A NEW METHOD FOR TESTING METALS IN OILS: WEAR METALS AND ADDITIVE ELEMENTS IN LUBRICATING OILS

Calibrating with Hybrid Aqueous/ Bio-based Organic Solvent Standards

Abstract

The analysis of wear metals and additive metals in oils by ICP-OES has traditionally depended on the use of organometallic certified reference materials (CRMs). Inorganic Ventures (IV) has developed a new approach to instrument calibration for testing metals in oils using aqueous CRMs diluted in an organic solvent. This new organic solvent, ASOSolv™, provides miscibility for both the inorganic metals standards and the oil samples. Aqueous inorganic Co and Y were added as internal standards to the organic solvent, making the dilution of standards and samples an easy, one-step process. A calibration method using the hybrid aqueous/organic solvent calibration standards was validated by analyzing both traditional organometallic CRMs and NIST SRM 1085c as samples for the lubricating oils. The benefits of using these hybrid aqueous/organic CRMs are discussed; including the ability to analyze for elements in oils that are currently difficult or not possible to test, such as the addition of sulfur to the calibration standards. This method analyzes all the elements prescribed for testing in ASTM methods D5185-18, ICP-OES Method for Metal Testing in Lubricating Oils. Optionally, an oils testing laboratory may continue to use traditional organometallic standards, but substitute this newly developed organic solvent, ASOSolv, as a diluent for standards and samples. ASOSolv offers a cleaner, less hazardous, and more environmentally friendly alternative to traditional organic solvents.

Introduction

The impetus for the development of a new type of certified reference material for metals in oil came from Dr. Paul Gaines, the founder of Inorganic Ventures. Paul was interested in developing wear metal standards using the aqueous, inorganic forms of the metals of interest. Inorganic Ventures has demonstrated that the inorganic forms of the 27 metals of interest, in dilute acid, are certified as stable for 5 years in sealed, unopened TCT™ (Transpiration Control Technology) bags. IV set out to make standards in which the metals in dilute acid would be miscible and stable in an organic solvent. This organic solvent needed to simultaneously dissolve the wear metals samples that are in a motor oil and allow the aqueous standards to be miscible. The common organic solvents that are traditionally used in this type of testing are quite toxic. Inorganic Ventures also sought to find a solvent that would be less hazardous for the analyst and the greater ecology.

Method Development

Many trials were needed to find a solvent that fit the stated requirements. This organic solvent is primarily made from green and sustainable resources. Having a solvent that is primarily sourced from greener and less hazardous materials helps push forward on increased environmental sustainability efforts.

Two metal concentrates in dilute acid are used for the two sets of calibration standards. These concentrates contain 1000 µg/mL of each element with the density recorded for the solutions. The first element concentrate is in a 10% v/v HNO_3 matrix. The second concentrate contains the elements that traditionally require HF for stability. The matrix of this concentrate is 20% v/v HCl / 0.6% v/v HF (**Figure 1**). After dilution, the highest concentration of HF in the working calibration standards is 0.03% v/v HF.

10% v/v HNO_3 Standard Concentrate	Analyte
1	Ag
2	Al
3	B
4	Ba
5	Bi
6	Ca
7	Cd
8	Cr
9	Cu
10	Fe
11	In
12	K
13	Li
14	Mg
15	Mn
16	Na
17	Ni
18	P
19	PB
20	S
21	V
22	Zn

20% v/v HCl / 0.6% v/v HF Standard Concentrate	Analyte
1	Mo
2	Sb
3	Si
4	Sn
5	Ti

Figure 1. *Elements in the HNO_3 and HCl concentrated standards.*

Each batch of the organic solvent, ASOSolv, is tested for trace metallic impurities. The solvent is accepted for use only if it is free from these elemental impurities. Aqueous, inorganic forms of cobalt (Co) and yttrium (Y) are used as the internal standards (IS) for this method. These IS elements are commonly used in the traditional ICP-OES testing methods for metals in oil. Inorganic Co and Y IS have been added to the organic solvent, which allows for easy preparation of the working calibration standards and dilution of samples.

There are two sets of calibration standards used in this method. One is made from the 10% v/v HNO_3 concentrate, and the other from the 20% v/v HCl / 0.6% v/v HF concentrate. Each set contains six calibration standards: 0, 1, 5, 10, 20, and 50 µg/g solutions of the metals. Metals testing laboratories may choose to use fewer than 6 calibration standards, e.g., 0, 5, 10 and 50 µg/g standards are commonly used. The matrix of the calibration standards is 1:10 w/w aqueous to organic solvent ratio. The two sets of working calibration standards contain 1% v/v HNO_3 and 2% v/v HCl, respectively.

The calibration standards may be prepared either by diluting the 1000 µg/mL aqueous concentrates to each of the required working concentrations, or diluting 10x aqueous concentrates of each calibration standard to the working standard concentrations. IV would suggest the easier preparation method of making 1:10 w/w dilutions of the 10x aqueous concentrates in ASOSolv organic solvent containing the cobalt and yttrium internal standards (**Figure 2**). This method replicates the procedure observed in wear metals testing laboratories.

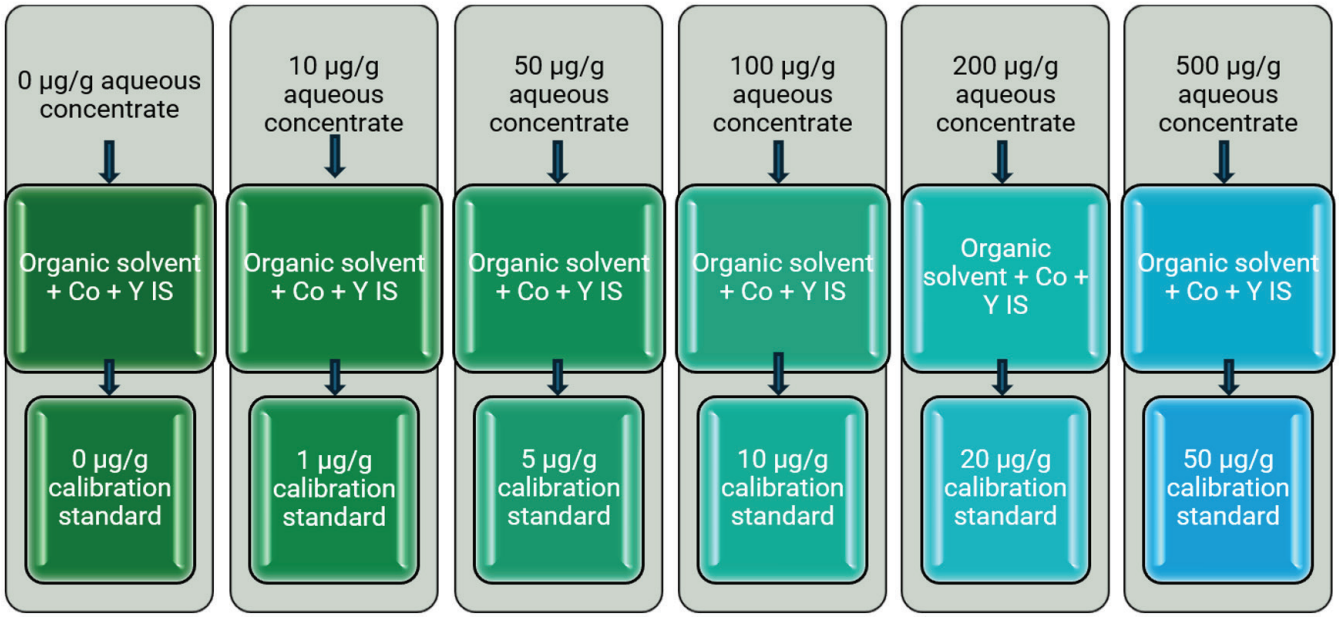

Figure 2. *Calibration standard preparation using 10x aqueous metals concentrates*

Oils testing laboratories often make volume to volume dilutions of samples. Because the density of the ASOSolv organic solvent is similar to the density of the oil samples, it is acceptable to dilute samples either by weight or by volume.

The standard sets contains a total of 27 elements. Sulfur is included in the HNO_3 standard. It has not been possible to test for sulfur using the traditional organometallic standards because the organometallic starting materials are commonly alkyl aryl sulfonates, which add large amounts of unquantified sulfur to the standards.

Inorganic Ventures has confirmed that it is possible to add the inorganic forms of Co and Y as internal standards directly to the ASOSolv organic solvent. The inorganic Co and Y are miscible and stable, with ongoing studies to determine the long-term stability of the solution. Having the internal standards in the ASOSolv organic solvent allows for ease of dilution when making the standards and the sample dilutions. The Co and Y internal standards are diluted to 15 µg/g Co and 5 µg/g Y in the calibration standards. In our experiments oil samples were diluted 1:10 w/w directly with the organic solvent + Co and Y. Industrial labs often use volume to volume dilutions, but as a standards manufacturer we prefer to make dilutions by weight because gravimetric preparation is more accurate.

Testing the Hybrid Aqueous/ Organic Solvent Standards

The Spectro Arcos III ICP-OES in radial mode was used for testing our standards. Solva Flex tubing was used for the sample and drain lines along with a Twister (baffled) cyclonic spray chamber, quartz torch, and the Guardian autosampler probe by Glass Expansion. Two different nebulizers were used. First, the Texas Scientific Products OptiMist Ultimate nebulizer (**Figure 3**), made from Ultem® plastic, making it HF resistant. Second, the Glass Expansion, Slurry nebulizer (**Figure 4**), a concentric nebulizer made from borosilicate glass. Both nebulizers are marketed to allow for the analysis of samples containing large particles. Excellent RSDs were achieved by both nebulizers, where results mostly ranged from < 0.2% to approximately 1% RSD. The % RSDs for the real-world wear metals samples were also very good, with most lines having < 1% RSD for samples run at 1:10 w/w dilutions. The torch was free from carbon buildup when running the hybrid aqueous/organic solvent calibration standards or samples made from organometallic standards. The instrument measure conditions are shown in **Figure 5**. The coolant and auxiliary Ar gas flow rates were set to what is commonly used for oils testing. The nebulizer flow rate of 0.9 L/min is the suggested optimal gas flow for the OptiMist Ultimate, and 0.8 L/min for the Slurry nebulizer.

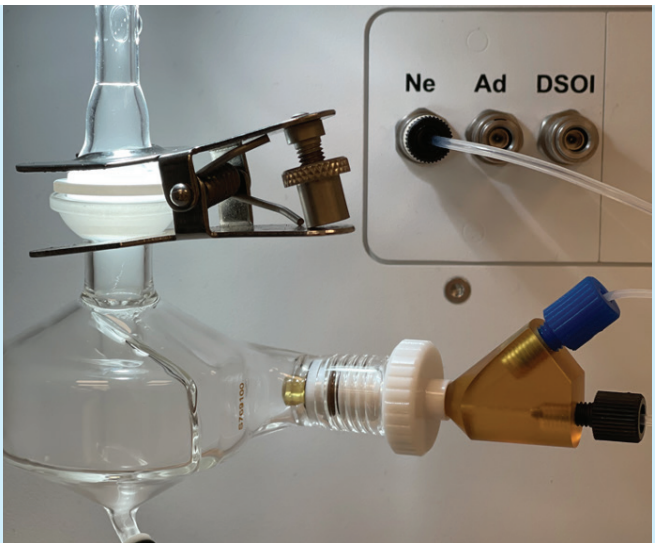

Figure 3. *OptiMist Ultimate nebulizer*

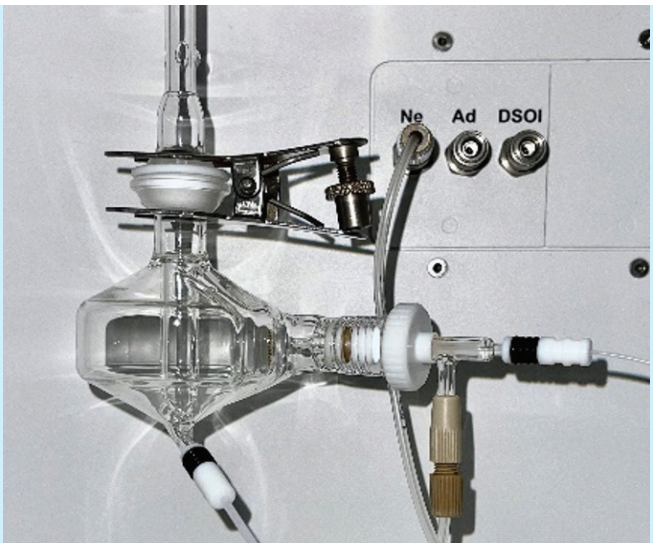

Figure 4. *Slurry nebulizer*

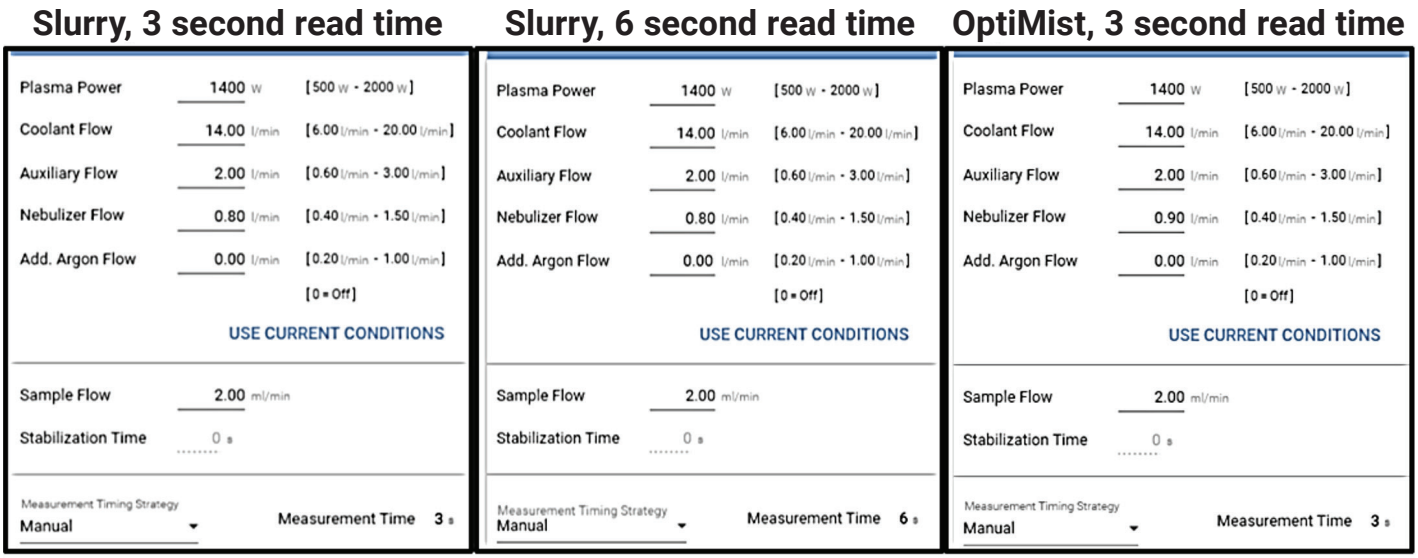

Figure 5. *Instrument measure conditions*

The read time was minimized for standards and samples to 3 sec, for a 60 sec total time / sample. An alternative 6 sec sample read time, with 75 sec total time / sample was also tested. The 6 sec read time results were marginally better than 3 sec read time results. Oils testing labs, for example, may have a total time / sample of 1 minute 30 seconds, with some labs having a much lower sample run time. The extremely high sample throughput of these oils testing labs, where hundreds of samples are run each day, make fast analysis time a necessity.

A 1 µg/g standard was included in our calibration curves because it is required that some elements, e.g., Al, Cr, Pb and Sn, be detected at concentrations as low as 1 µg/g. This addition allows for more confidence in low concentration results. **Figure 6** shows the 0 µg/g and 1 µg/g standards for Al 394.401 nm and Al 167.078 nm. Please note, Al 167.078 nm is recommended, if available, having a lower background equivalent concentration (BEC) and limit of detection (LOD) than Al 394.401 nm.

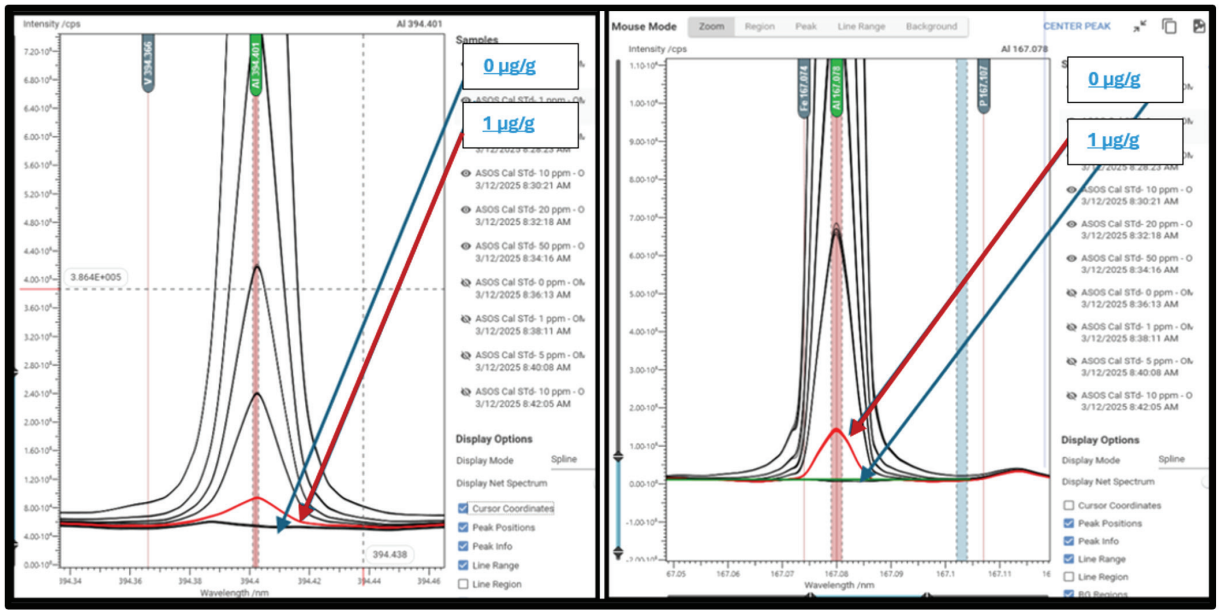

Figure 6. *6.0 µg/g and 1 µg/g standards for Al 394.401 nm and Al 167.078nm.*

To test the aqueous / organic calibration standards 1:10 w/w dilutions were made of several commonly used organometallic oil standards and NIST SRM 1085c, the wear metals in lubricating oil standard reference material. The diluent for all samples was our ASOSolv organic solvent + Co and Y internal standards, with Co and Y at 15 µg/g and 5 µg/g respectively, in the diluted samples.

The organometallic standards from two manufacturers, MFG 1 and MFG 2, were tested:

1) MFG 1 — Sulfur 1000ppm in Hydrocarbon Oil
    a) The organometallic sulfur standard was tested to confirm that sulfur in oils could be testing using the hybrid aqueous / organic standards.
2) MFG 1 — 26 element Wear Metal Standard in oil at 50 µg/g
3) MFG 1 — 26 element Wear Metal Standard in oil at 100 µg/g
4) MFG 1 — Metal Additives in oil (Ba, Ca, Mg, P, Zn at 1000 µg/g)
5) MFG 2 — 21 elements +K+Sb:50 µg/g
6) MFG 2 — 21 elements +Be+K+Li+Sb: 100 µg/g
7) MFG 2 — Metal Additives in oil (Ba, Ca, Mg, P, Zn at 1000 µg/g)

Results

The results presented in **Figures 7, 8, 9,** and **10** were obtained using the Glass Expansion Slurry nebulizer. **Figure 11** presents the results for NIST SRM 1085c, obtained using the TSP OptiMist Ultimate nebulizer.

Best Lines (nm)	Results (µg/g)	Percent Recovery for 50 µg/g organometallic standard certified value	Best Internal Standard (IS) Lines (nm)
Ag 328.068	48.8	97.6%	Co 341.234 / Y 324.228
Al 394.401	50.3	100.6%	Co 341.234
B 208.959	49.9	99.8%	No IS used
Ba 233.527	50.6	101.2%	Co 237.862
Bi 223.061	50.5	101.0%	Y 324.228
Ca 315.887	50.7	101.4%	Co 230.786
Cd 226.502	47.8	95.6%	Co 228.616
Cr 267.716	49.4	98.8%	Co 228.616
Cu 324.754	50.9	101.8%	Co 341.234
Fe 238.204	49.1	98.2%	Co 228.616
In 303.936	50.7	101.4%	Co 304.400
K 766.491	50.4	100.8%	Y 371.030
Li 670.780	50.9	101.8%	Co 304.400
Mg 279.553	50.4	100.8%	Co 238.892
Mn 257.611	49.6	99.2%	Y 324.228
Mo 203.909	50	100.0%	Co 238.892
Na 588.995	49.5	99.0%	Co 304.400
Ni 231.604	49.3	98.6%	Co 228.616
P 178.287	48.7	97.4%	Co 228.616
Pb 405.778	48.6	97.2%	Co 341.234
Sb 231.147	51.1	102.2%	Co 304.400
Si 288.158	49.3	98.6%	Co 304.400
Sn 242.949	50	100.0%	Y 371.030
Ti 334.941	50.1	100.2%	Y 371.030
V 309.311	49.7	99.4%	No IS used
Zn 334.502	49.9	99.8%	No IS used

Figure 7. *Results for 50 µg/g organometallic standard vs. aqueous/organic solvent standards using the Glass Expansion Slurry nebulizer.*

Best Lines (nm)	Results (µg/g)	Percent Recovery for 100 µg/g organometallic standard certified value	Best Internal Standard (IS) Lines (nm)
Ag 328.068	100	100.0%	Co 341.234 / Y 324.228
Al 394.401	101	101.0%	Co 341.234
B 208.959	100	100.0%	No IS used
Ba 233.527	102	102.0%	Co 237.862
Bi 223.061	101	101.0%	Y 324.228
Ca 315.887	102	102.0%	Co 230.786
Cd 226.502	96	96.0%	Co 228.616
Cr 267.716	99.9	99.9%	Co 228.616
Cu 324.754	102	102.0%	Co 341.234
Fe 239.562	100	100.0%	Co 228.616
In 303.936	101	101.0%	Co 304.400
K 766.491	101	101.0%	Y 371.030
Li 670.780	103	103.0%	Co 304.400
Mg 279.553	102	102.0%	Co 238.892
Mn 257.611	98.8	98.8%	Y 324.228
Mo 203.909	102	102.0%	Co 238.892
Na 588.995	101	101.0%	Co 304.400
Ni 231.604	98.2	98.2%	Co 228.616
P 178.287	98.1	98.1%	Co 228.616
Pb 405.778	98.4	98.4%	Co 341.234
Sb 231.147	101	101.0%	Co 304.400
Si 288.158	98	98.0%	Co 304.400
Sn 242.949	101	101.0%	Y 371.030
Ti 334.941	100	100.0%	Y 371.030
V 309.311	98.7	98.7%	No IS used
Zn 334.502	99.6	99.6%	No IS used

Figure 8. *Results for 100 µg/g organometallic standard vs. aqueous/organic solvent standards using the Glass Expansion Slurry nebulizer.*

Best Lines (nm)	Results (µg/g)	Percent recovery for 1000 µg/g organometallic Metal Additives certified value	Best Internal Standard (IS) Lines (nm)
Ba 233.527	990	99.0%	Co 237.862
Ca 315.887	1015	101.5%	Co 230.786
Mg 285.213	992	99.2%	Co 238.892
P 178.287	997	99.7%	Co 228.616
Zn 334.502	1030	103.0%	No IS used

Figure 9. *Results for 1000 µg/g metal additives organometallic standard vs. aqueous/organic solvent standards using the Glass Expansion Slurry nebulizer.*

Best Lines (nm)	Results (µg/g)	Percent recovery for 1000 µg/g organometallic Sulfur standard certified value	Best Internal Standard (IS) Lines (nm)
Sa 182.034	997	99.7%	Co 228.616

Figure 10. *Results for 1000 µg/g sulfur organometallic standard vs. aqueous/organic solvent standards using the Glass Expansion Slurry nebulizer.*

Best Lines (nm)	Results NIST SRM 1085c (mg/kg)	NIST SRM 1085c Certified Values (mg/kg)	NIST reported 95% Coverage Interval (mg/kg)	Percent Recovery NIST SRM 1085c Certified Values (mg/kg)
Ag 328.068	292	298	290–309	98.0%
Al 167.078	292	292	264–321	100.0%
B 182.641	311	304	301–308	102.3%
Ba 230.424	301	306	296–317	98.4%
Ca 315.887	302	299	269–330	101.0%
Cd 226.502	295	301	291–310	98.0%
Cr 267.716	305	302	289–314	101.0%
Cu 324.754	298	298	28310	100.0%
Fe 238.204	315	301	298–313	104.7%
K 766.491	282	295	282–309	95.6%
Mg 285.213	294	300	294–305	98.0%
Mn 257.611	298	299	289–311	99.7%
Mo 203.909	309	305	295–316	101.3%
Na 589.592	293	300	289–310	97.7%
Ni 231.604	299	306	295–316	97.7%
P 213.618	302	304	302–307	99.3%
Pb 220.353	308	303	294–312	101.7%
Si 288.158	297	293	288–297	101.4%
Sn 189.991	292	298	291–306	98.0%
Ti 334.187	299	300	288–311	99.7%
V 292.464	291	285	278–291	102.1%
Zn 334.502	281	285	273–296	98.6%

Figure 11. *Results for NIST SRM 1085c using the TSP OptiMist Ultimate nebulizer.*

Discussion

The organometallic standards tested vs. our hybrid aqueous / organic calibration standards yielded results that were largely within 2% of the element certified values. These results demonstrate the ability to use the organic solvent, ASOSolv with internal standards, as an excellent diluent for traditional organometallic standards and oil samples.

The ASOSolv organic solvent + Co and Y IS ensures ease of standard and sample preparation. The commonly used 1:10 dilution of sample to diluent was applied for all of the samples analyzed. Switching to the aqueous / organic standards could be done with minimal disruption to an oil testing laboratory's routine. The results presented showed that very short sample run times could be used to achieve accurate results with excellent reproducibility.

Our organic solvent, ASOSolv, was observed to be excellent for cleaning the glass / quartz ICP-OES introductory system and washing out residuals oils. No carbon buildup was observed on the torch injector while testing the organometallic standards vs. the aqueous / organic solvent calibration standards.

Conclusions

Inorganic Ventures has demonstrated that it is possible to make hybrid aqueous / organic solvent standards for the testing of wear and additive metals in oils. The stability of the aqueous standard concentrates is documented for up to five years when stored in TCT bags. The ASOSolv organic solvent that was developed is primarily sourced from green and sustainable materials, with lower health hazards than traditional solvents currently used in oils testing laboratories. The analysis of traditional organometallic standards as samples vs. the hybrid aqueous / organic solvent standards confirmed the accuracy of the hybrid standards. The sample preparation method for using the hybrid aqueous / organic solvent standards was demonstrated to be the same as the method using traditional organometallic standards, ensuring an easy transition from traditional standards. This method analyzes all the elements prescribed for testing in ASTM methods D5185-18 and D6595-16 plus several other elements. If a laboratory wishes to continue to use the traditional organometallic standards this organic solvent, ASOSolv with internal standards may be used as a diluent for those standards and samples while offering a cleaner, more environmentally friendly solvent.

– Madeline Gozzi

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