Analysis of Oils

Understanding Chemical Stability and ICP Matrix Effects

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Introduction

Elemental analysis is a commonly performed test in petroleum laboratories. Instruments and techniques used include Inductively Coupled Plasma (ICP), Atomic Absorption (AA), and Rotating Disk Electrode (RDE). Labs with a high throughput of samples may have multiple ICPs operating at the same time over multiple shifts. The ICP is a versatile instrument as it rapidly detects and quantifies the concentration of a wide range of specified elements in oil. The presence and relative concentration of these elements may signify abnormal wear, excessive contamination, and/or additive depletion, all of which require action by the end user or owner of the asset.

Once ICP results are obtained, one or more methods or routes are commonly used to determine if there is a concern requiring action. These methods include analyst experience, statistical analysis, and/or rate of change over time (trend analysis). Regardless of the ICP instrument or method used, consistent and knowledgeable operation of the ICP, choice of certified reference materials (CRMs) for calibration and control standards, and the use of a high-quality diluent matrix solvent are essential to accurately determine if corrective action needs to be performed based on the test results.

Calibration in Petrochemical ICP Analysis

ICP analysis of metals in petrochemical samples requires all samples, standards (calibrants), and control (check) samples to be stable and homogeneous over the course of their use. Typically, samples and calibration standards are treated similarly with respect to having a consistent dilution level using the same dilution solvent, and are then analyzed while relatively "fresh." While laboratory managers are inclined to maximize the useful lifetime of all prepared samples, Good Laboratory Practice (GLP) suggests that standards be made fresh daily. It is generally accepted that test samples and metallo-organic calibrants are not particularly stable for more than a few days or a week once blended with the solvent – sometimes even less.

Calibration of the ICP instrument is usually performed for each analytical run using "working standards" obtained from a handful of commercially available suppliers. Calibration verification is performed over the course of the analytical run with an independent set of control "check" standards. Only true Certified Reference Materials (CRMs) deliver the highest accuracy and confidence available in a standard. CRMs produced under an ISO scope of accreditation to acceptable quality levels, such as ISO 17034, are ideal for the purposes of calibration and/or control standards and these can be selected from a range of convenient "multi-element" metallo-organic analytes in base oil matrices.

A pivotal aspect affecting the integrity of data produced is the solvent used for dilution. The choice of solvent varies considerably in laboratories worldwide, and even different laboratory locations within a single company may use a variety of solvents. Some laboratories employ reagent grade aromatic solvents (e.g. xylene) while others select simple, locally available materials (e.g. lamp kerosene or "white spirits"). These materials often provide suitable solvency effects for the samples at hand, but their impurity levels and the stability of the samples prepared with these solvents often differ. Not surprisingly, inexpensive, lower purity solvent materials vary more in composition, as well as in lot-to-lot uniformity, resulting in even greater variability of analytical test data.

One distinct aspect of ICP calibration is that working standards and controls are seldom made from single-element stock CRMs or a single multi-element CRM (e.g. serial dilutions). Instead, they are prepared from a range of multi-element CRMs, so the working standards are all identically diluted from the commercial stock standards, which provides a more uniform matrix. Therefore, commercial CRMs are typically provided as multi-element blends, and as a series of "concentrates." By performing a one-step dilution, the resulting instrument calibration standard concentration arrives at the chosen value (e.g. a 1:10 dilution of 100 µg/g to 10 µg/g, 300 µg/g to 30 µg/g for standards #1 and #2, etc.). These are often referred to as "working standards."

Challenges with Prepared Metallo-Organic Standards

One common issue reported by ICP users is the tendency for element recovery in a standard to fail and "drop out" over time, despite no visual change. In many cases, the root cause is assumed to be a problem with the stock standard; however, careful ICP retesting of the same stock lot would prove that the CRM itself had not degraded. This problem of recovery degradation over time is commonly ascribed to the working standard "becoming contaminated" or the individual bottle of stock standard having a unique factor "ruining" it.

Boron is a commonly cited example of an element with the most problematic tendencies for petroleum ICP analysis. Also problematic, but to a lesser degree, are silver, molybdenum, lead, and vanadium. The VHG™ research and development team determined a root cause analysis (RCA) was necessary to evaluate this issue, and would involve looking at a wide range of potentially contributing factors. VHG™ initiated a project to investigate a variety of factors which influence the stability of these solutions over time.

As mentioned, boron has the greatest reported incidence of control outliers; as well as anecdotal reporting of other various measurement accuracy or precision issues. Causes were rarely traceable to the ICP analytical program since the issues were generally sporadic and nearly as frequent at laboratories with long-established processes as they were with new users.

Initial work to determine the root cause focused on possible lot variability of the CRM and mixing during production. Yet, it was known that boron measurement instability by ICP was also commonly reported with the use of entirely different alternative commercial suppliers of stock standards, suggesting a causal factor (or factors) existed within the instrument, method, or lab practices. The VHG™ team found it interesting that a seasonal component appeared to exist as a contributing influence. Other evaluated factors included the freshness of preparation, temperature, UV exposure of prepared samples, and interactions with other major or trace metal levels in samples.

A hyopothesis was developed that exposure of a prepared sample to air was the factor affecting boron, even while other elements present in the same solution did not have measurement recovery problems. It is known that prepared samples are commonly left open (e.g. on the auto-sampler rack) for lengthy periods of time, a condition found in a number of high-throughput oil laboratories. Furthermore, the association of this problem with laboratories located in more tropical conditions (such as the coastal region near the Gulf of Mexico) adds an additional humidity component.

Water and Oil Do Mix

Water (H_2O) as a liquid has well-known chemical repelling properties (hydrophobicity) when combined with neat non-polar oil / solvent materials. While solvents used as ICP diluents (e.g. kerosene type solvents) are generally free from significant amounts of liquid water, they can tolerate and hold varying degrees of dispersed water before an obvious phase separation or cloudy emulsion is visibly seen to occur. Once the phases separate and the solution becomes inhomogeneous, the metallo-organic components could follow suit and a distinct dropout or stratifying of the metal content would likely occur.

However, many oil products, prepared test samples, and metallo-organic calibrants may lose some of their hydrophobic qualities by virtue of additives present. For example, a sample of 15-40w diesel oil and a sample of a 75w base oil (group II oil) were tested by Karl Fischer (KF) titration for water content subsequent to open atmospheric exposure to different environmental conditions. Table 1 reveals that the 75w base oil maintained low water content, changed little, and maintained hydrophobic qualities (remaining <50 µg/g H_2O) while the 15-40w commercial oil either added or sloughed off water to its original water content value depending on the exposure conditions. Warm humid conditions added water to the diesel oil while warm, arid conditions removed water from the diesel oil. This implied that the open sample was chemically impacted by the atmospheric headspace above it, also that additive components in the oil increased reactivity between the oil and the atmosphere interface above it.

	# Days Exposed	Original bottle closed	High humidity, open exposure	Dry, open exposure
75wt Base Oil	3	<50 µg/g H_2O	<50 µg/g H_2O	<50 µg/g H_2O
15-40 Diesel Engine Oil	3	330 µg/g H_2O	420 µg/g H_2O	130 µg/g H_2O

Table 1. Karl Fischer results for open sample exposures (23°C)

The experimental concept was to determine the impact of environmental conditions on open auto-sampler tubes containing typical, solvent-diluted metallo-organic blends. The goal was to mimic the common laboratory situation of having loaded auto-sampler racks of prepared samples. An outcome of this understanding would be to produce materials with greater resilience to stress from environmental factors.

Experimental

Metallo-organic stock concentrate test blends (VHG™ V21 CRMs, prepared under our ISO 17034 scope of accreditation at our Manchester, NH facility) were used containing Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn in 75 cSt Mineral Oil. These included two stock blends that were identical except that they contained different forms of raw starting material for the boron component. The name "conventional boron" was used to describe a boron material used in V21 that met industry standards and had generally good qualities.

The second form of boron material, named "HI•Boron", also met industry standards for use as a boron metallo-organic material and was blended into an advanced forumlation of the VHG™ V21 CRM tested here. HI•Boron was developed by the VHG™ R&D team to enhance performance over a wide range of uses, including those where water (hydration) was an environmental factor.

Comparison to an alternate supplier's 21-element blend was also done. Samples' ICP analyses were prepared at 10 µg/g concentration with a diluent solvent proportion of 90% (1:10 dilution of the stock). Diluent solvents used were commercially available materials including laboratory grade xylenes, kerosene, and VHG™ V-Solv™. Water content in each of the solvents was tested by Karl Fischer (KF) titration, and confirmed to be low at <50 µg/g.

The test sample containers (50 mL centrifuge tubes) were placed into a controlled environment enclosure (Norlake Scientific) where temperature and relative humidity (RH) could be maintained. For the bulk of this work 24°C was defined as warm, 25% RH as dry, and 65% RH as humid (these settings being similar to those conditions found in a warm and humid laboratory environment in summertime or a warm climate).

The test samples were split between capped and open containers. They were not agitated during exposure and after approximately 24 hours the samples (1 Day Dry Conditions, 1 Day Humid Conditions, 6 Days Humid Conditions) were removed and analyzed (see Figure 1). Measurements were taken on a PerkinElmer® 7300V ICP run in radial view mode. As such, the "rack life" of exposed metallo-organic "working standards" compared to closed, capped ones both prepared for ICP measurements was the investigated component of the study.

Discussion

It is helpful to review the potential impact of samples placed into open sample tubes that are typical of those used with commercial ICP auto-samplers. The open top allows for evaporation, impurities to enter, and a location at which air can chemically interact with the material. Air is composed primarily of nitrogen gas (N_2) which can be reasonably considered to be inert; however the oxygen (O_2) present in air is, chemically speaking, a reactive molecule. In humid air the water (H_2O gas) content is an additional and potentially non-inert component. The mass amount of water in air is not trivial - between a cool and dry 15°C at 20% relative humidity to a warm and humid 24°C at 80% relative humidity, the absolute water content in air increases sevenfold from approximately 2.6 to 18.4 µg/cm^3. Note that the combined presence of oxygen and water represents a reactive duo, as in the rusting process of iron. A sample's exposure to this type of atmosphere can be even more impactful when the sample contains additive components that are capable of complexing with water or oxygen molecules.

As previously mentioned, cases involving recovery issues of boron in test samples do not typically involve any visual change in the sample. Similarly, in this test none of the samples exposed to conditions had visible precipitation, phase separation, or any distinct visual changes. Slight evaporative loss of samples occurred, with evaporation rates dependent on the volatility of the solvent, the open portion sample container cross section, RH (dryness), and airflow near the open top. The evaporation rate at 24°C in dry conditions was approximately 3% per day (24 hr) for xylene, 0.5% per day for kerosene, and negligible for V-Solv™, with the rate being somewhat less in high RH conditions.

A general conclusion for V-Solv™ and kerosene solvents was that day-to-day evaporation is not a large factor, however is a modest factor for xylene. Evaporation represents an ongoing concentrating of the metal components in the solution. It is important to note that the ICP results to follow were not corrected for the evaporative loss component which, in any case, was modest and would impact all element recoveries equally.

Figures 1-3 graphically show ICP data results (% recovery) for "conventional boron V21" and an "alternate supplier's 21-element blend" under parameters of atmospheric condtions and time. The baseline reference was the unexposed, but otherwise identical material. The solvent is indicated in the figure caption.

ICP results for conventional boron V21 had modest differences for all elements across the varied conditions of exposure, except for boron which exhibited drastically different results. Within as little as 24 hours a 75% reduction in the boron measurement (% recovery) was observed, suggesting over a 3% **per hour** loss rate under open, humid conditions! Elements other than boron demonstrated negligible or minimal change according to their specific environmental exposures condition and, assuming +/- 10% range designation for "in control," then other elements remained acceptable.

Note that the xylene samples (Figures 1 and 4) indicated an enhancement effect that can be associated with the modest evaporative loss of solvent that resulted in an apparent across the board increase in concentration. Results shown for kerosene dilution solvent (Figure 2) are similar – boron indicated poor recovery while those for other elements were stable. Kerosene had a much reduced evaporative loss component in the ICP results since the kerosene evaporation rate was low compared to xylene. Figure 3 summarizes short one-day sample exposures in humid conditions in both xylene and kerosene solvents using the alternative commercial supplier's 21-element blend. Boron loss was substantial after one day, and other elements (e.g. Ag, Mo, Pb, and V) were moderately impacted as well – particularly in the kerosene matrix.

In summary, the ICP data suggested that an unacceptably high rate of loss of the boron signal reliably occurred, and other analytes to a lesser degree, for samples left open to the atmosphere in common solvents in humid conditions using some available "state of the art" commercial stock standards.
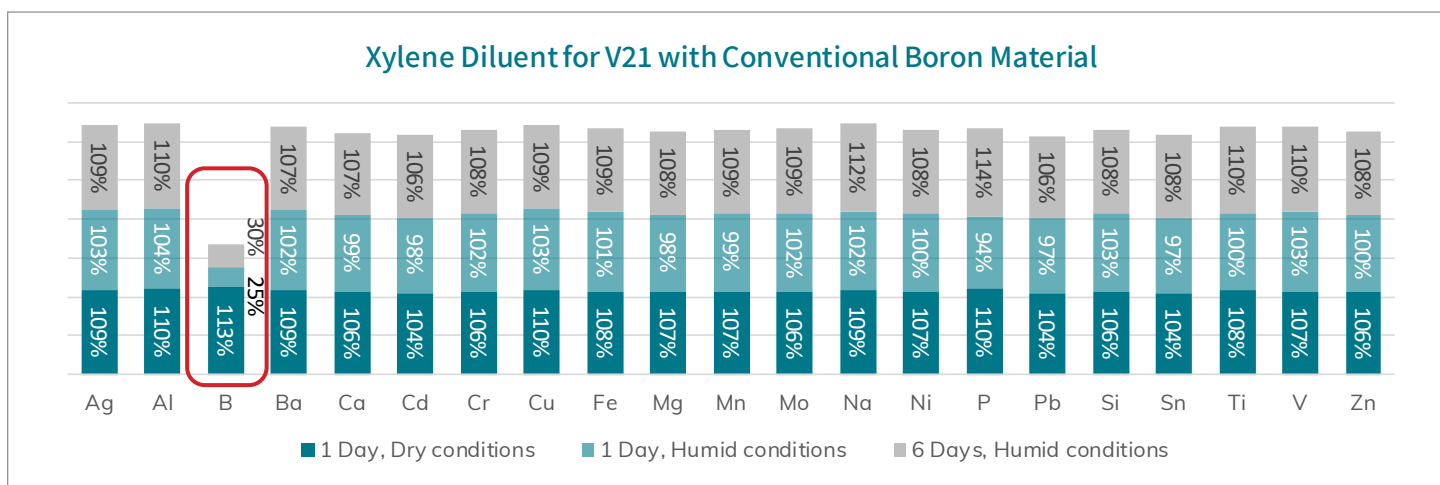

Fig 1. Percent recovery results for samples with open top, atmospheric exposures (xylene diluent)*
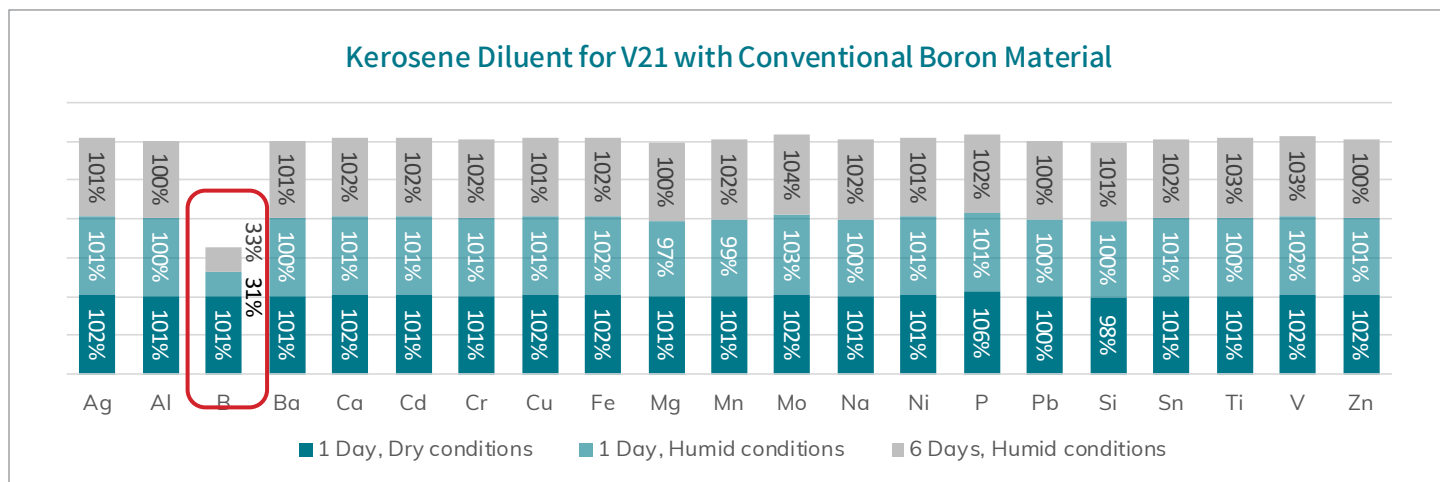*100% +/-10% recoveries with ICP are considered acceptable

Fig 2. Percent recovery results for samples with open top, atmospheric exposures (kerosene diluent)
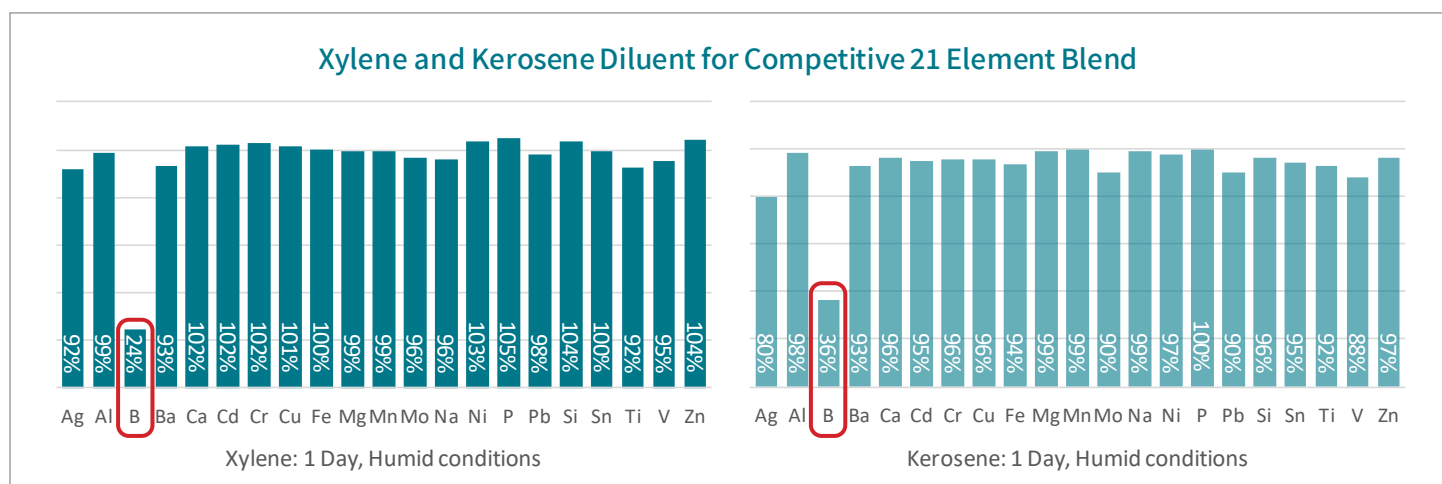
Fig 3. Percent recovery results for samples of an alternate supplier 21 element blend with humid condition, open top, one day atmospheric exposures in both kerosene and xylene matrix

Results in Figures 1-3 augmented by the anecdotal evidence for boron measurement issues by ICP, prompted VHG™ to develop an improved metallo-organic material of boron. The resulting boron material (HI•Boron) was designed to have greater resiliency for open sample tube conditions, especially those of high humidity situations.

Results for open sample exposure tests like those discussed in the previous paragraphs, but utilizing "HI•Boron V21", exhibited improved stability and measurement control for all elements including boron (Figures 4 and 5). After one day of exposure, the average recovery was 102.1% in xylene and kerosene diluent solvents (again, reflecting an evaporative enhancement across the board). In the xylene and kerosene matrices, exposure to humid conditions for six days began to show modest boron measurement loss, even with xylene's moderate evaporative enhancement portion evident for those data. After six days, the boron recovery in kerosene was approximately 88%, while the other elements were within +/- 5% other than silicon with a 108% recovery.

Overall, the data suggested that HI•Boron eliminated the rapid boron loss behavior for typically prepared standards in common solvents, but with longer exposure some issues still could be encountered depending on the environmental situation. Stability of the boron signal may also be impacted by the original purity state and water content of the diluent solvent. Thus, commercial xylene might be expected to have consistent quality; however commercial kerosene and white spirits solvents would likely range in their composition and trace impurities between manufacturer lots. Note that Figures 1-5 indicated that good signal stability was typical for dry, open exposure conditions regardless of the stock standard used.

Xylene Diluent for Advanced V21 with HI•Boron Material

	Ag	Al	B	Ba	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Mo	Na	Ni	P	Pb	Si	Sn	Ti	V	Zn
6 Days, Humid conditions	119%	121%	108%	116%	117%	117%	120%	121%	118%	118%	117%	121%	118%	118%	134%	114%	119%	113%	118%	120%	117%
1 Day, Humid conditions	104%	103%	98%	100%	98%	100%	103%	104%	103%	104%	104%	104%	104%	101%	98%	99%	105%	98%	106%	105%	101%
1 Day, Dry conditions	106%	108%	105%	106%	104%	103%	105%	109%	106%	106%	106%	105%	109%	105%	105%	101%	106%	100%	107%	107%	104%

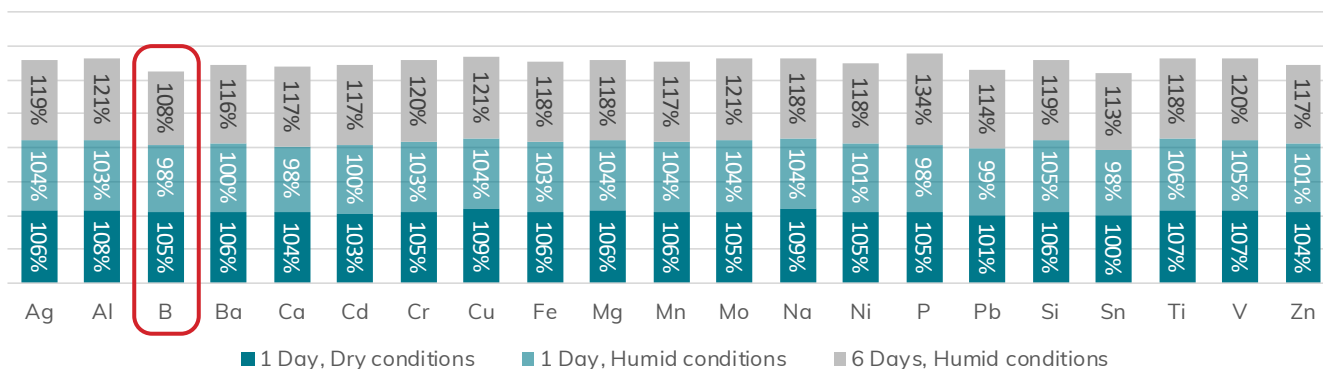■ 1 Day, Dry conditions   ■ 1 Day, Humid conditions   ■ 6 Days, Humid conditions

Fig 4. Percent recovery results for samples with open top, atmospheric exposures of a xylene matrix using the HI•Boron for the boron component

Kerosene Diluent for Advanced V21 with HI•Boron Material

	Ag	Al	B	Ba	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Mo	Na	Ni	P	Pb	Si	Sn	Ti	V	Zn
6 Days, Humid conditions	100%	98%	88%	95%	98%	101%	101%	99%	101%	100%	100%	101%	101%	99%	104%	99%	108%	98%	101%	101%	99%
1 Day, Humid conditions	104%	100%	98%	99%	103%	104%	103%	103%	104%	102%	102%	104%	102%	102%	99%	101%	104%	100%	102%	104%	103%
1 Day, Dry conditions	101%	100%	99%	101%	101%	100%	100%	101%	101%	100%	100%	101%	100%	101%	98%	99%	102%	99%	100%	101%	100%

■ 1 Day, Dry conditions   ■ 1 Day, Humid conditions   ■ 6 Days, Humid conditions
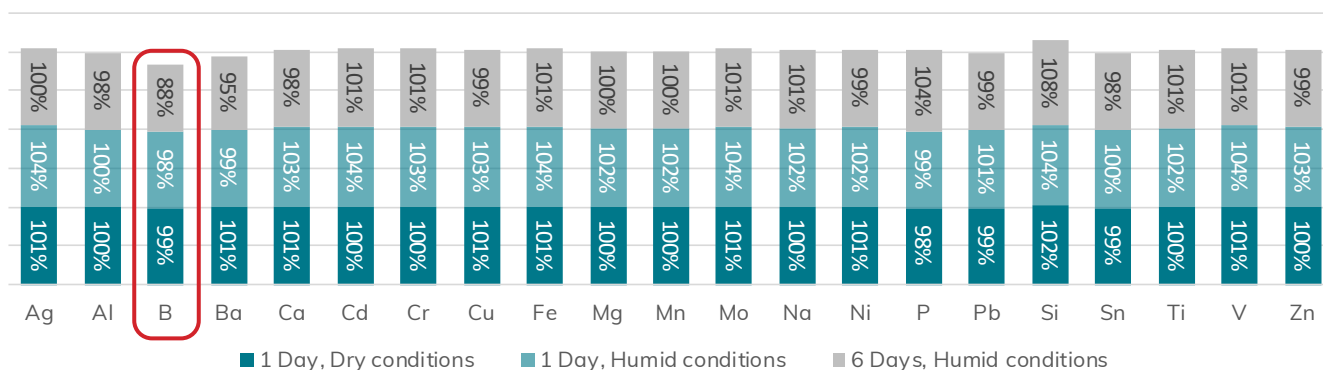
Fig 5. Percent recovery results for samples with open top, atmospheric exposures of a kerosene dilution matrix using HI•Boron for the boron component

While the development of the new HI•Boron metallo-organic material made strides towards greater humidity tolerance, a tandem approach utilizing a better solvent was also evaluated (Fig. 6 and 7). With VHG™ V-Solv™ as the diluent solvent for the stock standard, problems with rapid loss or even low recovery of boron were absent (< +/- 3%); hence V-Solv™ behaved as a solvent tolerant of warm, high humidity conditions for open and exposed samples and working standards (Figure 7). A portion of this performance is due to the low evaporation rate for V-Solv™ ,which is negligible under these conditions, as a source of bias in the ICP measurement.
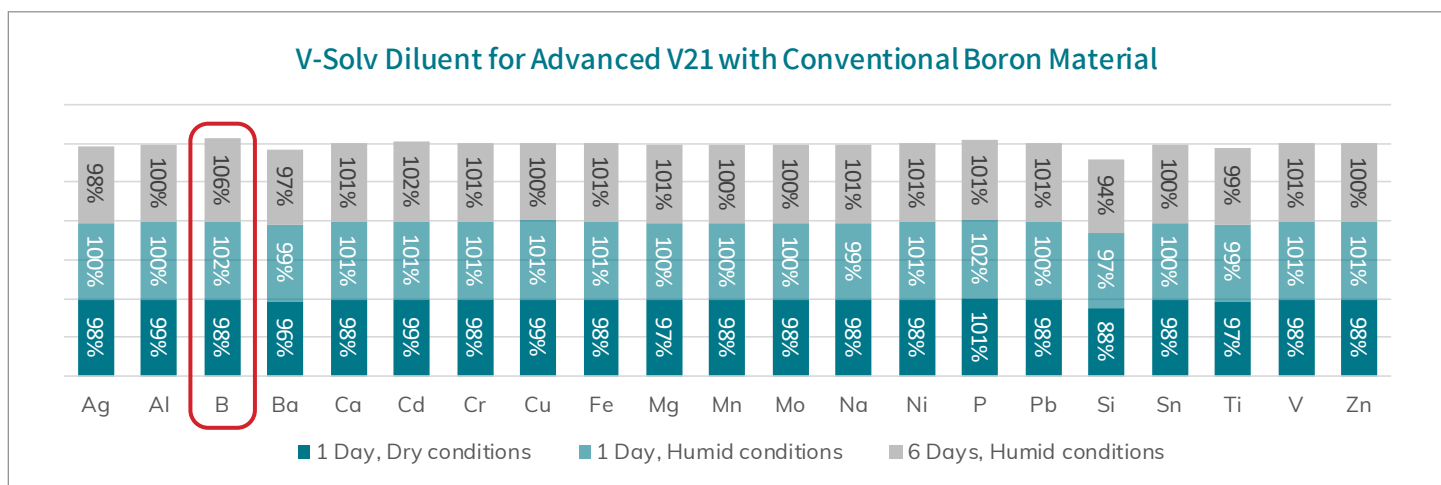

Fig 6. Percent recovery results for samples with open top, atmospheric exposures of a V-Solv™ matrix using "conventional boron" for the boron component
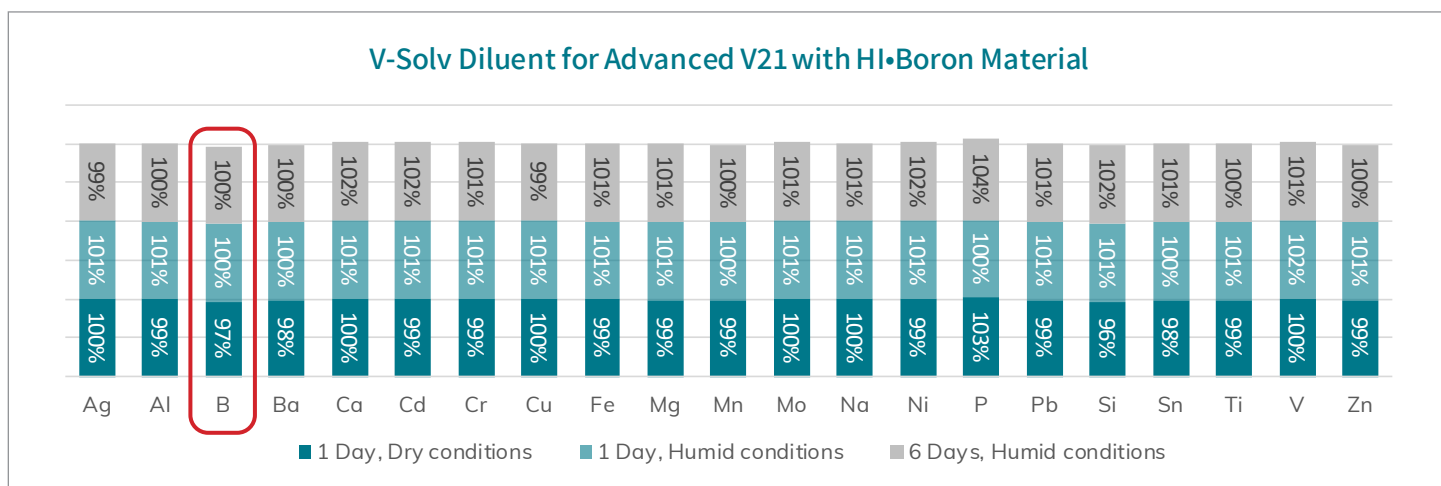

Fig 7. Percent recovery results for 10 µg/g samples with open top, atmospheric exposures of a V-Solv™ matrix using HI•Boron for the boron component

Summary

Dry-air exposed samples did not experience degradation in the signal recovery either for boron or other elements. However, under humid conditions in particular, boron showed pronounced signal loss for some of the materials and solvents studied. This was unsurprising in that boron had the most widespread reports of ICP signal variability (i.e. instability) compared to other metals. The VHG™ V21 blend made from HI•Boron did not experience the signal reduction exhibited by either the alternative supplier material, or the blend made with a "conventional boron material". Xylene and kerosene behaved similarly, while V-Solv™ ICP Solvent was effective at stabilizing all of the metals under all conditions.

If possible, covered (capped) or dry conditions are preferential for open tubes or containers of metallo-organic working standards, controls, and samples for ICP analysis. Care must also be taken to choose an appropriate solvent and CRM, especially where variance of temperature and humidity can occur.

The impact of holding samples in auto-sampler racks exposed and open to the atmosphere is not limited to important, elemental specific effects as discussed, but also to evaporative effects. These were attributable to the volatility of the solvent, air flow, and exposed cross section. This factor might be seen as an across the board drift in results, but could

Conclusion

As one may see from the data presented, the choice of the Certified Reference Material to be used as a calibration standard is critical to consistent ICP performance. The use of HI•Boron (VHG™) in conjunction with V-Solv™ ICP Solvent as the diluent corrects the stability issues commonly seen with boron and other elements, including silver, molybdenum, lead and vanadium.

As shown, ICP performance may be impacted by the choice of solvent, choice of Certified Reference Materials, environmental exposure, and length of time the CRMs are diluted in the base matrix. All of these actions rely on consistent calibrations of the ICP, otherwise, improper guidance will be suggested to the end user.

The results of improper guidance could cause poor results for the lab and risk to the asset, or operational difficulties for the end user ranging from unnecessary oil changes to overextended oil change intervals, from costly inspection and downtime to asset failure. In all, the guidance that the oil lab provides to the end user is truly dependent on proper ICP performance, and that is heavily reliant on choosing the optimal Certified Reference Materials and diluent matrix.

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