NEWS

Glass Expansion Newsletter | February 2015 | Issue 36

APPLICATION SPOTLIGHT

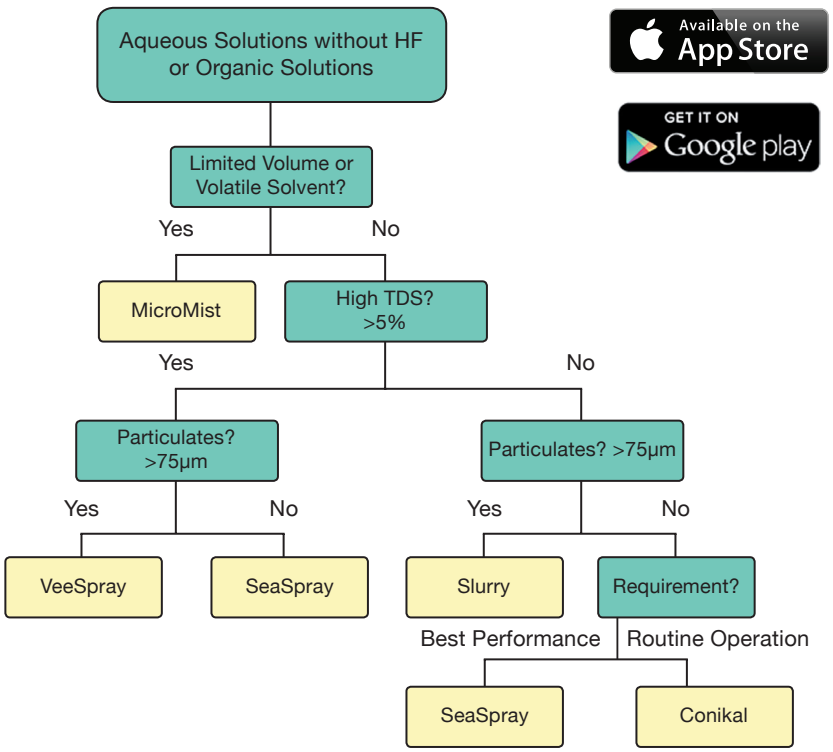
Optimizing your ICP Sample Introduction System for Improved Analysis of Oils and Organic Solvents

While ICP-OES technology has undergone considerable developments on the spectrometer side, challenges related to the sample matrix still remain. For example, oil analysis by ICP can be challenging due to the use of volatile organic solvents that typically results in plasma instability. Additionally, when organic solvents are introduced into the plasma, the temperature gradient along the axis of the ICP torch increases significantly, which can lead to premature failure of the standard quartz ICP torch. Oil analysis also often requires labor intensive sample preparation with volatile organic solvents. In this paper we will present sample introduction components specifically designed to optimize your ICP sample introduction system for improved oil and organic solvent analysis.

Nebulizer Selection

When dealing with oil analysis or an organic solvent, the first component you should select is a proper nebulizer. The Glass Expansion website features a very helpful nebulizer selection guide that will help you to arrive at a proper selection, including a new smart phone app (Figure 1).

Figure 1. Glass Expansion's nebulizer selection guide (aqueous or organic).



GLASS EXPANSION
Quality By Design

Glass Expansion News

Pittcon 2015

A wide selection of Glass Expansion products will be on display at Pittcon 2015, New Orleans, Louisiana, USA, March 9 - 12, 2015.

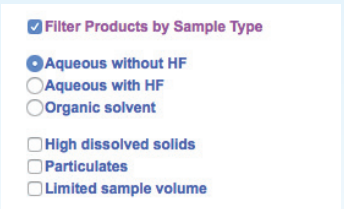
The display will include nebulizers, spray chambers, torches, RF coils, ICP-MS cones and accessories. You will also be able to see a demonstration of the Assist CM and Niagara Plus CM enhanced productivity systems. Glass Expansion specialists will be on hand to answer your questions and assist you to choose the optimum components for your ICP. Please visit us at Booth 2727.

You are invited to a seminar on "Tips for Career Advancement in Elemental Analysis". Email geusa@geicp.com to reserve your seat.

Wednesday 9:30 - 11:30 am, March 11th in Seminar Room SRB.

Website upgrade – new product selection guide

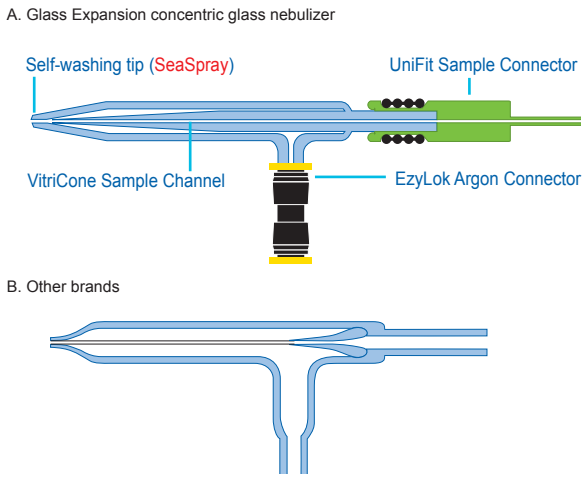
Our new product selection feature helps you to find the optimum sample introduction system for your particular application. Simply select your ICP model and you will see all products suitable for that model together with a product filter. Then click on any of the sample characteristics that apply to your samples. Any unsuitable products will be removed from the display and you will see only the products which suit your samples. Click here to check it out. If your samples do not fit the categories displayed, please send an email to enquiries@geicp.com and we will happily provide you with details of the most suitable sample introduction system.



In this issue:

The Conikal concentric glass nebulizer is a preferred nebulizer option in oil analysis, especially with kerosene-diluted oil samples. The Conikal provides low RSDs due to the highly accurate construction and a physical reproducibility of 1%. The Conikal is available in standard uptake rates of 1 and 2mL/min. When utilizing a more volatile solvent, like methyl isobutyl ketone or toluene, it is often required to reduce the sample uptake rate to below 1mL/min. Under these conditions we recommend the low flow MicroMist nebulizer. The MicroMist nebulizer provides high performance at uptake rates as low as 0.05 to 0.6mL/min. The small droplet sizes and lower sample volume produced with the MicroMist reduces the amount of solvent reaching the torch and provides a more robust plasma.

Figure 2. Unique features of Glass Expansion's concentric nebulizer design.



Unique to all Glass Expansion concentric glass nebulizers is the VitriCone sample channel and UniFit sample line connector (Figure 2). The VitriCone sample channel is created by machining constant bore heavy stock glass tubing to create the desired aerodynamic exterior while maintaining a consistent internal diameter. The UniFit sample line connector slides easily over the sample arm of the nebulizer creating an excellent seal and a zero dead volume connection. Together, the VitriCone sample channel and UniFit connector provide a uniform internal diameter from entry point to the nebulizer tip, reducing the chance of trapped particulates and improving washout. Further details and benefits of the VitriCone and UniFit are described in a previous Newsletter article.[1]

Both the Conikal and MicroMist nebulizer can handle particulates up 75µm. However certain applications, such as the determination of wear metals in used engine oils, often involve the presence of much larger particles. In this case we recommend the Slurry concentric glass nebulizer, which has the ability to handle particulates as large as 150µm. The Slurry is a popular choice in the oil industry due to the larger bore capillary (50% larger than Conikal & MicroMist) that reduces the possibility of particle blockage, while giving excellent signal stability. The optimum sample uptake rate for the Slurry is between 1.5 and 2.5mL/min.

To prevent even larger particles from clogging the nebulizer, the Glass Expansion re-usable inline filter assembly (Figure 3A) can be added. The filter is easily inserted in the sample tubing between the autosampler probe and nebulizer, providing a simple and effective way to eliminate the risk of a blockage. It incorporates a re-usable PEEK filter suitable for use with all of the most common ICP solutions, which can be conveniently back-flushed with the Eluo Nebulizer Cleaning Tool (Figure 3B). For more details on the inline filter assembly please click here.

Figure 3a. Glass Expansion Inline particle filter.

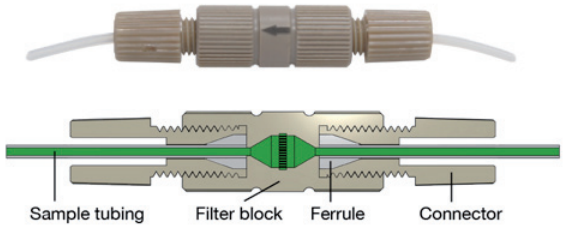
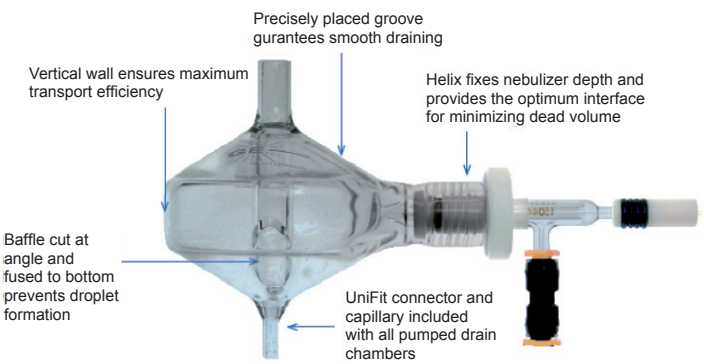


Figure 3b. Eluo Nebulizer Cleaning Tool

Spray Chamber Selection

As mentioned previously, volatile organic solvents can be troublesome due to the high transport efficiency to the plasma, creating an excessive load and typically resulting in plasma instability. In order to improve plasma stability, it is recommended that the sample transport be reduced. This can be accomplished by reducing the nebulizer uptake rate and using a baffled spray chamber. For this reason we recommend the use of the Glass Expansion Twister™ spray chamber. The Twister cyclonic spray chamber features a central transfer tube that prevents large solvent droplets and particulates from reaching the plasma (Figure 4). This helps to reduce the solvent load in the plasma and improve stability without compromising detection limits. Glass Expansion also offers a low volume spray chamber (20 mL) based on the Twister design. The Twinnabar™ provides a very fast washout for sample uptake rates in the range of 20 to 400 µL/min. Like the Twister, the center baffle of the Twinnabar offers a reduced solvent load and excellent precision, in addition to a very fast washout.

Figure 4. Characteristics of Glass Expansion Twister™ spray chamber.



All Glass Expansion spray chambers also feature the unique Helix nebulizer interface. The Helix design has many benefits. One that is particularly important for oil and organic solvent analyses is the absence of o-rings. Some organic solvents can cause o-rings to swell and degrade rapidly, leading to potential contamination, and require frequent replacement. The Helix o-ring free nebulizer

interface features a compression seal made from Teflon, which is totally inert to all organic solvents typically used in ICP analysis. Another important design feature of the Helix is the elimination of dead volume around the nebulizer seal. Eliminating dead volume leads to faster washout times[2] and higher sample throughput, which is especially important for high throughput operations such as wear metals in used engine oils.

Even when using a low-flow nebulizer combined with the Twister or Twinnabar spray chamber, some solvents may prove to be too volatile for ICP. Dilution with a less volatile solvent may degrade detection limits unacceptably. In these cases a cooled spray chamber is utilized to reduce the volatility to an acceptable level. The IsoMist™ is the perfect accessory for an ICP laboratory in the petroleum industry or others dealing with volatile solvents. With the IsoMist you can achieve a temperature of -5°C in less than 15 minutes, allowing for the direct analysis of naphtha without dilution (a common solvent analyzed by ICP).

Figure 5. IsoMist™ control panel with temperature scale.

The powerful inbuilt Peltier device of the IsoMist achieves a temperature as low as -10°C and is programmable in 1°C increments. Unique to the IsoMist is a Twister spray chamber encapsulated with a temperature conductive resin (Figure 6A). The encapsulated spray chamber provides a uniform temperature from top to bottom and an air-tight fit within the IsoMist module to prevent condensation build-up and freezing (Figure 6B). This unique design provides an unmatched temperature stability of +/- 0.1°C.

Figure 6a. Spray chamber

Figure 6b. Glass Expansion IsoMist

The otherwise difficult analysis of naphtha is made simple with the IsoMist. Table 1 shows a portion of data taken from Thermo Application Note: 40899, "The Analysis of Trace Elements in Naphtha", which utilizes the IsoMist set at -5°C on an iCAP 6500 Radial ICP. The majority of RSDs are below 0.5% and the recoveries are within 5% of the spiked value. Calibration plots with the IsoMist indicate excellent precision and linearity at relatively low concentrations.[3] For very volatile solvents and the analysis of gasoline we recommend the new IsoMist XR with the ability to reach -25°C while still achieving a temperature stability of +/- 0.1°C (Figure 5). The IsoMist XR provides superior plasma stability for the ICP laboratory that requires an extended temperature range of -25 to +60°C.

Table 1. Results of spiked Naphtha based on three replicate measurements with IsoMist.[3]

Wavelength (nm)	Naphtha spike (2.4mg/kg)	%RSD (3 Reps)	Detection Limit (µg/kg)
Ag 338.389	2.39	0.56	0.8
As 189.042	2.44	0.30	15
Ba 223.527	2.35	0.64	1.3
Cd 214.438	2.38	0.98	1.0
Cr 267.716	2.37	0.25	0.8
Fe 238.204	2.39	0.55	1.8
Mg 279.553	2.40	0.10	0.8
Mn 293.930	2.38	0.23	0.8
Na 589.592	2.41	0.55	13
P 178.284	2.40	0.44	15
Si 212.412	2.40	0.47	10.5
Zn 213.856	2.39	0.24	0.8

Torch Selection

As mentioned earlier, when organic solvents are introduced into the plasma the temperature gradient along the axis of the ICP torch increases significantly, shortening torch life. The main reasons for this increase in temperature gradient are:

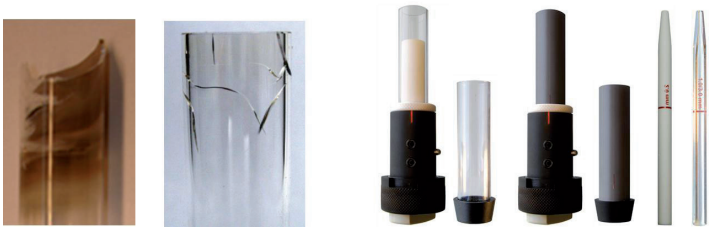
1. Higher RF powers are typically used when analyzing organic solvents.
2. Carbon based molecules will emit large amounts of infrared (IR) light which is absorbed by the quartz, increasing the temperature.

Glass Expansion developed the D-Torch™ to specifically deal with difficult sample matrices such as organic solvents and reduce torch replacement costs. The pertinent characteristics of the D-Torch are as follows:

- Direct replacement of the standard ICP torch, with no comprise of performance.
- Supplied with a ceramic intermediate tube which resists wear and tolerates high temperatures well.
- A demountable quartz outer tube so that just the outer tube can be replaced when worn rather than the whole torch.
- An optional ceramic (sialon) outer tube which prevents premature torch failure and provides low level Si background.
- Interchangeable injectors available in quartz, alumina, and sapphire.

The sialon material of the ceramic D-Torch outer tube eliminates the common premature failures of the torch (see Figure 7) when analyzing organic solvents. The sialon ceramic material can withstand a much higher temperature than quartz and is not prone to cracking like quartz when running organic solvents.

Figure 7. Glass Expansion's patented D-Torch demountable ICP torch.



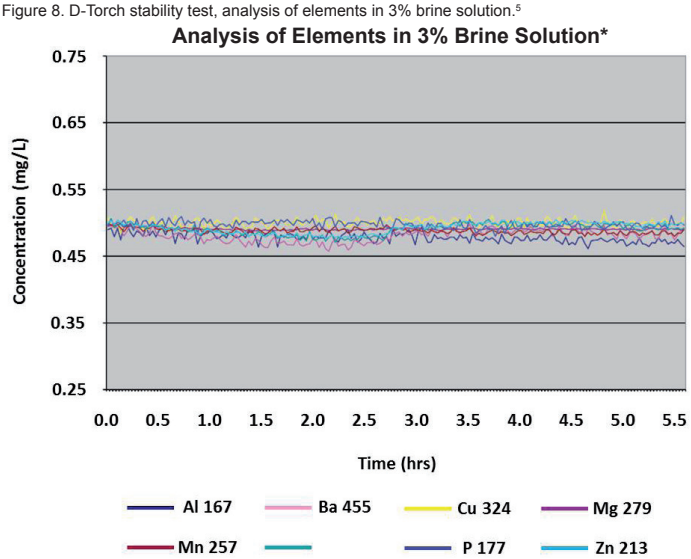
Torch Failure Problem? **Your Solution**

The performance of the D-Torch has been evaluated in several technical notes[4,5,6] to compare the analytical performance to a standard quartz torch. Table 2 compares the detection limits of a standard radial torch and the ceramic D-Torch for selected elements. The results show little difference between the detection limits obtained from the two torches. Another key indicator of ICP torch performance is stability. Figure 8 shows a plot of selected elements at 0.5 mg/L in a 3 % NaCl matrix. The stability exhibited by the ceramic D-Torch over a period of 5.5 hours in this high matrix sample is exceptional. The ceramic D-Torch proves to provide equivalent or better analytical performance to a standard quartz torch with the added advantage of resistance to devitrification and premature failures with specific sample matrices, including organics and high dissolved solids samples such as fusions. The D-Torch Kit is available for several different ICP and ICP-MS models. Click here to find the kit to suit your laboratory needs.

Table 2. Detection limit comparison of standard quartz torch and ceramic D-Torch.[5]

	Detection Limit (µg/L)	
Element (λ)	**Radial Quartz Torch**	**Radial Ceramic D-Torch**
Al 167	1.6	1.1
Ba 455	0.07	0.12
Cu 324	0.88	0.62
K 766	25.5	11.7
Mg 279	0.05	0.05
Mn 257	0.36	0.25
Ni 221	1.6	1.3
P 177	5.1	5.0
Zn 213	0.23	0.28

Figure 8. D-Torch stability test, analysis of elements in 3% brine solution.[5]



Sample Preparation

Oils are typically diluted in an organic solvent such as kerosene prior to being introduced into the ICP. A 5x or 10x dilution is usually adequate to reduce the viscosity of the oil to allow the oil to be nebulized. When high accuracy is required for elemental concentrations, these dilutions are typically performed by weight rather than volumetrically due to varying viscosities and densities. When oils are analyzed for trend analysis, an automated oil dilution accessory is often employed by high throughput labs to save sample preparation time. However, there are issues associated with utilizing automated offline oil dilutors. Due to the viscosity of the oil, it can "stick" to the probe or probe tip that is used for taking up the oil to be diluted. The variation in viscosity leads to a difference in the amount of time required to completely fill or empty the probe. The oil dilution accessories may not account for the difference in time required to fill or empty the probe and thus the volume of oil to be diluted can vary. In contrast, the diluent is delivered with an accurate volume, which leads to variations in the oil/diluent ratio. In the end, this can result in a poor calibration curve or produce inaccurate results. These same issues can also be associated with manual dilutions, in addition to varying results due to human error.

Diluted oil standards and samples can also stand for long periods of time before being analyzed. Depending on the solvent used, this sitting time can cause layer separation and produce inaccurate results. To negate settling, many labs employ a shaker or mixer prior to introduction, bringing the total number of accessories needed for dilution to three. The type of solvent used for dilution can play a large effect in the mixing of the oil sample and the settling of different analytes in a diluted sample.

Figure 9. Assist Oils Package with custom diluter probe.

In order to alleviate the negative effects of oil sample preparation, Glass Expansion designed the Assist Oils Package (Figure 9).[7,8] This system is configured specifically for the analysis of wear metals in raw (undiluted) lubricating oils. It incorporates three syringe drives, a Niagara switching valve, and a custom designed stainless steel diluter probe for the ICP autosampler. The Assist works with the existing ICP autosampler, taking a sample of the oil, mixing it with a solvent such as kerosene and precisely delivering the diluted oil to the ICP. It eliminates the need for off-line manual or automated dilutions and increases the speed of analysis. Each sample of oil is diluted at the tip of the autosampler probe using the same syringe drives immediately prior to introduction into the ICP, thus eliminating the need for a shaker and improving measurement accuracy. With the Assist, varying viscosity was shown to have

very little effect on the accuracy of the online dilution. The data in Table 3 shows a 10x online dilution utilizing the Assist with a Mo spiked diluent. The results show a variation of less than 3%, from a straight solvent, to a base oil, a 50% 460 grade oil and a 100% undiluted 460 grade oil. The precision syringe delivery also eliminates pulsations from peristaltic pumps, improving signal precision (RSD).

Table 3. Performance of online dilution using Assist with varying viscosity.

Sample Type	Element (λ)	Counts
Kerosene	Mo 202.032	74910
Base Oil	Mo 202.032	70700
50% 460	Mo 202.032	71800
100% 460	Mo 202.032	72900

The data shown in Table 4 was provided courtesy of WesTrac in Australia.[8] The results were achieved using a Varian Vista Radial ICP-OES. The Assist Oils Package provides correlation coefficients of at least five nines for the wavelengths examined, demonstrating excellent correlation. Mean % recoveries are between 99 and 107%, showing the Assist is capable of providing accurate online dilution and measurement reproducibility. Any carryover is reduced due to the totally inert sample path of the Assist Oils Package.

Conclusion

Optimizing your ICP sample introduction system to best suit your matrix and sample type increases the accuracy and speed of your analysis, but also reduces consumable cost and maintenance.

The ability to reach -10°C with the IsoMist and -25°C with the IsoMist XR allows for the direct analysis by ICP of the most volatile solvents, including naphtha and gasoline. The Assist Oils package eliminates the need for manual dilutions, allowing for a sample of undiluted oil to be diluted in-line with a solvent and precisely delivered to the ICP. The fully demountable D-Torch provides the ICP lab with the ability to reduce torch replacement costs. Additionally, when configured with the ceramic outer tube, the D-Torch eliminates premature torch failure and reduces Si background.

Table 4. Performance of online dilution using Assist Oils Package.

Element and λ	Mean % Recovery	Mean Wash Concentration (ppm)
Ag 328	103	(-) 0.21
Al 308	99	(-) 0.17
B 249	99	(-) 0.21
Ba 233	101	(-) 0.01
Ca 317	107	0.84
Cd 228	101	(-) 0.06
Cr 357	101	0.12
Cu 327	101	(-) 0.17
Fe 259	101	(-) 0.03
K 766	102	0.00
Mg 279	100	(-) 0.14
Mn 257	101	(-) 0.16
Mo 202	101	(-) 0.09
Na 588	100	(-) 0.09
Ni 231	101	(-) 0.12
P 214	106	0.03
Pb 220	101	(-) 0.02
Si 212	101	0.01
Sn 283	101	(-) 0.03
Ti 334	101	(-) 0.18
V 310	101	(-) 0.19
Zn 213	107	(-) 0.47

References

1. June 2013 Glass Expansion Newsletter, “A Nebulizer Update.”

2. October 2014 Glass Expansion Newsletter, “ICP Spray Chamber Update.”

3. Thermo Application Note: 40899, “The Analysis of Trace Elements in Naphtha.”

4. June 2012 Glass Expansion Newsletter, “Examining the Benefits of a Ceramic Torch for ICP.”

5. Thermo Application Note: 43053, “Radial Demountable Ceramic Torch for iCAP.”

6. October 2013 Glass Expansion Newsletter, “How to Achieve High Accuracy with Difficult Samples.”

7. February 2011 Glass Expansion Newsletter, “Comparison of Enhanced Productivity ICP Approaches for Engine Oil Analysis.”

8. February 2012 Glass Expansion Newsletter, “Characteristics of a Syringe-driven Sample Introduction System for ICP Spectrometry.”

INSTRUMENT NEWS

From Shimadzu - New ICPE-9800 series - Ultra high speed meets minimum argon consumption

A single method for elemental analysis across a wide concentration range

Analytical service and quality control laboratories will benefit from the new ICPE-9800 series of simultaneous ICP optical emission spectrometers Shimadzu has just released. The systems combine higher throughput with reduced operating costs and feature easy-to-use software, a sophisticated design and the Eco mode which brings savings of 50% or more in power and argon gas consumption, independent of sample matrix, whether aqueous or organic samples are aspirated. The vacuum optical system does not require any purge gas, thereby eliminating gas consumption when the plasma is switched off.

ICP optical emission spectrometers are used in a variety of fields involving environmental samples, drinking water, foods, pharmaceuticals and petrochemical materials. All-wavelengths acquisition allows users to add elements and wavelengths post-analysis without time-consuming reanalysis of samples.

The ICPE-9800 series consists of the ICPE-9810 which provides axial view plasma observation in a direction coaxial to the plasma, and the ICPE-9820 which, in addition to axial view, provides radial view plasma observation in the perpendicular direction. This dual view capability allows measurements to switch automatically between high-sensitivity axial view and high-accuracy radial view, enabling analysis of elements across a broad concentration range with a single method.

For more information please download the application note "Determination of Heavy Metals in Wine using simultaneous ICP – OES" or visit shimadzu.eu

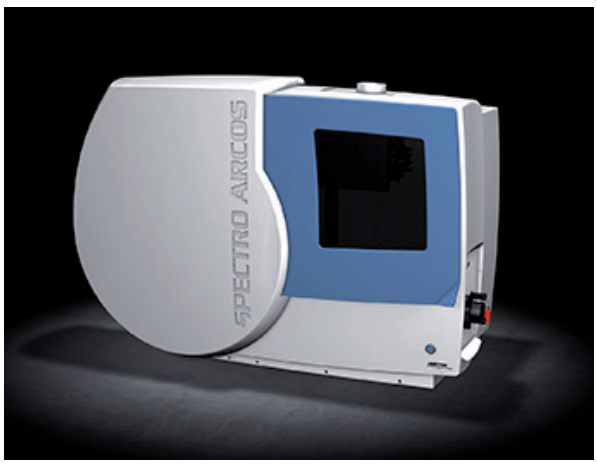
From SPECTRO - New SPECTRO ARCOS high-resolution ICP-OES spectrometer for elemental analysis surpasses performance limitations

SPECTRO Analytical Instruments has announced its new SPECTRO ARCOS high-resolution ICP-OES spectrometer, the first and only spectrometer featuring the fast and convenient selection of axial plasma or radial plasma observation in a single instrument - without any optical compromise.

Designed for use in the most demanding elemental analysis applications in industry, science, and academia, the new SPECTRO ARCOS easily surpasses the performance limitations of conventional ICP-OES instruments - dramatically improving sensitivity, stability, and precision, while lowering operating costs with the introduction of innovative components, unique capabilities, and optimum flexibility.

Features of the new SPECTRO ARCOS include:

- Axial or Radial Plasma Observation: SPECTRO's unique new MultiView capability delivers unmatched performance improvements in accuracy and stability and allows for the fast and convenient selection of axial plasma or radial plasma observation with no optical compromise.
- ORCA Optical System: The CCD optic system with a Paschen-Runge mount assembly delivers a matchless resolution of 8.5 picometer in the wavelength range from 130 to 340 nm.
- Innovative Power Generator: A unique new solid-state generator design that provides the highest plasma power available for extreme or quickly changing plasma loads.
- Elimination of the Need for Purge Gases: SPECTRO's UV-PLUS sealed optical chamber ends the need for the purging of argon or nitrogen gases — along with the related supplies, maintenance costs, and downtime.
- No External Cooling System: Air-cooled interface technology and the completely air-cooled generator eliminates the need for an external cooling system — along with the associated, and often substantial, equipment, power, and maintenance costs.



The new-generation SPECTRO ARCOS is available immediately from SPECTRO Analytical Instruments.For more information, visit www.spectro.com or email Spectro.info@ametek.com.