NEWS

Glass Expansion Newsletter | June 2015 | Issue 37

APPLICATION SPOTLIGHT

Optimizing the Analysis of Naphtha by ICP-OES

Introduction

Trace metal content in naphtha is important for a number of reasons[1]. The presence of metals such as nickel during the cracking process can poison the expensive catalyst, while vanadium causes corrosion problems. During the refining process, release of toxic metals such as lead, mercury, and arsenic must be monitored and minimized. The presence of trace metals is also used to gain insight into the geological origin and migration of crude oil to aid in exploration. The analysis of naphtha by ICP-OES is complicated by the high volatility of the sample, which can overload the plasma. It is therefore often diluted with a suitable solvent such as kerosene or xylene to facilitate the analysis. Unfortunately, due to the low levels of detection desired, dilution may not always be a viable course of action. In this paper, we will determine the optimum parameters to analyze naphtha directly without dilution.

Experimental

An iCAP 6500 Duo ICP spectrometer (ThermoFisher Scientific, Waltham, MA) was used for all measurements. The following components were incorporated (all from Glass Expansion, Melbourne, Australia):

- Spray chamber: IsoMist XR Programmable Temperature Spray Chamber
- Torch: D-Torch with alumina inner tube and ceramic outer tube
- Injector: Quartz tapered 1.0mm bore
- Nebulizer: SeaSpray glass concentric with 0.4mL/min uptake
- Pump tubing: Contour Flared-end Solva two tag, Orange/Yellow 0.51mm ID.

The instrument parameters employed are listed here	
Plasma gas flow rate (L/min)	16
Auxiliary gas flow rate (L/min)	2
Forward Power (watts)	1350
Nebulizer gas flow rate (L/min)	0.28 and 0.38
Sample uptake rate (mL/min)	0.5
Spray chamber temperature (°C)	-10 and -25

The IsoMist XR (Glass Expansion) was used to control spray chamber temperature. The IsoMist XR has a range of -25°C to +80°C in increments of 1°C and accuracy of + /-0.1°C. It is controlled with proprietary software via a USB port or wireless Bluetooth® technology. Photos of the IsoMist XR and the encapsulated glass spray chamber (which resides inside the IsoMist housing) are shown in Figure 1.

Glass Expansion News

Upcoming Exhibitions and Conferences

A wide selection of Glass Expansion products will be on display at the following exhibitions. The display will include nebulizers, spray chambers, torches, RF coils, ICP-MS cones and accessories. Glass Expansion specialists will be on hand to answer your questions and assist you to choose the optimum components for your ICP.

Environmental Measurement Symposium
Chicago IL, USA, July 13 to 17
(Booth #59)
www.nemc.us/index.php

NY & PA Association of Approved Environmental Laboratories Annual Convention (NYPaAAEL)
Corning NY, USA, July 20 to 21
www.nyaael.org/

JASIS 2015
Tokyo, Japan, September 2 to 4
www.jasis.jp/en/

SOS Fluid Analysis 2015 Dealer Conference
Scottsdale AZ, USA, October 5 to 8

Gulf Coast Conference
Houston TX, USA, October 20 to 21
(Booth # 313).
www.gulfcoastconference.com/

In this issue:

GLASS EXPANSION
Quality By Design

Figure 1: IsoMist XR™ Controlled Temperature Spray Chamber Accessory and encapsulated cyclonic spray chamber

The encapsulation resin is temperature conductive to achieve rapid heat transfer. The resin is also molded to fit the chamber cavity so that there is no dead volume. This is particularly important at temperatures well below the freezing point as were employed here in order to eliminate condensation and freezing. A screen display of the temperature vs. time graph is shown in Figure 2. Due to the enhanced insulation and temperature conductivity, the device is able to go from room temperature to -25°C in about 20 minutes. Similar to all IsoMist models, the one used here includes a torch interface kit specific to the iCAP Duo. Although also available in quartz and PFA, the chamber used here was made of borosilicate glass.

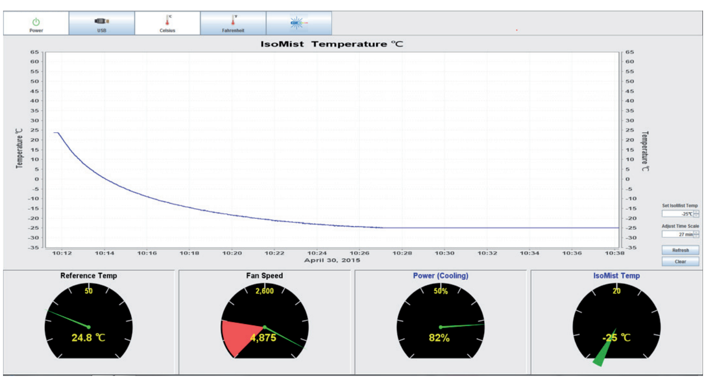


Figure 2: PC Screen showing IsoMist Graphic Software

The uptake rate of the naphtha was measured with a TruFlo sample monitor (Glass Expansion) which was calibrated for naphtha. The standard TruFlo is calibrated for aqueous matrices but Glass Expansion offers a service to calibrate it for other solvents. Figure 3 shows how the TruFlo device was installed in the sample line (a) and shows a graphical display of flow rate vs. tension of the peristaltic pump platen (b). You can see the amount of tension that achieves a consistent flow rate. Excess tension only hastens degradation of the pump tubing.

The torch used is the ceramic D-Torch shown in Figure 4. The D-Torch incorporates an alumina intermediate tube, an optional demountable ceramic outer tube, and a demountable 1.0mm bore injector. The Duo version has a built-in optic fiber so that the plasma is observed by the interlocked ignition system when the opaque ceramic outer tube is installed.

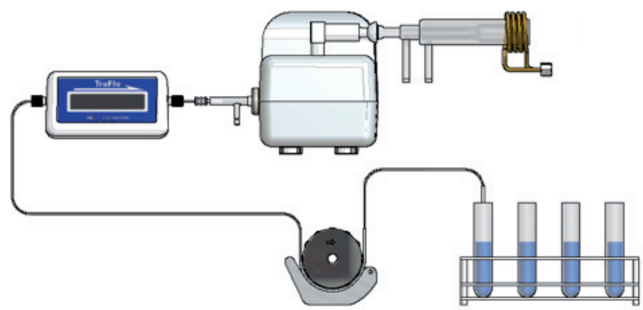


Figure 3a: Naphtha uptake rate measurement

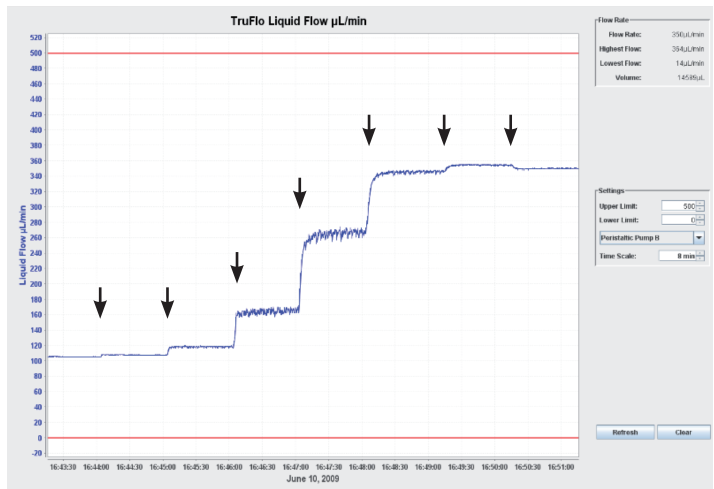
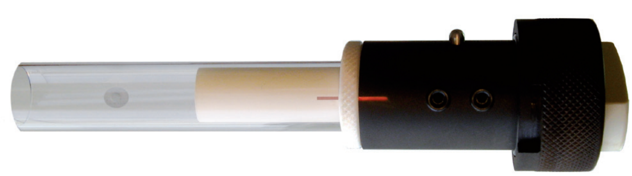


Figure 3b: Naphtha uptake rate measurement.
The pump tubing clamp was tightened by a half turn at each arrow.

Quartz Injector - 31-808-2833

Ceramic outer tube - 31-808-2863



D-Torch - 30-808-2844

Figure 4: Ceramic D-Torch for Thermo iCAP Duo

Results and Discussion

Standards were prepared by gravimetric dilution of Conostan S21 stock standard (SCP Science, Champlain, NY) in naphtha to achieve 5.4, 10.08, and 100mg/L of analytes. Standards were run as samples following standardization.

Optimizing nebulizer gas flow

Realizing from previous work that the optimum nebulizer gas flow rate should be lower than that used for aqueous solutions, we compared the results at 0.38 and 0.28 L/min. The 0.38 setting was approximately equal to that used in Reference 2 and the 0.28 setting was the minimum flow capable of “piercing” the plasma with the injected sample. The results in Figure 5 show a consistently higher intensity at the lower flow rate for the analyte lines investigated with one exception, potassium, which would be expected since the potassium atom line “prefers” a cooler plasma. On average, for the remaining lines, a 15% increase in intensity was observed. The remainder of the work was carried out at 0.28L/min.

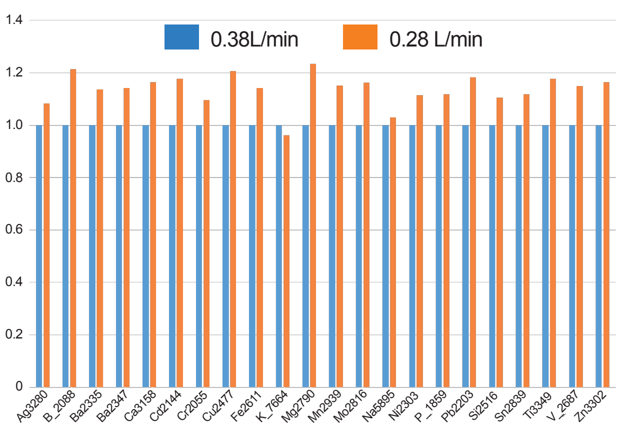


Figure 5: Optimizing the nebulizer gas flow rate; effect on normalized intensities

Optimizing Spray Chamber Temperature

Previous work with naphtha[2,3] was performed with a standard IsoMist which was limited to -10ºC for the low end. With the IsoMist XR, temperatures as low as -25ºC could be achieved and maintained. We therefore compared the results at -10ºC and -25ºC to see if improvement could be realized. Figure 6 shows an approximate 100% increase in intensities on average for all lines. Figure 7 compares the precision at the low and high standards. At the low end (a), some of the lines run at -10ºC appear to show intensity-related poor precision not seen at -25ºC. This goes away in large part for the high concentration standard (b) but the precision is still consistently better at -25ºC. As expected then, accuracy is also higher at the -25ºC temperature (Figure 8, page 4).

Reproducibility

Short term reproducibility was examined over a two hour period and the results shown in Figure 9 (page 4) are quite acceptable with an average difference of 3.3 %. To test longer term reproducibility, the experiment was repeated 5 days later. Results in Figure 10 (page 4) show a high degree of consistency with an average deviation of 2.6% for the 5.4 ppm standard and 3.1% for the 10.08ppm standard.

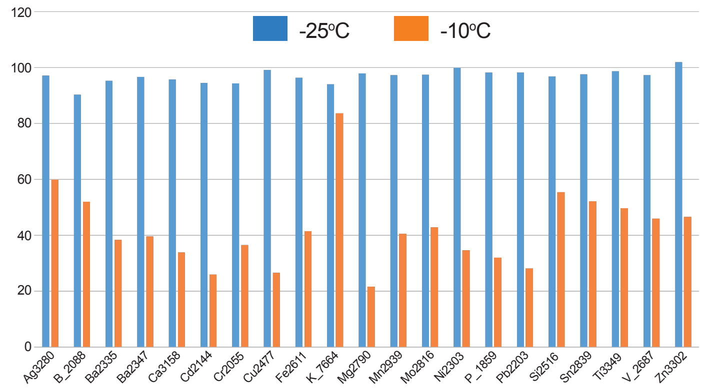


Figure 6: Effect of Spray Chamber Temperature on Intensity

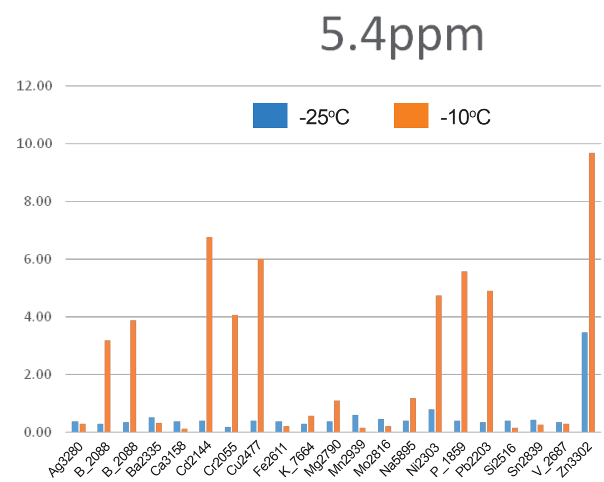


Figure 7a: Precision Comparison (%RSD)

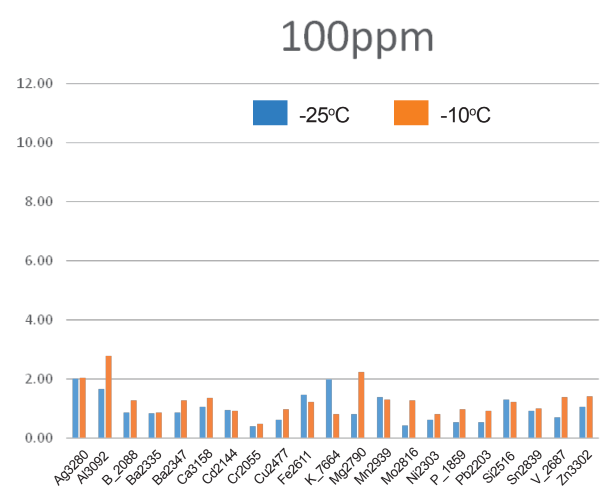


Figure 7b: Precision Comparison (%RSD)

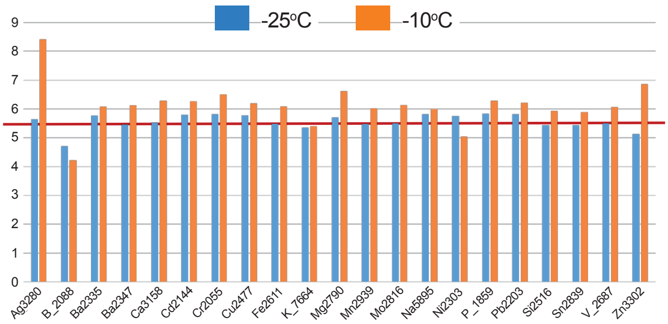


Figure 8: Accuracy Comparison at 5.4ppm

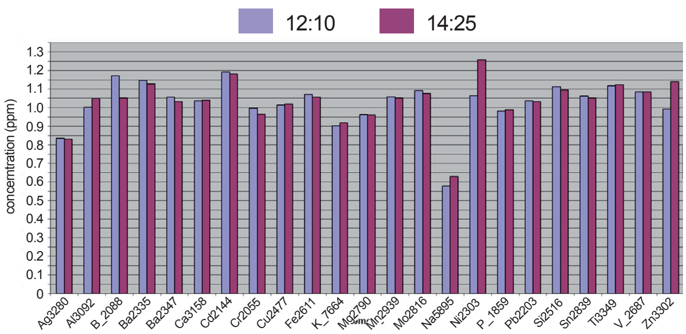


Figure 9: Intensity Reproducibility over two hours

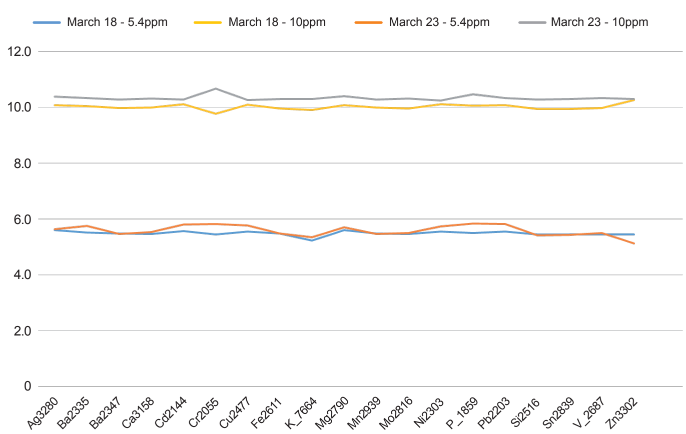


Figure 10: Five Day Reproducibility

Detection Limits

Both method detection limits (MDL) and method quantification limits (MQL) were calculated and are shown in Table II. In almost all cases, MDL's are in the ppb range. All are adequate for measuring metals in naphtha for the purposes described in the introduction.

Summary

For the optimum analysis of naphtha, it was found that the lowest practical nebulizer gas flow of 0.28L/min gave the best performance. Using the IsoMist Programmable Temperature spray chamber at a temperature of -25ºC rather than -10ºC gave higher intensities, better precision, and higher accuracy. Using the proper sample introduction components and the stated parameters, accurate, precise, and reproducible results could be achieved without dilution of the naphtha.

Table II: Limits of Detection and Quantification

Line	Predicted MDL(ppm)	Predicted MQL(ppm)
Ag3280	0.0013	0.0045
B_2088	0.0442	0.1473
Ba2335	0.0004	0.0014
Ba2347	0.0132	0.0442
Ca3158	0.0034	0.0114
Cd2144	0.0004	0.0014
Cr2055	0.0028	0.0094
Cu2247	0.0031	0.0102
Fe2611	0.0021	0.0072
K_7664	0.0058	0.0194
Mg2790	0.0147	0.0489
Mn2939	0.0017	0.0055
Mo2816	0.002	0.0067
Na5895	0.0042	0.0139
Ni2303	0.0075	0.0249
P_1859	0.0112	0.0375
Pb2203	0.0045	0.0149
S_1826	0.0696	0.232
Si2516	0.00194	0.0064
Sn2839	0.0074	0.0249
V_2687	0.0022	0.0073
Zn3302	0.151	0.5035

References

1. S. J. Kumar and S. Gangadharan, J. Anal. At. Spectrom., 1999, 14, 967-971.

2. M. Cassap, Thermo Fisher Applications Note #40899, 2010.

3. J. Dulude, V. Dolic, and R. Stux, Glass Expansion Application Note # 010407, 2007.

NEW PRODUCTS

New Elegra™ Argon Humidifier

An Argon Humidifier is commonly used in ICP analyses involving samples with high concentrations of dissolved solids. It helps to alleviate salt deposits in the nebulizer and torch injector, allowing uninterrupted and maintenance-free operation. Glass Expansion is pleased to introduce the new Elegra™ Argon Humidifier

- Compact, cost-effective design
- No heating or electric power required
- Non-pressurized water reservoir
- An easy-to-use bypass switch allows you to take the Elegra off-line without disconnecting argon lines
- Highly efficient membrane humidification technology
- Improved signal stability for samples with high TDS
- Simple to use and maintain
- Facilitates long, uninterrupted run times
- Inert metal-free construction eliminates possibility of contamination
- Rugged and durable polymer casing
- Maximum and minimum fill marks ensure that you are always operating under optimum conditions
- Compatible with all ICP-OES and ICP-MS models. Direct connection to argon outlet provided for most models.
- Two-channel configuration available for ICP-MS instruments using auxiliary argon

Product Number:	Description:	Suitable for:
70-803-1265	Elegra argon humidifier	Agilent/Varian Vista/700-ES
70-803-1266	Elegra argon humidifier	Agilent 5100 or Thermo iCAP 6000/7000
70-803-1267	Elegra argon humidifier	Agilent 4500/7500
70-803-1268	Elegra argon humidifier	Agilent 7700/7800/7900
70-803-1269	Elegra argon humidifier	PerkinElmer Optima or Spectro
70-803-1270	Elegra argon humidifier	PerkinElmer Elan/NexION
70-803-1271	Elegra argon humidifier	Other models
70-803-1272	Elegra Dual two-channel argon humidifier	Agilent 4500/7500
70-803-1273	Elegra Dual two-channel argon humidifier	Agilent 7700/7800/7900
70-803-1274	Elegra Dual two-channel argon humidifier	PerkinElmer Elan/NexION
70-803-1275	Elegra Dual two-channel argon humidifier	Other models

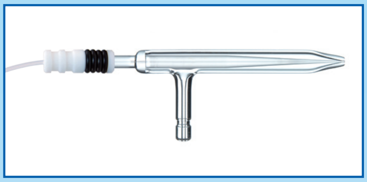
CONSUMABLES FOR

Agilent 5100 ICP-OES

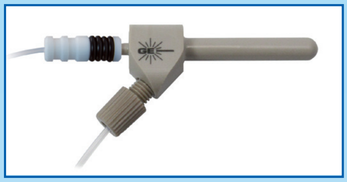
We can now supply a full range of consumables for this model.
Click **here** to see the full range.

Spray chamber 20-809-3452

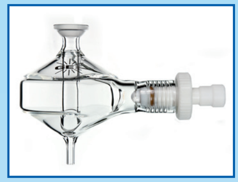
SeaSpray Nebulizer



DuraMist Nebulizer



Spray chamber 20-809-9199HE



Torch 31-808-3557

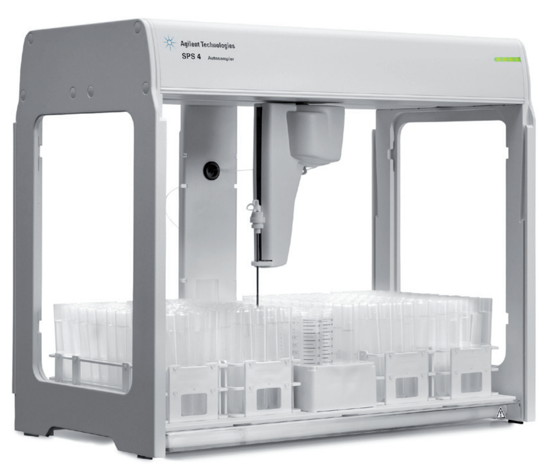
INSTRUMENT *NEWS*

From Agilent Technologies - New 7800 ICP-MS and New SPS 4 Autosampler

Agilent Technologies has introduced the Agilent 7800 ICP-MS, a system that sets a new standard for routine elemental analysis. The latest addition to Agilent's industry-leading ICP-MS portfolio, the 7800 provides wide dynamic range, exceptional matrix-tolerance, and superior interference removal, together with optimization tools and documentation to simplify method development and operation. The Agilent 7800 ICP-MS system was designed to meet the needs of industry and contract laboratories that want to simplify method development and increase productivity.

Agilent has also announced the availability of a new SPS 4 autosampler to help laboratories maximize productivity. The new four-rack autosampler is compatible with the company's entire portfolio of Flame AA, MP-AES, ICP-OES and ICP-MS products.

Agilent 7800 ICP-MS



SPS 4 Autosampler

From Teledyne Leeman Labs - New Application Note on the Analysis of Trace Elements in Edible Oils using ICP-OES

Teledyne Leeman Labs has released a new application note on the Analysis of Trace Elements in Edible Oils using ICP-OES. Edible oils are derived from a wide variety of plants and plant seeds and refined for global use in foods such as salad dressings, margarine, shortenings, snack foods and frying oil. Oils contain unsaturated fatty acids and relatively high levels of phospholipids which can react with oxygen to produce unpleasant flavors and odors in the oil. The presence of trace concentrations of metals such as Ca, Cu, Fe, Mg and Ni promote oxidation and can significantly reduce shelf life. Vegetable oils are very high in P, Ca and Mg as well as traces of Fe. Accurate trace metals analysis is a required quality control measure throughout the refining process. ICP-OES's sensitive and selective methodology meets this requirement with the ability to determine up to 70 elements in a sample throughout the various stages of the refining process.

This application note describes the analysis of edible oils using a Teledyne Leeman Labs' radial view Prodigy 7 ICP and provides the most suitable wavelengths, background correction and integration times. Results of a detection limit study are presented. The accuracy of the analytical method is validated using soybean, olive and corn oil matrices.

To receive a copy of application note 1503, The Determination of Trace Elements in Edible Oils using ICP-OES,
please visit http://info.teledyneleemanlabs.com/AN1503_Edible_Oils

From Spectro - How New Spectrometer Technologies Substantially Cut Operating Costs — New Whitepaper from SPECTRO Analytical Instruments

A new whitepaper detailing how new ICP-OES spectrometer technologies are substantially cutting operating costs in environmental, industrial, and academic laboratories is available to download from SPECTRO Analytical Instruments at http://icp-oes.spectro.com.

Traditional spectrometers bear the burden of a number of inherent problems in their design. A new whitepaper, titled "How New Spectrometer Technologies Substantially Cut Operating Costs," explores how engineering innovations have addressed design issues to enable significant savings while improving performance. The advancements, detailed in the paper, include:

- New system designs that deliver improved uptime and throughput while reducing operating costs.
- A unique sealed optical system that abolishes the need for the constant purging of argon or nitrogen, eliminating purge gas consumables cost and purging delays.
- Improved spectrometer technology that removes the need for a separate, external, water-based cooling system along with the associated purchase, installation, power and maintenance costs.
- Innovations in optical technology that improve performance measures such as sensitivity and stability.
- A robust generator design that provides ample power reserves, so it can handle extreme plasma loads, and adapt to quickly changing demands.

Such advancements, according to the whitepaper, cut operating costs by enabling easier, less expensive installation, operation, and maintenance, while improving both ICP-OES performance and usability. Download "How New Spectrometer Technologies Substantially Cut Operating Costs" at http://icp-oes.spectro.com.