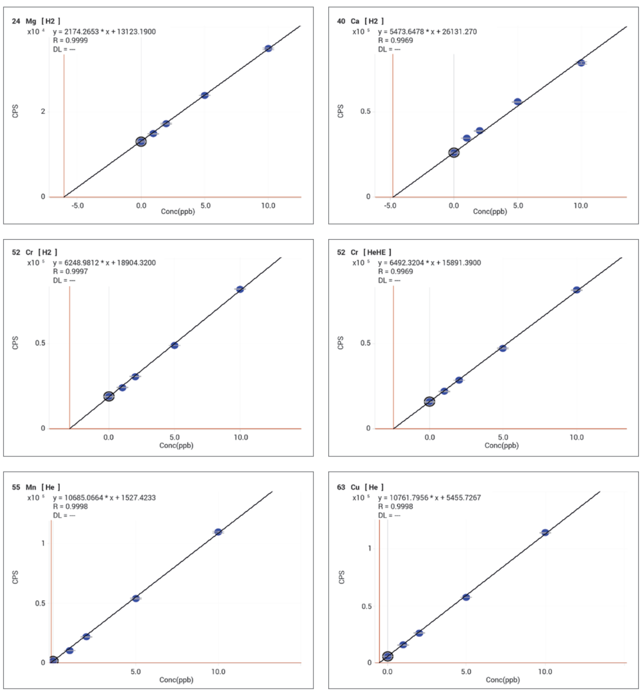


Figure 2. Calibration plots for elements spiked into DMC:EMC. Mg, Ca, and Cr in H_2 cell gas mode; Cr in HEHe mode; Mn and Cu in He mode.

Most analytes were present at low or sub-ppb levels in the solvents, so the results were processed using only the standards up to 10 ppb for most elements. The quantitative results are given in Table 1. Some significant differences were observed in the levels of the elements measured in the two different solvents, with DMC:EC containing higher levels of most elemental contaminants. For example, Ca, Fe, Zn, and Mo were all around an order of magnitude higher in DMC:EC than in DMC:EMC.

Table 1. Quantitative results for elements in electrolyte solvents.

Element	Mass	Cell Gas	Concentration (ppb)	
			DMC:EMC	DMC:EC
B	10	No Gas	8.78	35.1
Na	23	No Gas	2.60	3.66
Mg	24	H_2	6.04	36.4
Al	27	He	12.6	86.0
P	31	HEHe	52.0	61.5
K	39	H_2	4.63	7.17
Ca	40	H_2	4.77	64.5
Ti	47	He	4.77	11.4
V	51	He	0.04	0.40
Cr	52	HEHe	2.45	7.72
Mn	55	He	0.14	0.40
Fe	56	H_2	0.49	6.42
Ni	60	He	0.09	0.57
Cu	63	He	0.53	1.95
Zn	66	He	3.52	61.3
Mo	95	He	0.37	4.31
Ag	107	He	0.10	1.04
Cd	111	He	0.31	0.22
Sn	118	He	0.12	0.11
Ba	137	He	0.16	0.61
Pb	208*	He	0.17	0.64

Conclusion

The demand for high performance rechargeable batteries means manufacturers are urgently seeking to improve the performance of the current generation of batteries and develop new battery technologies. Controlling elemental impurities and contamination at low levels in battery components is a key part of these developments.

An Agilent ICP-MS configured for organic solvent analysis can be used for the analysis of trace elemental contaminants in battery electrolyte solvents. Excellent control of carbon-based spectral overlaps on elements such as Mg and Cr gives accurate results for critical contaminants even at low and sub-ppb levels.

Reference

1. Xu, K., Chem. Rev., 104, 4303–4417, **2004**
2. Enhanced Analysis of Organic Solvents using the Agilent 7700 Series ICP-MS, Agilent ICP-MS publication 5990-9407EN

Analysis of Urine Reference Materials Using IntelliQuant Trace Element Screening With the Agilent 7900 ICP-MS

Darren Allen, Christopher Warnholtz, Alexandra Kane, and Brett McWhinney, Pathology Queensland, Queensland, Australia

Access full mass range scan data

ICP-MS is a multi-element technique, capable of measuring almost all of the elements in the periodic table. But quantitative methods often focus on a few elements of interest, so much of the potentially useful information in the mass spectrum is missed. This situation can be addressed using the Quick Scan function in the Agilent ICP-MS MassHunter software, which makes it easy for operators to acquire a full mass scan as part of their normal quantitative methods.

Combined with helium (He) collision cell mode to control common polyatomic ion overlaps, Quick Scan adds only two seconds of additional acquisition time for each sample. Data is processed using the ICP-MS MassHunter IntelliQuant calibration function, providing surprisingly accurate semiquantitative results without requiring element-specific standards.

IntelliQuant is based on the fact that the Agilent ICP-MS mass/response, corrected for isotopic abundance and degree of ionization, follows a predictable curve from low to high mass, as shown in Figure 1. In each sample, the measured response for a few reference masses, such as the internal standards, is used to calculate results for the remaining elements by interpolation.

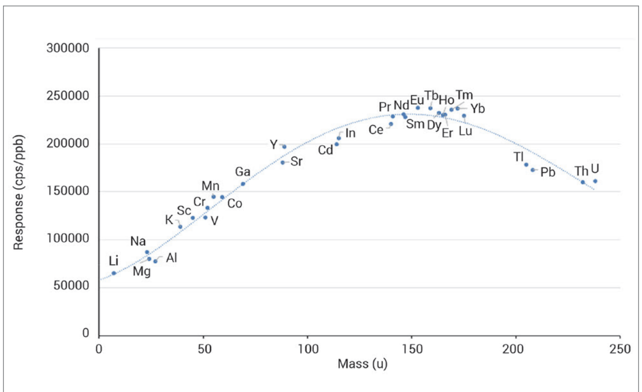


Figure 1. Agilent 7900 ICP-MS measured mass response curve, corrected for isotopic abundance and degree of ionization.

IntelliQuant results for urine reference materials

The accuracy of the semiquantitative calibration was investigated for several elements in commercial urine standards from Recipe (ClinChek) and Sero (Seronorm). The analytes selected are not routinely measured in urine but may be of interest in some applications, for example research into occupational exposure (*1*).

In total, 70 elements were measured using IntelliQuant, of which eight were of interest and had certified values in one or more of the reference materials. The recoveries of these elements are shown in Figure 2. All elements were recovered within ±20% except Ag, which was consistently ~40% higher, probably because of chemical instability in the standard solution, which contained trace chloride.

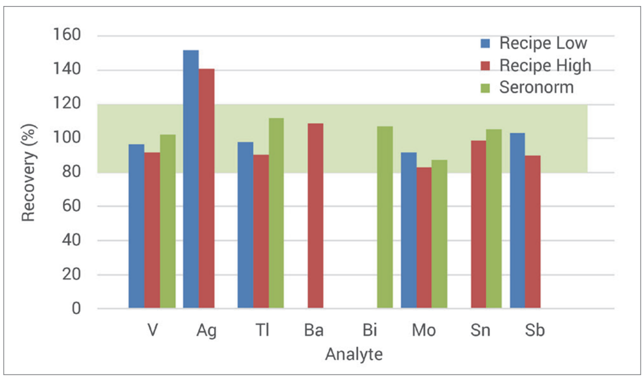


Figure 2. Recoveries of unusual elements in urine reference materials. Missing elements are not certified in that material. Shaded range ±20%.

Conclusion

Combining He mode Quick Scan with IntelliQuant calibration gives analysts access to a vast amount of useful information in addition to the quantitative results.

Reference

1. Baselt, R. C., Disposition of Toxic Drugs and Chemicals in Man, 12th ed., 2020, Biomedical Publications

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

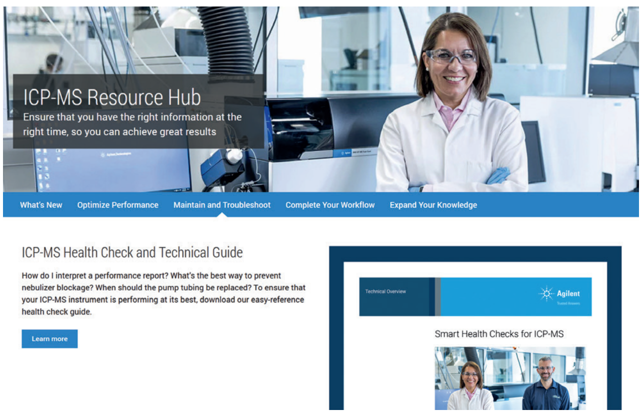
ICP-MS Resource Hub: From Instrument Health Checks and Tutorials to Online Selector Tools

Alain Desprez and Kate Lee, Agilent Technologies, Inc.

Your gateway to practical advice

Since its launch in 2017, the Agilent ICP-MS resource hub has become a much-visited site for analysts looking for technical information and guidance on operating and maintaining their Agilent ICP-MS.

The ICP-MS resource hub includes a wide range of practical information from how to optimize performance to best practices for instrument operation and routine maintenance. The hub gives you instant access to how-to videos, maintenance procedures, training courses, selector tools, and more, helping you achieve reliable, high-quality ICP-MS results and avoid costly downtime.

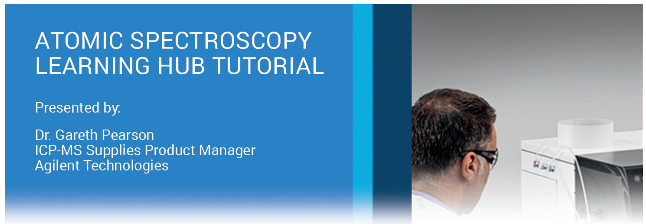


Keep your ICP-MS productive

A technical overview 5994-4380EN on Smart Health Checks for ICP-MS, explains how Agilent instruments are designed for ease of use and intuitive workflows. The instruments include predefined templates to simplify method setup, and auto-optimization tools, performance checks, and self-diagnostic sensors and monitors to streamline routine operation. Download the guide to ensure that your instrument is performing at its best.

How to check the health of your ICP-MS (agilent.com)

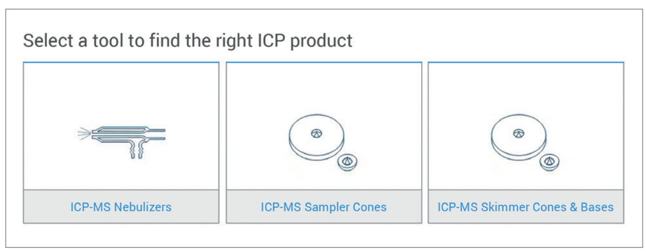
Atomic spectroscopy learning resources



The Atomic Spectroscopy Learning Hub: ICP-MS is a free access e-learning portal produced by Separation Science in collaboration with Agilent. Users can access course content, track their learning progress, and receive a completion certificate once all modules have been successfully finished. The course comprises four modules on Sample Introduction, Application-specific ICP-MS Setup; Speciation Applications with ICP-MS; and Laser Ablation ICP-MS.

You can also register to access four video tutorials on How to Make ICP-MS Easier: ICP-MS MassHunter Software; Simplifying Workflows with Easy-fit Supplies; ICP-MS Configuration Tools; and Questions & Answers.

New e-selector tool for nebulizers and cones



Using the ICP-MS nebulizer and interface cones that are best suited to your application will help you generate the highest quality results. The ICP-MS nebulizer and cone selector will guide you to the best match for your application needs. ICP MS and OES Selector | Agilent

Learn more at www.agilent.com/chem/icp-ms-resource

Addressing Analytical Techniques for Alternative Protein Products

In this timely and interesting on-demand webinar, Agilent specialists and food industry experts provide an overview of the alternative protein industry and current testing approaches. The opening presentation from Agilent's Dr Lorna De Leoz summarizes the alternative protein market and shows how Agilent instruments can meet industry and regulatory testing requirements. Application Specialist Jenny Nelson then explains how ICP-MS can be used to characterize the elemental content of alternative proteins using the established FDA EAM 4.7 food method.

Moving on to organic compounds, Application Specialist Seok Hwa shows how LC/Q-TOF, combined with MPP for chemometric data processing, can give more objective assessment of the key flavor compounds, compared to traditional, subjective, sensory trials. The flavor theme continues with talks from Dr. Youngmo Yoon of Hanbit Flavor and Fragrance Co., Ltd., Korea, and Dr. Li Li Zyzak of Eastern Kentucky University. The talks show how food manufacturers use GC Olfactometry (GC-O) to identify combinations of plant proteins and additives that will give the product a nutrient profile, aroma, flavor, texture, and price that is acceptable to consumers. In the final presentation, Dr. Stephan van Vliet of Utah State University shows how metabolomic profiling reveals the underlying differences in meat- and plant-based products, even when the nutritional label shows similar composition. This suggests a balanced diet is the best way to obtain all the essential nutrients.

Latest Agilent ICP-MS publications

- **Application note:** Determination of Ultratrace Impurities in Semiconductor Photoresist Using ICP-MS/MS, 5994-6089EN
- **Application note:** Automated Surface Analysis of Metal Contaminants in Silicon Wafers by Online VPD-ICP-MS/MS, 5994-6135EN
- **Application note:** Analysis of Elemental Impurities in Synthetic Oligonucleotides by ICP-MS, 5994-6470EN
- **Case study:** Agilent Case Study: Source Certain: Using Elemental Fingerprints To Confirm The Geographic Origin Of Products, 5994-5593EN
- **Catalog:** Spectroscopy Supplies, 5994-5574EN

Published in the USA, July 20, 2023
5994-6227EN
DE41020392

Agilent
Trusted Answers