

Comparing Disposable Sensor ASV to ICP-MS for Lead in Water Analysis

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Introduction

For over 20 years¹ Palintest has provided US EPA approved disposable anodic stripping voltammetry (DS-ASV) sensors for rapid analysis of lead in water. Palintest's easy to use technique combines the high selectivity associated with ASV with the maintenance-free and calibration-free benefits of single use disposable sensors. As the only fully approved² field test kit capable of measuring lead in drinking water, disposable sensors give accurate on-site results in 3 minutes down to 2 parts per billion (ppb).

During the original EPA review of the disposable sensor technology, the benchmark laboratory technique was GF-AAS (Graphite Furnace Atomic Absorption Spectroscopy). Palintest's sensor technology was approved based on its equivalent performance to GF-AAS on known standards, real world drinking water samples and spiked drinking water samples³.

In recent years, inductively coupled plasma mass spectrometry (ICP-MS) has taken over as the standard laboratory technology. ICP-MS offers significantly lower detection limits than previously possible, as well as allowing for increased analytical flexibility and higher sample throughput⁴.

So how does Palintest's sensor technology compare to this new standard?

DS-ASV, GF-AAS and ICP-MS

There are distinct benefits and drawbacks between ICP-MS and GF-AAS as dedicated laboratory instruments. When considering them solely as a tool to benchmark the performance of DS-ASV however, both methods remain equivalent.

For example, both ICP-MS and GF-AAS, have sub-ppb detection limits and greater resolution than Palintest's DS-ASV technology. As such, ICP-MS' improved detection limit over GF-AAS does not make it a better benchmarking tool considering DS-ASV has a method detection limit (MDL) of 2 ppb.

Additionally, DS-ASV and ICP-MS do not report routine matrix interferences for the analysis of lead in drinking water^{5,6}. While broadband spectral interference can occur in GF-AAS, trained operators can easily overcome such interferences through background correction devices⁷.

Therefore, both laboratory methods remain valid benchmarks, even today. The correlation between DS-ASV and ICP-MS should not be significantly different than the correlation between DS-ASV and GF-AAS over the range of 2-100 ppb.

This is demonstrated from two separate sources. Figure 1 is a reproduction of data published comparing DS-ASV to ICP-MS on real world drinking water samples collected in 2012 in

¹ US EPA Method 1001 was originally Approved on December 1st 1999

² US EPA Approved for monitoring lead in drinking water

³ Please contact Palintest USA for a full copy of our Three Laboratory Study submitted to the US EPA

⁴ AAS, GFAAS, ICP or ICP-MS? Which technique should I use? An elementary overview of elemental analysis, Thermo Elemental, 2001

⁵ US EPA Method 1001, Section 4

⁶ US EPA Method 200.8, Section 4

⁷ US EPA Method 200.9, Section 4

Montreal, QC⁸. Figure 2 compares DS-ASV to GF-AAS on real world drinking water samples from two independent laboratories used as part of the original EPA method approval submission³.

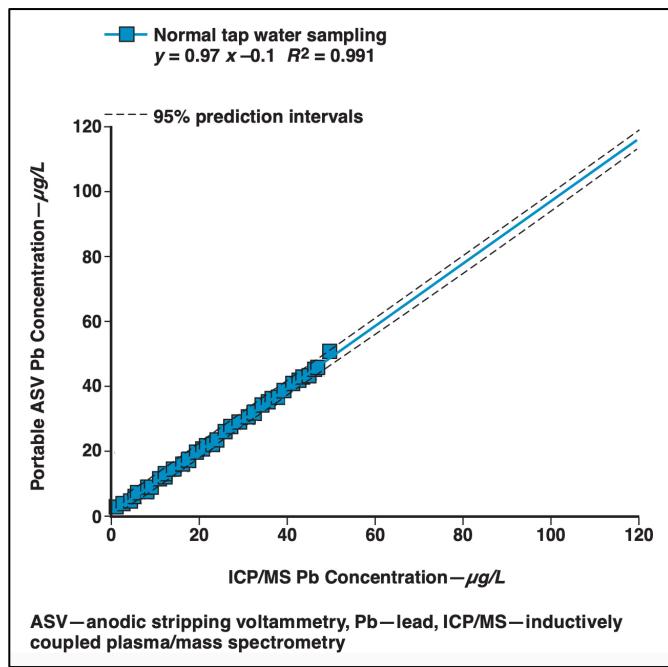


Figure 1, Modified reproduction of data from Cartier et al⁸ showing DS-ASV compared to ICP-MS on drinking water samples. n=89. Unmodified version shown in figure 3.

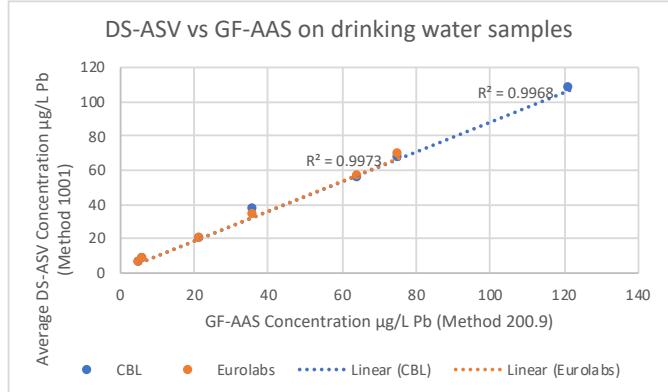


Figure 2, DS-ASV vs GF-AAS from CBL and Eurolabs studies, 1996³

Both the ICP-MS and GF-AAS benchmarking data above show good correlation to DS-ASV testing. It is important to remember that meaningful comparisons can only be drawn when analyzing the same forms of lead compounds between both methods.

Dissolved and Particulate Lead

Palintest's DS-ASV technology is approved for dissolved lead and, with acid digestion, total recoverable lead in drinking water. When performing an in-field analysis however, it can be difficult to safely and practically perform an acid digestion.

Being able to test in-field has numerous benefits, being often cheaper than expedited laboratory testing and returning a result within minutes without requiring highly trained operators. This allows more fixtures and distribution points to be tested and action taken more quickly for those flagged as dangerous.

Where a drinking water system has an elevated level of particulate lead, but digestion is not performed for in-field analysis, results from field testing can be lower than samples sent to a laboratory and digested.

As a fully approved method, DS-ASV can be used in a laboratory setting to replace or free capacity on traditional multi-parameter instruments like ICP-MS for compliance reporting. In this setting, where digestions can be routinely and safely performed, particulate lead will be solubilized and included in the result.

Understanding when and how particulate lead will be present can help to mitigate the likelihood of under-reporting potentially dangerous levels of lead when in-field digestions are not performed.

Arguably the worst-case scenario would be a sample containing high levels of particulate lead but low levels of dissolved lead. This is most likely to occur when corrosion control of the water is good, but lead containing scale or sediments from pipes or fixtures is not durable⁹. A disturbance or shock event, such as pipe work or even elevated flow rates, could agitate lead containing scale and cause distribution into the water supply which may not be detected by a dissolved lead test.

An example of this relationship is reported in Cartier et al⁸ and is shown below in Figure 3.

⁸ Cartier, C., Bannier, A., Pirog, M., Nour, S. and Prévost, M. (2012), A rapid method for lead service line detection. Journal - American Water Works Association, 104, E596-E607. dx.doi.org/10.5942/jawwa.2012.104.0143

⁹ Clark, B., Masters, S., Edwards, M. (2014), Profile sampling to characterize particulate lead risks in potable water. Environ. Sci. Technol., 48, 6836–6843. dx.doi.org/10.1021/es501342j

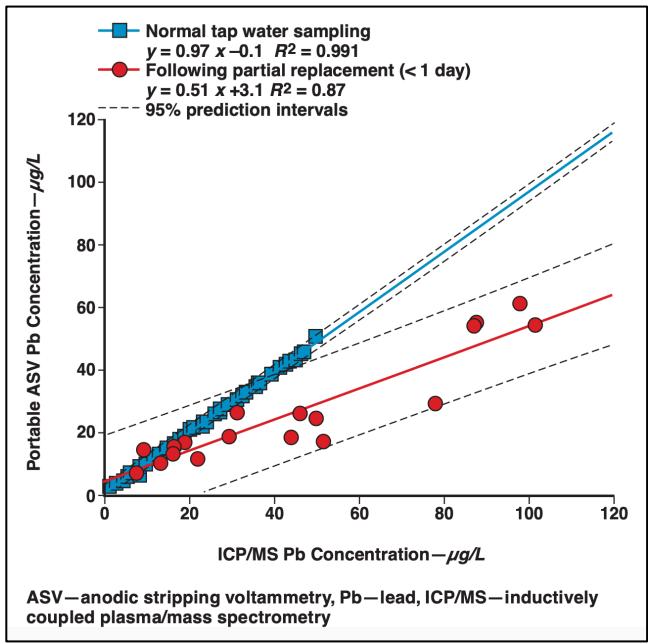


Figure 3, DS-ASV without digestion vs ICP-MS before and after a disturbance event. Reproduction from Cartier et al⁸

Figure 3 shows that after partial replacement of the lead service line, DS-ASV begins to under-report lead concentrations compared to ICP-MS. The authors attribute this to the replacement of the pipe causing a scale or sediment release event, temporarily increasing the concentration of particulate lead in the system. Similar trends have also been reported in other field-testing comparisons¹⁰.

The challenges with such a scenario are not limited to field testing. Lead releasing events can be sporadic, and the particulates may rapidly settle, making it difficult to collect a truly homogenous sample. These factors could contribute to under reporting in both lab and field testing, even with digestion.

Additional factors that can lead to significant under-reporting with laboratory testing include sample collection technique, sample mixing, and transferring the sample between containers¹¹. Immediate on-site field testing can actually eliminate some of these issues.

There are a number of risk factors that can be considered to help anticipate potential under-reporting from non-digested field analyzed samples.

Risk Based Turbidity Limits

Disturbance events that release lead-based scale or sediment are highly likely to also release non-lead containing scale or sediment. Increases in sample turbidity are therefore likely to follow such events.

Some reports suggest when particulate matter is visible to the naked eye, total lead concentrations can be on average 4 times higher than samples with no visible particulates⁹. It follows that using digital instruments that can detect differences in turbidity imperceptible to the naked eye can be an even more useful tool in assessing the risk of particulate lead.

In methods 200.8 and 200.9, the EPA recommends that acid digestion is not needed for samples below 1 NTU in turbidity and that total lead can be read directly. The rationale being that low turbidity is indicative of an overall low number of suspended particulates and therefore there is lower risk of particulate lead.

It is worth noting that samples sent to or received by labs are acidified to pH 2 using nitric acid and held for at least 16 hours. Studies by the EPA¹² and others¹¹ show that unless much stronger levels of nitric acid are used, particulate lead compounds such as lead oxides are not solubilized during this room temperature pH 2 acidification process¹². While weaker bound lead complexes may be solubilized after 16 hours at room temperature and pH 2¹², the DS-ASV methodology includes the addition of a decomplexation agent to release lead from weak-bound complexes such as polyphosphates¹.

It can therefore be concluded that in relation to field testing, the use of a turbidity screening test could be introduced where if samples were above 1 NTU (or other appropriately determined value), they would

¹⁰ McCormick, L., Lovell, S. (2018), Putting children first: Tackling lead in water at child care facilities, Environmental Defense Fund, https://www.edf.org/sites/default/files/edf_child_care_report_01-19.pdf

¹¹ Triantafyllidou, S., Nguyen, C.K., Zhang, Y. and Edwards, M.A. (2013), Lead (Pb) quantification in potable water samples.

Environ Monit. Assess., 185, 1355-1365.
dx.doi.org/10.1007/s10661-012-2637-6

¹² Effectiveness of the Preservation Protocol within EPA Method 200.8 for Soluble and Particulate Lead Recovery in Drinking Water, EPA/600/R-13/222, 2013.

be sent for laboratory analysis irrespective of the field-testing result. This would reduce the likelihood or magnitude of field test underreporting compared to the same sample analyzed at a laboratory (via direct analysis).

Risk Based Action Limits

Another tool that can be implemented to reduce the risks of under-reporting is changing the action limit value that is used in the decision-making process.

After the lead service line replacement in Cartier et al field testing results without digestion under-reported the newly introduced particulate lead⁸. Despite this under reporting, all field results still showed the presence of some lead above the detection limit. Further analysis showed DS-ASV was able to obtain 25-30% recovery of standards prepared entirely from particulate lead *without* digestion. Based on this and a wider pilot study an action limit of 3 ppb was chosen. In real testing, results at or above the 3 ppb action limit for undigested samples predicted the presence of lead service lines to 96% accuracy across 468 sites in Montréal.

When using DS-ASV as a screening tool without digestion, setting a more stringent limit, such as 3 ppb (or other appropriately determined value) could significantly reduce the risk of leaving a potentially harmful water source in service.

Other Factors

Several other factors could be considered to help identify increased potential for particulate lead, including;

- Service line length
- Age and quality of fixtures
- Knowledge of recent pipe or water works
- Knowledge of water pressure or flow rates

Conclusion

DS-ASV shows excellent correlation to both GF-AAS and ICP-MS techniques when comparing like-for-like samples and lead species in real world drinking water samples. DS-ASV shows no routine

matrix interferences and through its disposable sensor technology, eliminates complex maintenance and calibration requirements.

Because DS-ASV can be utilised as both a laboratory and field technique, careful consideration of particulate lead is necessary when screening without digestion. In water with higher turbidity or potential particulate lead issues, the use of field testing via DS-ASV should be thought of as a complimentary tool to laboratory analysis, and not a complete replacement.

Screening techniques enable rapid, low cost testing without the need for highly qualified operators and can dramatically reduce the number of samples that need to go to the lab. This enables lead testing programmes to cover more facilities more economically, and in less time. When field screening is combined with an appropriate protocol based on particulate lead risk factors, resource can be dedicated to where it is needed most.

Although no screening program can guarantee 100% detection of all unsafe lead levels, it must be remembered that significant issues in underreporting persist with laboratory testing too. Understanding the factors leading to elevated lead water levels and *routinely* testing those fixtures with the greatest risk is the only way to ensure ongoing safe water supply.

Finally, in a laboratory setting where digestions can be performed safely, DS-ASV can be used to rapidly analyze fully compliant lead testing samples. When a certified laboratory is performing a large number of lead in drinking water analyses, DS-ASV allows for a substantial increase in analytical capacity without the need for significant capital investment.