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## Analysis of Trace Metals in Organic Solvents Using prepFAST M5, PC<sup>3x</sup> and ICP-OES

**Keywords:** Organic Solvent, Trace Metals, prepFAST M5, Autocalibration, PC<sup>3x</sup>

### Introduction

Metal impurities need to be determined in organic solvents used in pharmaceuticals production, electronics manufacturing, food oil or fat extraction, and many other applications. ICP is an excellent choice for ppb level detection of metals in organic solvents. This note demonstrates a specialized automation and sample introduction system optimized for organic solvents analysis using a sequential ICP detector.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is an effective tool for measuring trace metals. However organic solvents can present problems to the plasma stability due to the vapor loading caused by the volatility of the samples. Using the ESI prepFAST M5 and PC<sup>3x</sup> in combination with an ICP-OES allows for undiluted organic samples to be cooled before the ICP-OES to reduce the vapor loading of the sample. The increased stability resulting from the PC<sup>3x</sup> allows for the accurate analysis of undiluted organic solvents.

The organic samples were syringe loaded, due to viscosity, by the ESI prepFAST M5 into the ESI PC<sup>3x</sup> + ICP-OES. In addition, using the prepFAST M5 allows for autocalibration and inline dilutions which reduce sample handling, leading to increased linearity of calibration curves.

For this study, IPA (isopropyl alcohol, 2-propanol) and ethyl lactate were chosen as the organic solvent for validating the method. The method was calibrated using the autodilution feature, implementing dilution factors of 100x, 40x, 20x, 10x, 2x and 1x. Figures of merit for As, Cu, K, Mn, Na, Ni, Pb, S, Si and Zn are presented here, as well as precision for undiluted IPA and ethyl lactate samples analyzed over a ~5 hour time period.



**Figure 1.** ESI PC<sup>3x</sup> Peltier cooled/heated spray chamber with hydride inlet for Avio 200



## Sample Preparation

A 2 L solution of 2% HNO<sub>3</sub> in IPA was prepared using 99.9% IPA (Kanto Corporation, Portland, Oregon) and used as the carrier/diluent, and preparation of the stock standard and internal standard. The carrier/diluent is used to matrix match the standards and samples throughout all experiments. A stock solution was prepared using 1000 µg/L single element standards of As, Cu, K, Mn, Na, Ni, Pb, S, Si and Zn. The concentrations of the stock standard are listed in Table 1. The internal standard consisted of 1 µg/L Y in the HNO<sub>3</sub>/IPA or HNO<sub>3</sub>/ethyl lactate matrix.

**Table 1.** Concentration levels of stock standards

Stock Standard Concentration (µg/L)	
Element	Concentration
Arsenic	2
Copper	1
Potassium	5
Manganese	1
Sodium	5
Nickel	1
Lead	5
Sulfur	100
Silicon	1
Zinc	1



**Figure 2.** ESI prepFAST M5

## Equipment

A PerkinElmer Avio 200 ICP-OES system was used for all sample analysis. An ESI SC-2 DX autosampler was used to automate the sample uptake. An ESI prepFAST M5 syringe valve assembly was used to autocalibrate and load samples into the ICP-OES instrument. The prepFAST M5 allows for a smoother loading of the sample which avoids cavitation within the lines. A 3 mL sample loop and a 2 mL dilution loop were used to ensure enough of the sample was captured for direct analysis.

An ESI PC<sup>3x</sup> Peltier cooled/heated spray chamber (Fig. 1) was used to increase the stability of the plasma. The PC<sup>3x</sup> incorporates the ESI baffled cyclonic spray chamber and is completely O-ring free making it chemically resistant to organic solvents. The PC<sup>3x</sup> allows for the heating or cooling of the spray chamber to increase the sensitivity or lower the vapor loading of the sample, respectively. The PC<sup>3x</sup> has a working range of -10°C to 80°C. In this case, the PC<sup>3x</sup> was operated at -10°C to decrease vapor loading of the sample and increase stability of the plasma (e.g. flash point of IPA = 13° C). An ESI quartz, baffled cyclonic spray chamber with a hydride inlet was employed. The hydride inlet allows for the addition of oxygen to prevent any carbon buildup during the analysis.

An ESI PFAST3-70 nebulizer was used to produce a fine aerosol for high transport efficiency and high sensitivity. The PFA is also chemically resistant which is ideal for the analysis of organics. A quartz injector (0.8 mm I.D.) was used to produce a stable plasma during direct analysis of undiluted organic solvents. The smaller internal diameter helps restrict the amount of organic sample introduced into the plasma.



**Figure 3.** PerkinElmer Avio 200

## Instrumental Conditions

**Table 2.** Instrumental parameters used during the analysis of undiluted organic solvent

Plasma Conditions	
<b>Spray Chamber</b>	Glass, Baffled Cyclonic with Hydride Inlet
<b>Injector</b>	Quartz, 0.8 mm ID
<b>Nebulizer</b>	ST3-70
<b>Plasma Gas Flowrate</b>	9 L/min
<b>Auxiliary Gas Flowrate</b>	0.5 L/min
<b>Nebulizer Gas Flowrate</b>	0.45 L/min
<b>O<sub>2</sub>/Argon Gas Flowrate</b>	24 mL/min
<b>Power</b>	1500 Watts
<b>Plasma View Mode</b>	Axial
<b>Peristaltic Pump Tubing Settings</b>	Black/Black
<b>Peristaltic Pump Tubing (Carrier)</b>	Orange/Green (Solva)
<b>Replicates</b>	3
<b>Wash Flowrate</b>	2.6 mL/min
<b>Wash Time</b>	83 Seconds
<b>Sample Flowrate</b>	2.6 mL/min
<b>Purge Gas Flow</b>	Normal
<b>Delay Time</b>	170 Seconds
<b>Source Equilibration Delay</b>	15 Seconds
<b>PC<sup>3x</sup> Temperature Set Point</b>	-10°C
<b>Peristaltic Pump</b>	ESI DXi

## Quantification

The calibration curves were produced by autocalibrating the stock standard using dilution factors of 100x, 40x, 20x, 10x, 2x and 1x dilution (1x = undiluted). The autocalibration function is easily set within the Avio 200 software. Yttrium was used as the internal standard and was added to each sample inline using the prepFAST M5 internal standard addition feature.

An example of the autocalibration curves can be found in Figures 4 and 5. All analytes showed excellent linearity over the calibrated range with a calibration coefficient of > 0.999 for each analyte (Table 3).

As, Cu, K, Mn, Na, Ni, Pb, S, Si and Zn were monitored during the analysis. The method integration times are listed in Table 4. The calibration curve results show that the Avio 200 can be successfully used for trace elemental analysis of IPA and ethyl lactate in conjunction with the prepFAST M5, PC<sup>3x</sup> Peltier cooled/heated spray chamber and a SC-2 DX autosampler.

**Table 3.** Calibration coefficients

Element	R <sup>2</sup>	
	Isopropyl Alcohol	Ethyl Lactate
Arsenic	0.9999	0.9999
Copper	0.9993	0.9999
Potassium	0.9998	0.9995
Manganese	0.9999	0.9999
Sodium	0.9991	0.9996
Nickel	0.9997	0.9995
Lead	0.9998	0.9993
Sulfur	0.9999	0.9999
Silicon	0.9996	0.9997
Zinc	0.9999	0.9999

**Table 4.** Elements with the minimum and maximum integration times sorted by wavelength

Element	Element Auto Integration Time		
	Wavelength (nm)	Min Time (s)	Max Time (s)
Arsenic	228.812	4	10
Copper	327.393	4	5
Potassium	766.490	4	10
Manganese	257.610	4	5
Sodium	588.995	4	10
Nickel	231.604	4	10
Lead	220.353	10	10
Sulfur	181.975	5	10
Silicon	251.611	4	10
Zinc	206.200	5	10
Yttrium*	371.029	2	2

\* Yttrium was the internal standard

## Ethyl Lactate

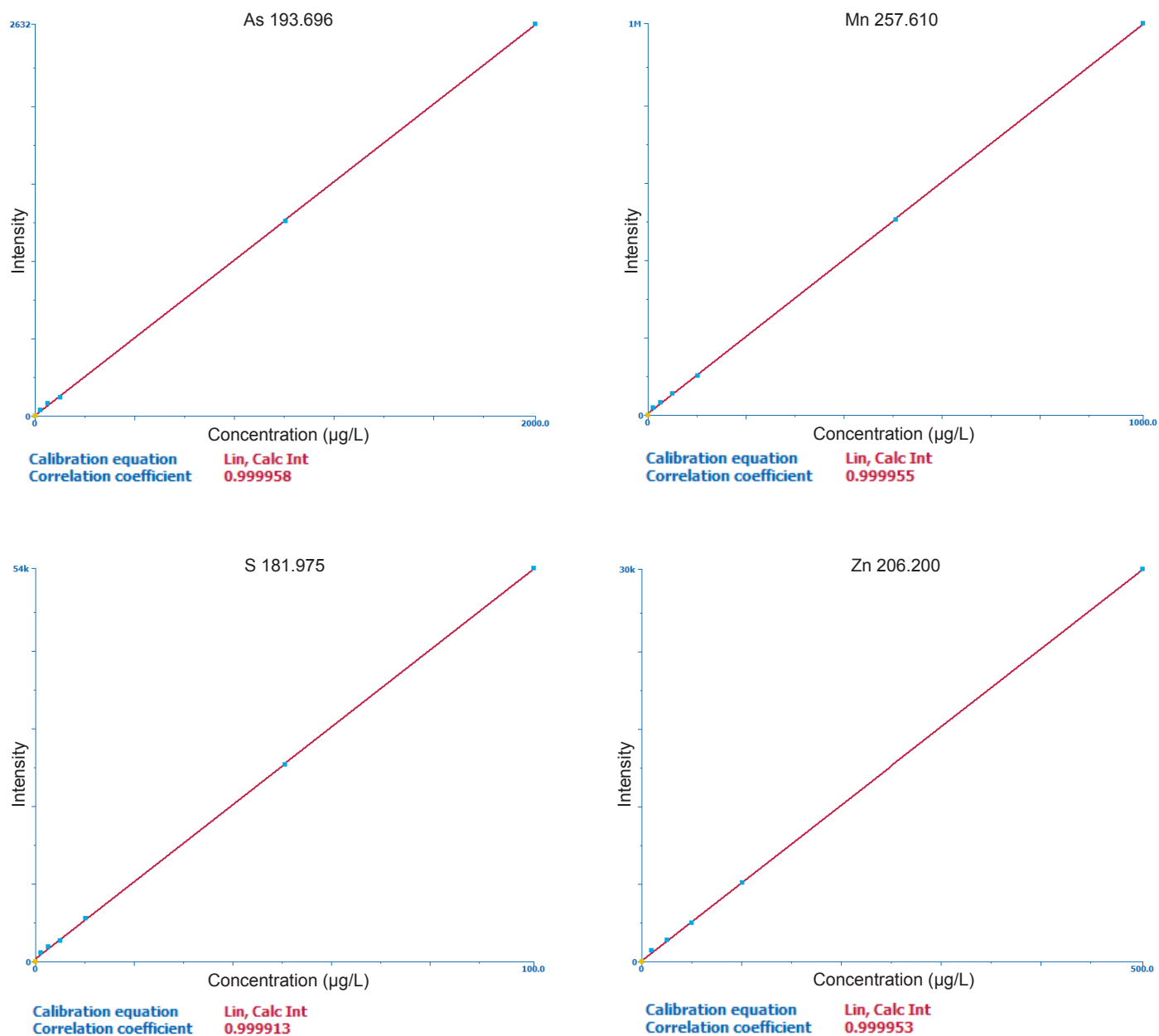


Figure 4. As, Mn, S, and Zn calibration curves for ethyl lactate created using the autocalibration feature (Screen shots captured in Syngistix software)

## Isopropyl Alcohol

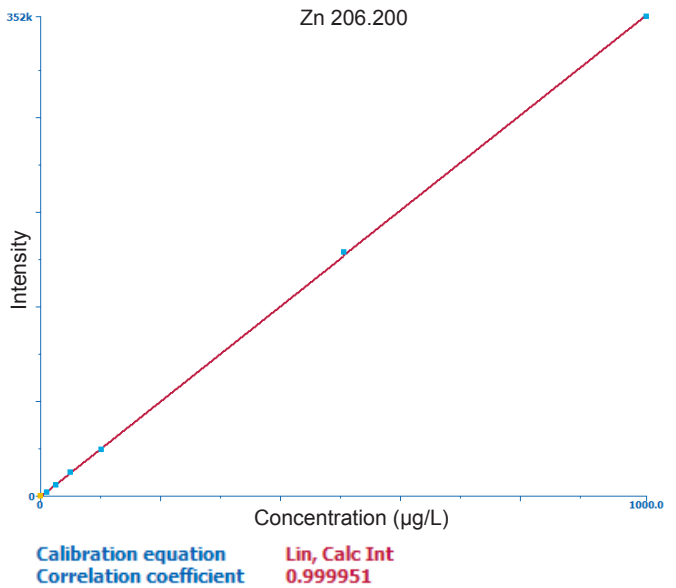
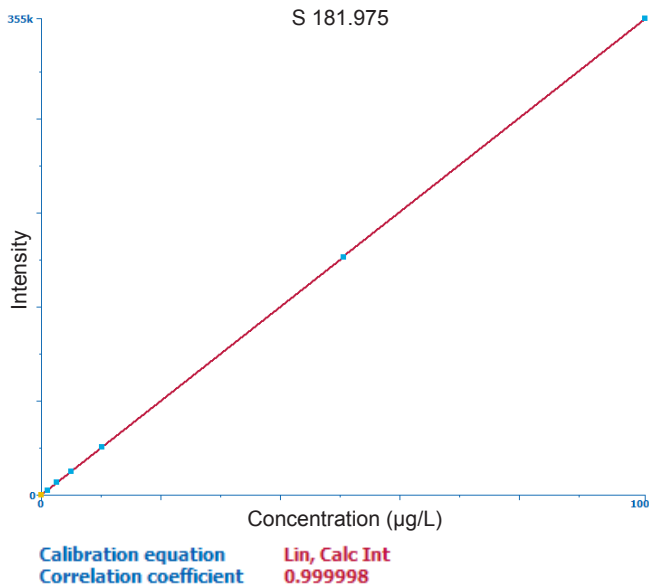
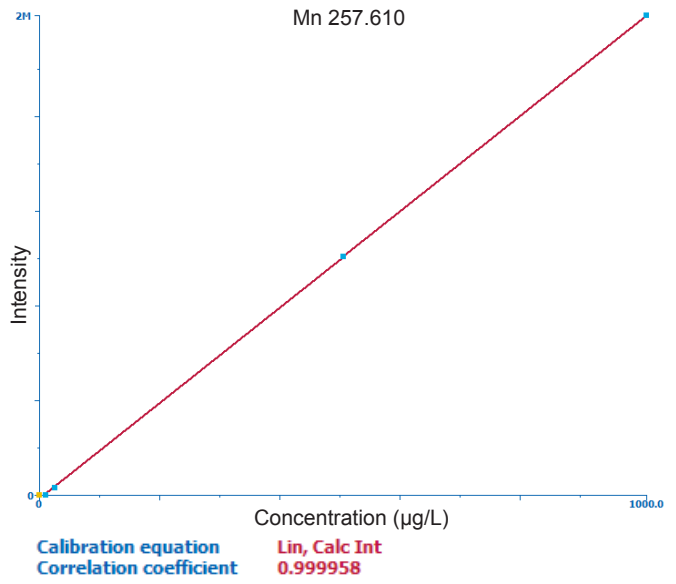
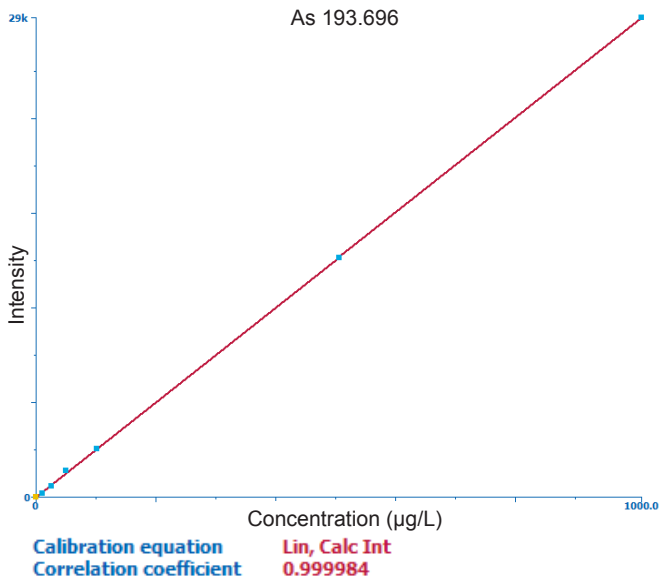


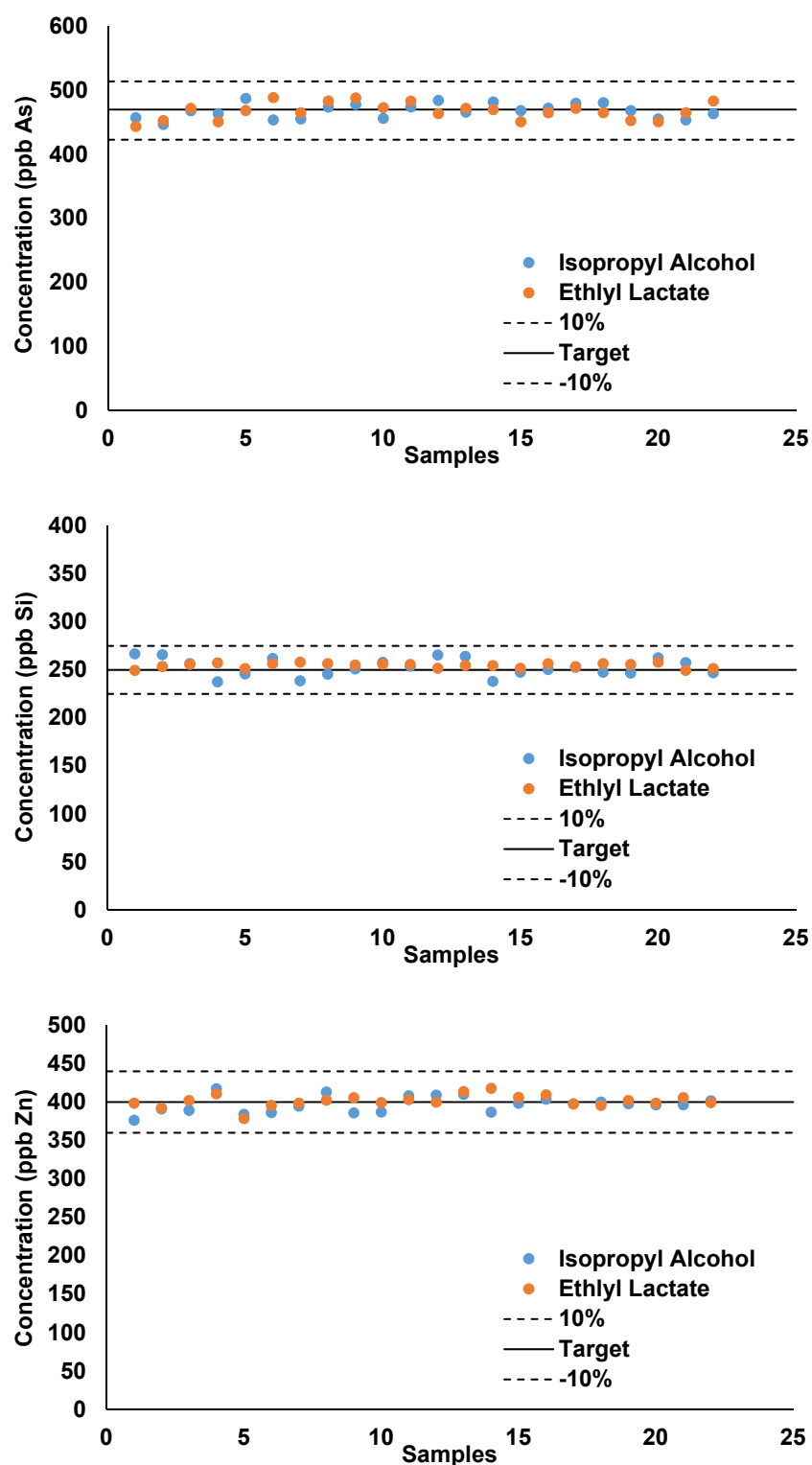
Figure 5. As, Mn, S, and Zn calibration curves for isopropyl alcohol created using the autocalibration feature (Screen shots captured in Syngistix software)

## Precision

In order to show that the stability of the method was indeed improved using the ESI prepFAST M5 and PC<sup>3X</sup> combination, an IPA and ethyl lactate matrix sample was prepared and analyzed over a 5 hour time period (blanks, calibration standards, and samples). Table 5 displays the precision measured over these 20+ undiluted samples. The %RSD measured was < 4% for the IPA and ethyl lactate samples for all elements measured. Figure 6 represents the sample to sample measurement for As, Si, and Zn for both matrices. For As, Si, and Zn in IPA the %BIAS to the expected value was 1.2%, -0.4%, and -0.7%, respectively. As, Si, and Zn in ethyl lactate resulted in a %BIAS of 1.8%, -0.6%, and 0.4%, respectively.

**Figure 6.** Precision for undiluted, spiked isopropyl alcohol and ethyl lactate samples over a typical analytical run (n ≥ 20)

Element	%RSD	
	Isopropyl Alcohol	Ethyl Lactate
As	2.5	2.8
Cu	2.5	2.7
K	3.9	2.2
Mn	2.3	1.3
Na	3.7	2.6
Ni	3.0	2.8
Pb	2.7	3.4
S	3.0	1.9
Si	3.7	1.0
Zn	2.6	2.0



**Figure 7.** Sample results for As, Si and Zn over ~five-hour analytical run with isopropyl alcohol and ethyl lactate

## Detection Limits

The limit of detection (LOD) was determined in both the IPA and ethyl lactate matrices (Table 6). For comparison purposes only, water was used as a matrix under the optimal organic solvent conditions to show the performance compared to a non-organic solvent. The LODs for IPA and ethyl lactate compared reasonably with the water matrix, with only Pb and S resulting in a slightly higher LOD. Please note that the LODs for water do not reflect the best case scenario that could be found when optimizing for water based solvents.

**Figure 8.** Detection and quantification limits for each analyte

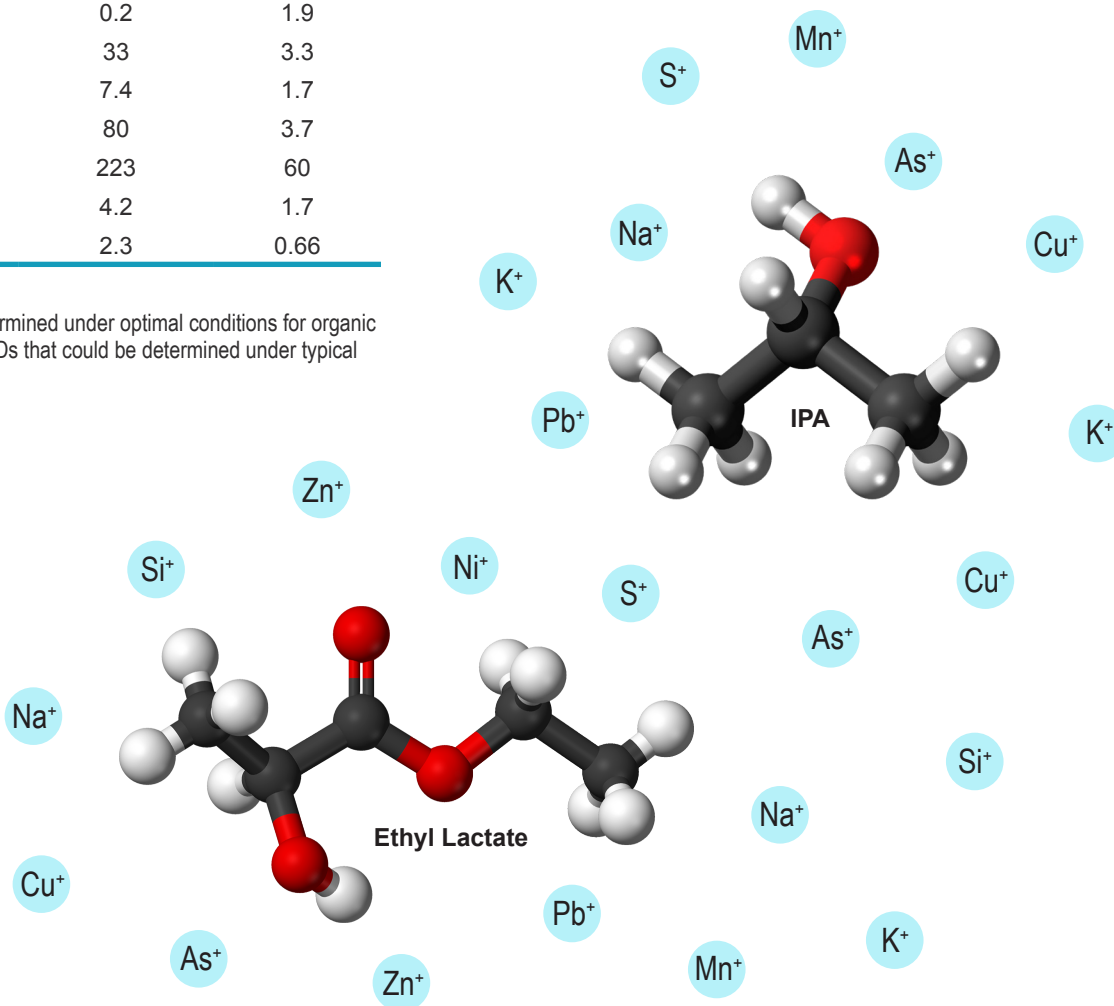
Element	LOD (µg/L)		
	IPA	Ethyl Lactate	Water*
As 193.696	23	8.7	13
Cu 327.393	1.7	0.4	1.1
K 766.490	73	35	20
Mn 257.610	0.5	0.2	1.9
Na 589.592	81	33	3.3
Ni 231.604	14	7.4	1.7
Pb 220.353	56	80	3.7
S 181.975	56	223	60
Si 251.611	8.3	4.2	1.7
Zn 206.200	2.4	2.3	0.66

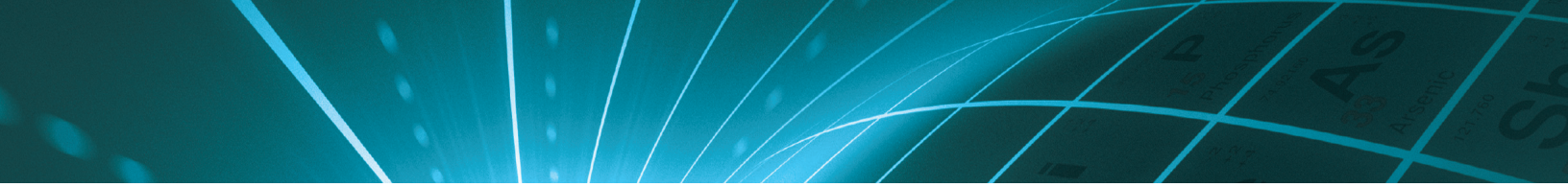
$$\text{LOD} = (3 \times \sigma_{\text{blank}}) / \text{slope}$$

\*Note that these LODs were determined under optimal conditions for organic solvent and do not reflect the LODs that could be determined under typical instrument conditions.

## Conclusions

The data presented here supports that the PerkinElmer Avio 200 can be used successfully for trace elemental analysis of undiluted organic solvents when used in conjunction with the ESI prepFAST M5, PC<sup>3x</sup> Peltier cooled/heated spray chamber, and SC-2 DX autosampler. This setup provided excellent linearity over the calibrated range with calibration coefficients > 0.999 for all analytes. The precision within a given sample was < 3 %RSD and the repeatability of > 20 undiluted organic samples in a single analytical run was < 4 %RSD. Limits of detection for the trace elements measured in this study were in the sub-ppb to ppb range for isopropyl alcohol and ethyl lactate.





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