

APPLICATION SPOTLIGHT

COMPARISON OF ENHANCED PRODUCTIVITY ICP APPROACHES FOR ENGINE OIL ANALYSIS

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Introduction

The measurement of metals in used engine oils provides valuable information about the engine and the state of the lubricant, information which can be used to increase the efficiency of the equipment in which the engine resides and lower the cost of maintenance. Table 1 lists the metals which are typically of interest and their sources (1-4). The presence of wear metals is important because it can pinpoint a specific component for maintenance. For example, copper is an indication of bearing wear while lead may come from bushings and chromium from piston rings and seals. Other elements such as calcium, magnesium, and zinc are added to the oil to produce a "soap" to protect engine components. So it is important to ascertain that these metals remain at an optimum concentration. Also, dirt may contaminate the oil which would be evidenced by the presence of elements like silicon and sodium.

Wear Metal	Contaminant	Additive
Copper	Boron	Calcium
Iron	Silicon	Phosphorus
Lead	Sodium	Zinc
Cadmium	Potassium	
Aluminum		

Table 1: Significance of metal determinations in used engine oil

Element/wavelength		
Ag 328.068	Fe 238.204	Pb 220.353
Al 309.215	K 766.491	S 181.972
B 249.678	Mg 285.213	Sb 217.582
Ba 493.408	Mn 257.610	Sn 283.998
Ca 317.933	Mo 202.032	Ti 336.122
Cd 226.502	Na 588.995	V 292.401
Cr 267.716	Ni 231.604	
Cu 324.754	P 177.434	

Table 2: Element wavelengths selected

Parameter	Setting
RF power	1.40 KW
Coolant gas flow	18 L/min
Auxiliary gas flow	2.25 L/min
Nebulizer gas flow	0.75 L/min
Replicate read time	2 s
Number of replicates	2

Table 3: ICP operating parameters

Despite the importance of these measurements, the need for fast analysis (high volumes of samples) and the undemanding accuracy requirements (trend determination only is required), speed of analysis is often one of the most critical requirements of the industry. In this paper, we will compare two methods of oil analysis, one using off-line dilution followed by high speed analysis, and the other employing in-line dilution and analysis with a single high productivity system. The preference of one approach over the other will depend more upon the individual laboratory's operational set-up than on anything else.

Experimental

All work was performed on a Varian Vista Pro radial ICP-OES system (Agilent Technologies, Melbourne, Australia) configured with a Twinnabar spray chamber (20ml internal volume with baffle), a ceramic VeeSpray modified Babington nebulizer, and a single piece quartz torch with 0.8mm bore injector (all from Glass Expansion, Melbourne, Australia). Organometallic standards were used throughout (Conostan, Ponka City, OK). The elements selected for monitoring and the associated wavelengths of measurement are listed in Table 2. The plasma conditions are listed in Table 3.

GE NEWS

Pittcon 2011

A wide selection of Glass Expansion products will be on display at Pittcon 2011, Atlanta, Georgia, USA, March 13 – 18, 2011. 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 new Assist syringe-driven ICP sample introduction system. 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 2947.

New ICP Chemist

Our customer support team has been strengthened by the appointment of Dr. Ryan Brennan to our USA office. Ryan has a PhD in analytical chemistry from The George Washington University and has recently been working at the Analytical Chemistry Division of the National Institute of Standards and Technology (NIST). Throughout his career, he has focused on solving difficult analytical problems with ICP-MS and ICP-OES. When he joins us on March 7, he will enhance our ability to help ICP users to get the best possible analytical performance.

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GLASS EXPANSION
Quality By Design

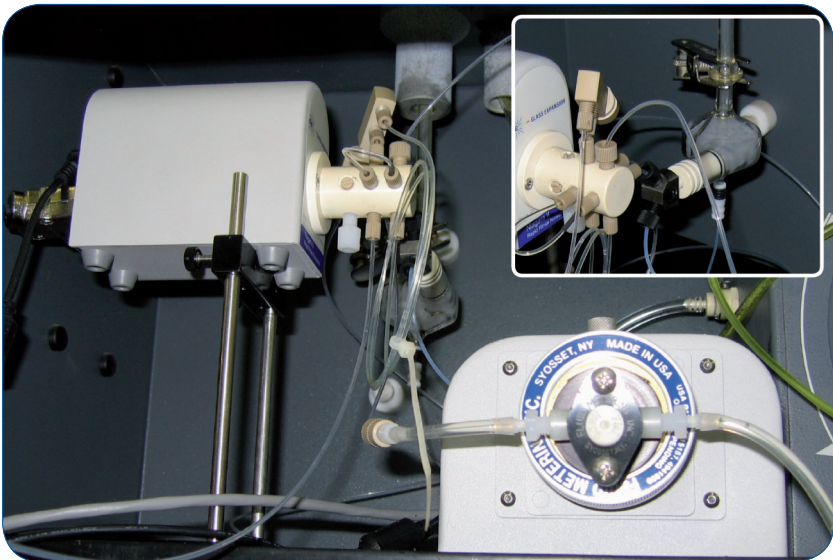


Figure 1: Niagara Plus mounted on the Varian Vista Pro ICP-OES

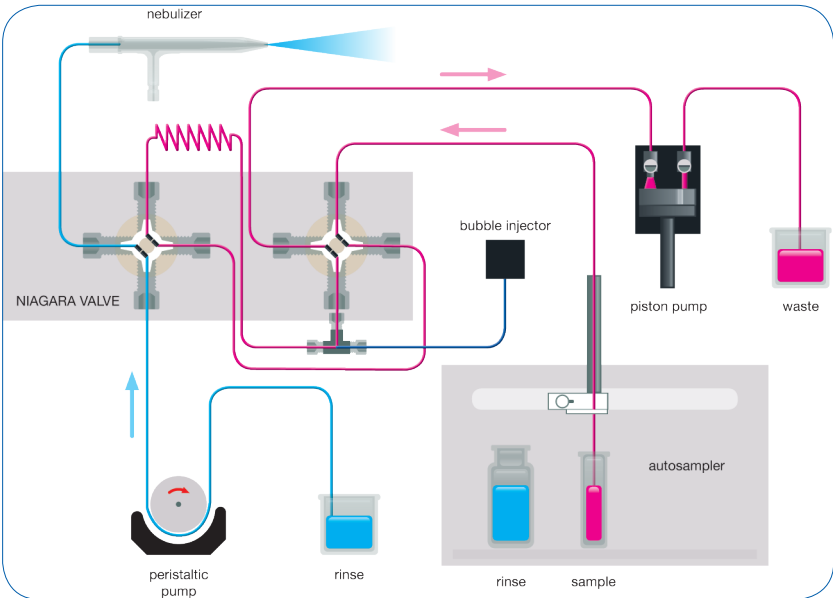


Figure 2: Niagara Plus flow schematic, Rinse/Refill stage

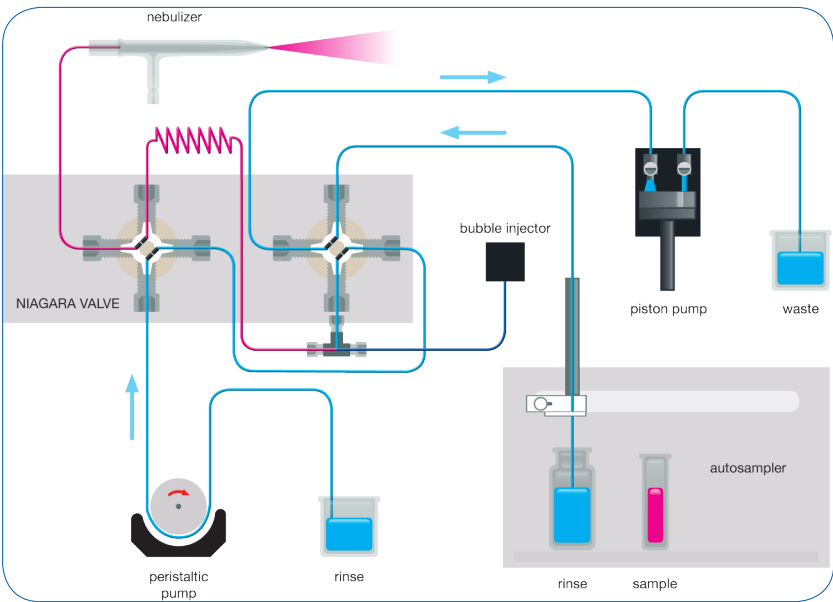


Figure 3: Niagara Plus flow schematic; Home/Inject stage

Off-line Dilution Approach

For this approach, a Hamilton ML500 Series auto diluter (Reno, NV) was used to affect a 10x dilution of the raw oil. Diluted samples were then placed in an AIM High Capacity autosampler (Clontarf, Australia), and analyzed via a Niagara Plus sampling accessory (Glass Expansion). This device was previously described for the analysis of environmental waters (5). The Niagara Plus accessory utilizes a recently developed switching valve and a positive displacement pump to speed both delivery of the sample to the nebulizer and subsequent washout. The switching valve was designed for minimum carryover and fast washout and has the following characteristics.

- Minimal swept volume
- Constant sample path ID
- Rigid rotor
- Replaceable PTFE stator
- Color-coded ports for ease of assembly

The design and material of the rotor and stator are of particular importance for this application due to the need for a rugged analytical protocol. Wear metals exist as small particles in a slurry of oil (6) and may cause damage to the valve if the wrong materials are employed. In this case the rotor is composed of PEEK and is quite resistant to scoring, while the less wear-resistant stator is designed for easy removal, cleaning, and installation. Figure 1 shows the Niagara Plus system mounted on the Varian ICP. Note the proximity of the nebulizer to the valve (inset) which is mounted on an adjustable height stand. This proximity contributes to the speed of the system. Figures 2 and 3 demonstrate the operation of the switching valve in its two modes of operation. In the “Rinse/Refill” mode, the sample loop is being loaded via the positive displacement pump while the nebulizer is rinsed with solvent. In the “Home/Inject” mode, the sample in the loop is injected into the nebulizer while the remainder of the system is rinsed with solvent.

The Niagara Plus method parameters are given in Table 4. Note that the positive displacement pump is programmed to use different speeds during the two modes, a faster speed while loading the sample loop and a slower speed while rinsing the system (inject mode). This not only conserves solvent and reduces waste, but we have found that the slower speed also improves washout. Two other fields merit explanation.

Parameter	Setting
Loop uptake delay (fill time)	4.5 s
Uptake pump speed (refill loop)	350 rpm
Uptake pump speed (inject)	220 rpm
Time in sample	3.5 s
Bubble inject time	4.4 s
Instrument stabilization delay	4 s
Sample uptake delay	0 s
Rinse time	0 s

Table 4: Niagara Plus (off-line dilution) parameters



Figure 4: Assist accessory mounted in front of the Varian ICP-OES

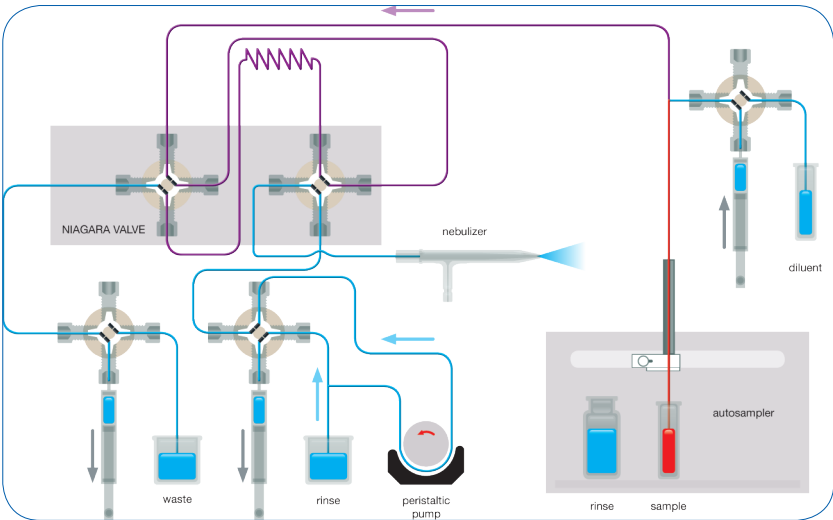


Figure 5: Assist flow schematic; Rinse/Refill stage

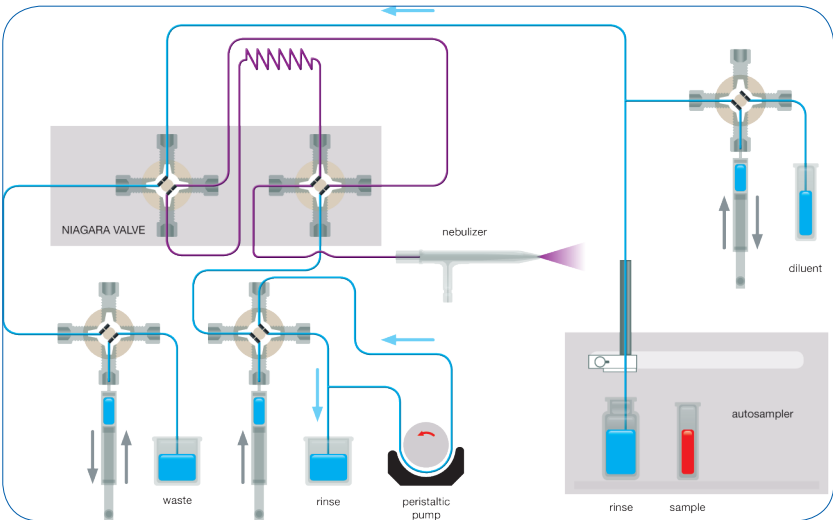


Figure 6: Assist flow schematic; Home/Inject stage

“Time in Sample” allows the autosampler probe to be programmed to come out of the sample while the sample loop is being loaded thus reducing the cycle time even more. The “Bubble Inject Time” defines when the bubble injector activates to place several gas bubbles in the sample line to limit boundary diffusion. Note the rinse time in the instrument method is set to zero, since the Niagara Plus is rinsing during the sample loading step anyway. For the sake of comparison, we also employed a method with a 1 second rinse programmed (which due to the autosampler and processor overhead contributed several seconds to the cycle time).

Method parameters	
Loop uptake delay	15 s
Purge time	0 s
Purge rate	0 rpm
Syringe refill time	5 s
Time in sample	11 s
Neb flow rate	1.75ml/min
Total read time	4 s
Read delay	4 s
Instr. Stabil. Delay	13 s
Uptake syringe	
Barrel volume	10 ml
Sample uptake vol.	3.5 ml
Sample uptake rate	15ml/min
Sample empty rate	580ml/min
% dilution	90
Diluter barrel vol.	10 ml
Diluter refill rate	50ml/min
Line flush vol.	2 ml
Line flush rate	35ml/min
Sample syringe	
Barrel volume	2.5 ml
# of priming cycles	3
Priming flow rate	2ml/min

Table 5: Assist (in-line dilution) parameters

In-Line Dilution and Analysis

This approach substituted the Assist accessory (Glass Expansion) for the auto diluter system and is shown mounted in front of the ICP spectrometer in Figure 4. The three syringes that are part of the Assist system are used to load the sample loop, inject the sample, and dilute the oil. As shown in Figure 5, during the Rinse/Refill stage, the diluter syringe pumps kerosene diluent while the sample uptake syringe draws sample. The two syringes are programmed to affect a 10x dilution of sample. During this time, the rest of the sample introduction system is rinsed with diluent. During the Home/Inject stage (Figure 6), the diluter and sample uptake syringes are 180 degrees out of sync to continuously pump diluent through the sample lines while the inject syringe delivers the diluted sample to the nebulizer.

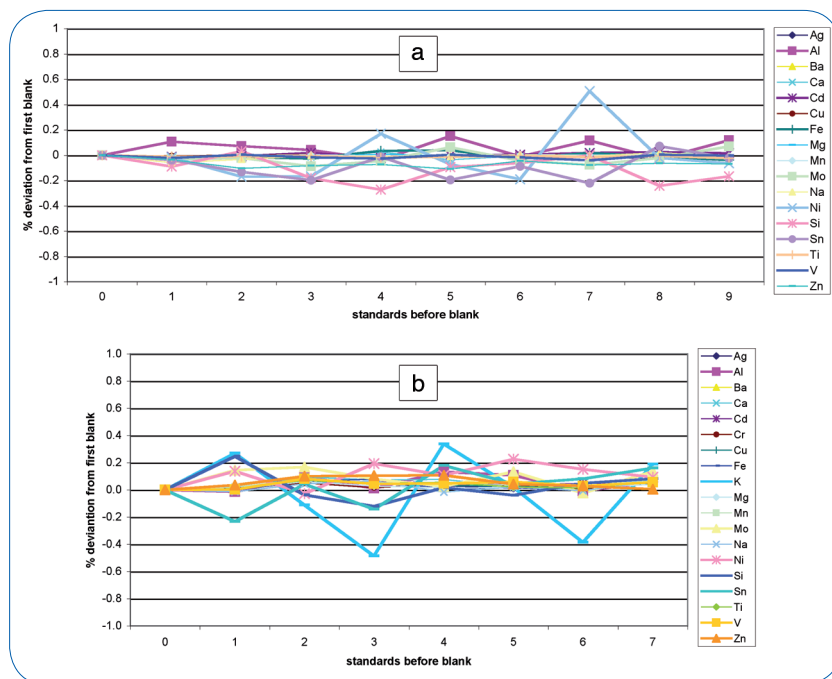


Figure 7: Carryover test for diluted oil on Niagara Plus;
a.) with one second programmed rinse;
b.) without a programmed rinse.

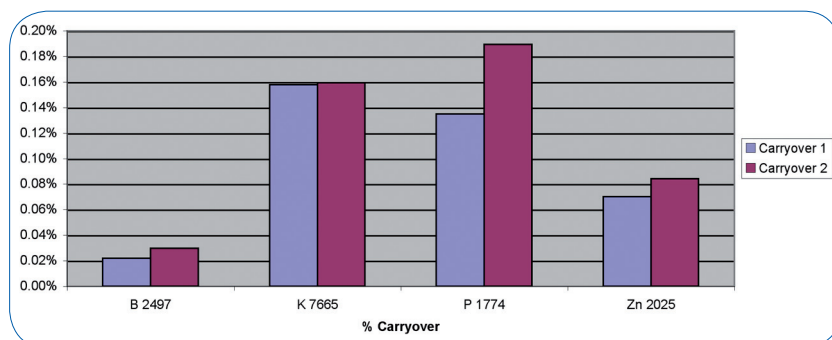


Figure 8: Carryover test for high concentration elements for diluted oil on Niagara Plus with one second programmed rinse

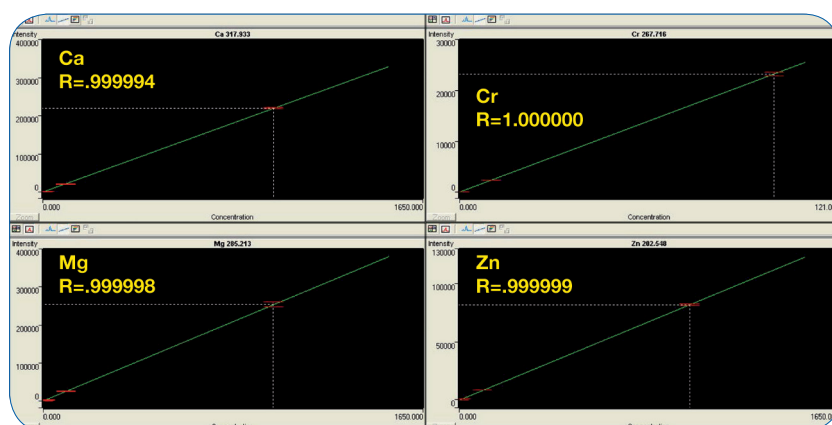


Figure 9: Assist generated calibration curves

The Assist method parameters are given in Table 5. While the sample loop was being filled for 15 seconds, the autosampler probe started moving to the rinse after only 11 seconds (Time in Sample). Standardization was performed by auto dilution of the stock standard with the Assist accessory. Again the programmed rinse time was zero.

Results

Using the Niagara Plus (off-line dilution), we evaluated carryover with and without a programmed one second rinse (Figure 7). The data was obtained by running successive blank/100ppm standard pairs and monitoring the blanks as a per cent of the high standard in comparison to the first blank. The theory is that if carryover is significant, an increasing trend in the blanks would result. In either case the level did not increase with increasing numbers of standards run, indicating no significant improvement using the 1 second programmed rinse method, we took a second look at carryover for several elements by running a blank subsequent to a very high concentration sample (3000ppm of boron and potassium and 1500ppm of phosphorus and zinc). The test was run twice to gauge reproducibility (Figure 8). Carryover did not exceed 0.2% for any element monitored. The sample cycle time without a programmed rinse was 18.5 seconds.

Using the Assist accessory (in-line dilution), we first examined the linearity of in-line standard dilution and analysis. The resultant calibration curves for 4 elements are shown in Figure 9. All have correlation coefficients of at least five nines demonstrating excellent correlation. Figure 10 examines the difference between the first and second replicate of an analysis. To attain confident results, we averaged 10 first replicate results of a high standard and compared it to the average of 10 second replicate results. Note that there is no significant difference between replicates for the Assist program (blue) used. This test is a valuable test protocol to ascertain that the method is adequately developed. The red bars represent a hypothetical case of insufficient uptake volume. In this case, if the sample loop has not been adequately filled, the second replicate will be lower than the first. The yellow bars represent a hypothetical case of insufficient read delay, where the signal is being measured prior to the sample reaching equilibrium in the torch.

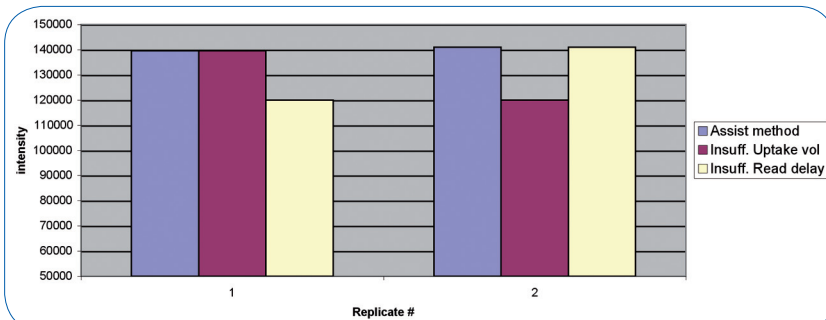


Figure 10: Replicate study for Assist; average of ten 100ppm standard results for 21 element lines

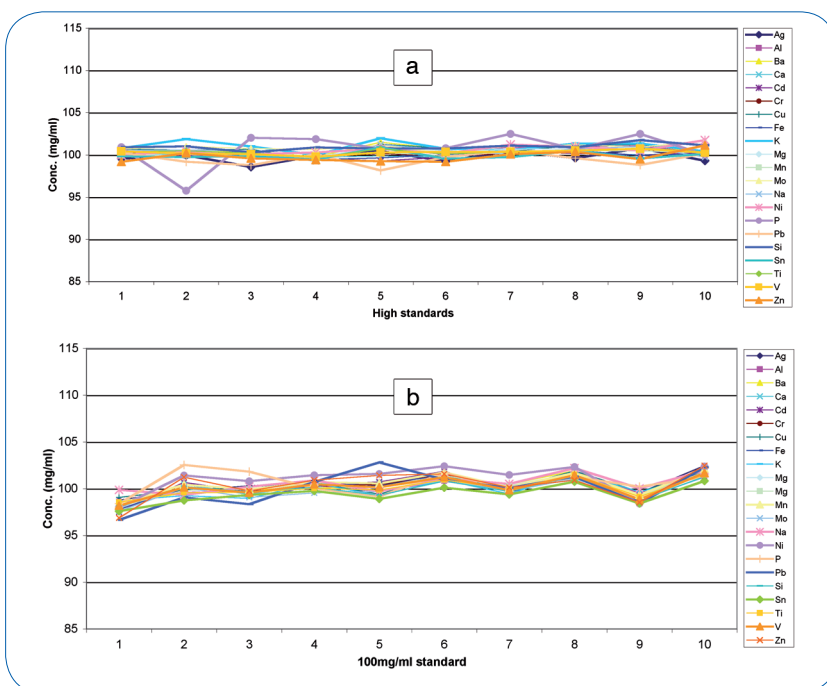


Figure 11: Reproducibility study;
 a.) Diluted oil on Niagara Plus without a programmed rinse;
 b.) Undiluted oil with Assist without a programmed rinse

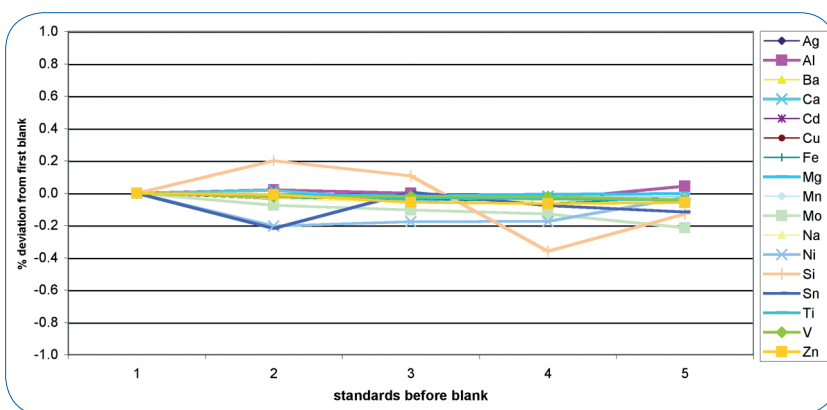


Figure 12: Carryover test for undiluted oils on Assist system without a programmed rinse

Reproducibility of a 100ppm standard was compared and the data is shown in Figure 11. Although the Niagara Plus data shows slightly better reproducibility, the Assist data is still well within the 10% deviation goal. Better reproducibility can be obtained by reducing the uptake rate of the undiluted oil, and incorporating a non-laminar flow path in the sample loop and uptake lines (putting bends such as figure eights in the lines). This leads to greater mixing of the sample and diluent at the expense of slightly longer analysis time. Figure 12 shows the carryover found with the Assist by running a succession of blank/100ppm standard pairs. Note that the results compare well with those shown in Figure 7b for the Niagara Plus system (no programmed rinse for either). The sample cycle time with the Assist was 28 seconds.

Conclusions

We have shown that acceptable reproducibility and washout can be achieved with two enhanced productivity approaches to the analysis of engine oils for metals. The faster sample cycle time of 18.5 seconds was achieved with the Niagara Plus off-line dilution method, while the less labor intensive Assist in-line dilution and analysis method still attained a cycle time under 30 seconds. Without these enhanced productivity accessories, sample cycle times from 45 to 60 seconds are typical.

Based on a paper presented at PITCON 2010, Orlando, Florida, USA, March 1 to 4, 2010

References

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2. B. E. Buell, App. At. Spectrosc. 2, 53 (1978).
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5. J. Dulude and V. Dolic, Spectroscopy Supplement, Nov., 16-23 (2009).
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NEW PRODUCTS

ASSIST

The Assist™ is an automated sample introduction system for ICP-OES or ICP-MS. It consists of purpose-built programmable syringe drives with an integrated valve system. The Assist delivers the highest level of accuracy, stability and sample throughput by controlling the delivery of both sample and internal standard or diluent, eliminating the inaccuracies and pulsations caused by peristaltic pumps.

The Assist provides you with:

- **Twice the sample throughput.** The rinse time, stabilization time and the time for the sample to move from the autosampler to the nebulizer are all reduced. This reduces the time for a typical analysis by at least half.
- **Better precision.** The sample is delivered by a precisely controlled syringe, eliminating the signal pulsation problem which occurs with the usual peristaltic pump delivery system.
- **Better accuracy.** The internal standard is delivered by a second precision syringe drive, ensuring that the ratio of internal standard to sample is accurately maintained. The fluctuations in this ratio that occur when the internal standard is delivered by peristaltic pump are eliminated, greatly improving the analytical accuracy.
- **Automatic dilution.** The second syringe drive can also be used to deliver a diluent, enabling accurate dilution by a factor of up to 20:1 to be carried out automatically.
- **Reduced carryover.** The sample does not contact any peristaltic pump tubing and the sample path is totally inert. This allows for a faster rinse and reduces carryover.
- **Low sample and internal standard usage.** The volumes required are substantially reduced, resulting in lower cost of reagents and less wastage.
- **Flexibility in the selection of the ratio of sample to internal standard.** The syringe system allows you to use sample to internal standard ratios of up to 20:1 and still get accurate correction.
- **Longer life of consumables.** The lower sample volume and reduced analysis time mean that you save on consumables such as torches and ICP-MS cones as well as argon.
- **Compatibility.** The Assist software is configured to operate with almost all models of ICP-MS, ICP-OES and autosampler.



Configured to suit the application

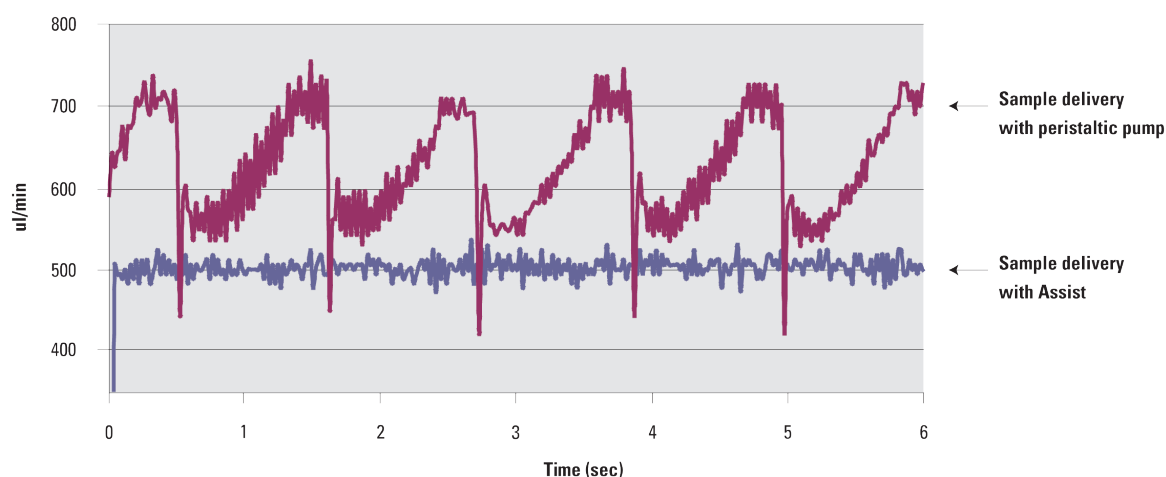
The Assist is a modular system of syringe drives and switching valves and it can be configured to suit specific applications.

Premium Package. This is the most common system and is the system described above. It incorporates two syringe drives and a Niagara switching valve. It provides for the inline delivery and mixing of the sample and internal standard or diluent.

Basic Package. This system is used when inline delivery of internal standard or diluent is not required. It incorporates a single syringe drive and a Niagara switching valve. It provides all of the benefits listed above with the exception of those relating to delivery of internal standard or diluent.

Oils Package. This system is configured specifically for the analysis of wear metals in raw (undiluted) lubricating oils. It incorporates three syringe drives and a Niagara switching valve. It takes a sample of the oil, mixes it with a diluent such as kerosene and precisely delivers the diluted oil to the ICP spectrometer. It eliminates the need for manual dilutions and increases the speed of analysis.

Part No.	Description
KT-1076	Assist Premium Package (2 syringe units)
KT-1100	Assist Basic Package (1 syringe unit)
KT-1095	Assist Oils Package (3 syringe units)



NEW PRODUCTS

DURAMIST NEBULIZER

The DuraMist is a new model HF-resistant nebulizer. It provides excellent sensitivity and precision at an affordable price. The PEEK material is resistant to most chemicals used in ICP applications, including HF. The DuraMist is a concentric, self-aspirating nebulizer and models are available with argon flows of 0.7 and 1.0L/min and natural sample uptake rates of 0.4 and 1.0mL/min.

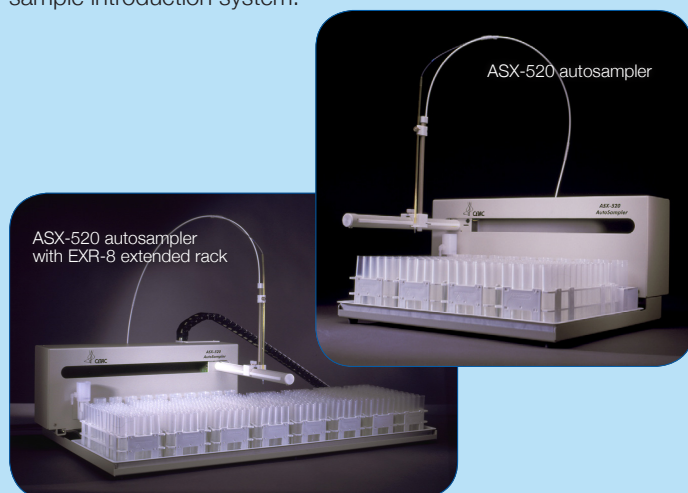


Part No.	Description
AR40-07-DM04	DuraMist nebulizer 0.4mL/min
AR40-07-DM1	DuraMist nebulizer 1mL/min
AR40-1-DM04	DuraMist nebulizer 0.4mL/min
AR40-1-DM1	DuraMist nebulizer 1mL/min

AUTOSAMPLER

The ASX-520 autosampler is now available through Glass Expansion. This is the most commonly used ICP autosampler throughout the world. Almost every ICP-OES and ICP-MS model incorporates software to drive the ASX-520, making installation straightforward. We are also offering the ASX-520 with extended rack, which expands the capacity to 8 racks and up to 730 samples.

The ASX-520 autosampler can be teamed with the Niagara Plus or the Assist to provide a complete automated high performance sample introduction system.



Part No.	Description
KT-1098	ASX-520 Autosampler
KT-1099	ASX-520 Autosampler with EXR-8 Extended Rack

INSTRUMENT NEWS

From Bruker – Analysis of Chromium Species in Waters

In September 2010 the US-EPA released a draft assessment on hexavalent chromium in US drinking water (Sept 2010 draft human health assessment for chromium-6). The EPA is proposing to classify chromium-6 as likely carcinogen to humans via ingestion and expects to complete the health risk assessment and make a final determination about the carcinogenicity of chromium-6 in 2011. When this assessment is finalized, it is anticipated that the USEPA will change the current standard.

Common forms of chromium in the environment are trivalent (chromium-3), hexavalent (chromium-6) and the metal form (chromium-0). Chromium-3 occurs naturally and is an essential micronutrient while chromium-6 is typically produced by industrial processes and is a likely carcinogen.

Liquid Chromatograph (LC) interfaced to Inductively Coupled Plasma Mass Spectrometer (ICP-MS) is a very powerful analytical tool for measuring ultra-trace concentrations of chromium species. The Bruker 820-MS, with its innovative patented Collision/Reaction Interface (CRI) technology, efficiently removes polyatomic interferences formed in the plasma, allowing for low ng/L (parts per trillion) detection of the trivalent (chromium-3) and hexavalent (chromium-6) chromium species.

The Bruker 820-MS with HPLC interface includes an integrated LC and ICP-MS software platform providing complete hardware control, real-time data collection and post-analysis data management.

For further information on this application (CA-274195) please visit the following web site for a free download:

www.bdal.de/products/icp-ms/810-820-ms/learn-more

From Spectro – Whitepaper on the Analysis of Precious Metals

Today, precious metal dealers, refineries, mining companies and service laboratories are more dependent on powerful elemental analysis than ever; techniques that can handle precious metal contents of almost 100 percent just as well as they can deal with traces of just a few parts per billion.

It's amazing what precious metal analyzers have to be able to do these days. And which instruments are most convincing? Find out in our new whitepaper "All that glitters is not gold." Here we have documented three equally well tested and powerful analytical procedures for metal analysis:

- Energy dispersive X-ray fluorescence analysis (ED-XRF) for non-destructive screening
- Optical emission spectrometry with inductively coupled plasma (ICP-OES) for the examination of highly pure precious metals and minimal trace element contents
- Stationary spark emission spectrometry for precise onsite metal analysis

The new whitepaper provides detailed information about the strengths of the different analytical procedures and, using various measurement series as examples, illustrates the possibilities that the SPECTRO instruments can open for your precious metal analysis. Sound interesting? Then download the free-of-charge "All that glitters is not gold" whitepaper today at spectro.com. You'll see: We have the perfect instrument for all your needs.