

Analysis of Heavy Metals in e-Liquids using the Agilent 5110 ICP-OES

Routine method meets requirements of the world's
first quality and safety standards for e-cigarettes



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Introduction

According to the World Health Organization, tobacco is responsible for about seven million deaths a year worldwide (1). Most smokers who are aware of the dangers of tobacco want to stop. An increasing number of people are switching to electronic cigarettes (e-cigarettes), which are seen as a safer alternative to smoking conventional cigarettes. The global market for vapor products is expected to continue its rapid growth. Already by 2014, 466 brands and 7764 flavors of electronic cigarette refill fluids (e-liquids) were commercially available (2). Although e-cigarette vapor doesn't contain the harmful combustion products found in tobacco smoke, questions remain about the long-term impact of vaping on human health.

In May 2016, the European Union's Tobacco Products Directive (2014/40/EU) came into force. The Directive specifies rules on tobacco and related products, including safety, quality, and notification requirements for e-cigarettes (3). Similarly, in August 2016, the US FDA finalized a rule extending its regulatory authority to cover all tobacco products, including e-cigarettes (4).

The French National Organization for Standardization (AFNOR) recently published two voluntary quality and safety standards for e-cigarettes (XP D90-300-1) and e-liquids (XP D90-300-2) (5). In addition to various organic compounds, the AFNOR standard specifies that manufacturers and test laboratories must also determine some heavy metals in e-liquids.

In this study, arsenic, cadmium, mercury, lead, and antimony were determined in two e-liquid samples using ICP-OES. Since variable ratios of propylene glycol (PG), glycerol (VG) and ethanol (EtOH) are typically used in different e-liquid products, all analytical standards were matrix matched. The aim was to develop a reliable method suitable for the routine testing of heavy metals in e-liquids at the concentration levels specified in the AFNOR standard method.

Experimental

Instrumentation

All measurements were performed using an Agilent 5110 Vertical Dual View (VDV) ICP-OES fitted with an SPS 3 autosampler. The sample introduction system consisted of a SeaSpray nebulizer, double-pass glass cyclonic spray chamber, and a standard 1.8 mm ID injector torch. Scandium was used as an internal standard. 1 mg/L of Sc was added manually to each solution to compensate for any variation in the e-liquid matrices arising from different ratios of PG, VG, and EtOH.

All measurements were performed in axial plasma viewing mode, as only trace level elements were of interest. The instrument operating conditions are summarized in Table 1 and the wavelengths selected for the analysis are given in Table 2.

Table 1. Agilent 5110 VDV ICP-OES method and instrument operating parameters.

Parameter	Setting
RF power (kW)	1.2
Aux flow (L/min)	1
Plasma flow (L/min)	12
Nebulizer flow (L/min)	0.7
Pump speed (rpm)	10
Sample pump tubes	PVC, 1.02 mm White/White
Drain pump tubes	PVC, 1.65 mm Blue/Blue
Read time (s)	20
Replicates	3
Sample uptake delay (s)	30 (fast pump)
Stabilization time (s)	20
Rinse time (s)	30 (fast pump)
Autosampler rinse solution	1% HNO ₃ – 1% HCl

Table 2. Wavelengths used in the analysis.

Element	Wavelength (nm)	Background correction
As	193.696	FACT
Cd	226.502	FACT
Hg	253.652	Fitted
Pb	220.353	FACT
Sb	217.582	FACT

FACT background correction

Spectral interferences originating from the carbon present in propylene glycol and glycerol generate an elevated and complex background. Fast automated curve-fitting technique (FACT), which is a spectral deconvolution tool supplied with Agilent's ICP Expert software, was used for background correction. Traditional off-peak background correction cannot effectively determine the background signal under the analyte peak with adequate accuracy or precision.

FACT simplifies method development by eliminating the need to manually determine correction points for all elements. A more accurate measurement of the analyte signal is possible using the software to model the complex background structure due to carbon-emissions. FACT models are easily created, based on the spectra of a blank and analyte.

FACT can lower the quantitation limit of elements present in organic matrices by an order of magnitude, with no increase in analysis time (6).

Standard and sample preparation

A blank solution was prepared by diluting a mix of propylene glycol (48.5%), vegetal glycerin (49.5%), and ethanol (2%) five times with pure water.

Standard solutions containing 1 g/L of arsenic, cadmium, mercury, lead, and antimony were diluted using the blank solution. Matrix matched calibration standards were prepared at 0, 50, 100, 200 µg/L.

The rinse solution comprised 1% HNO₃ and 1% HCl (v/v).

Two different samples received from manufacturers were analyzed in this study. Sample 1 comprised 100% glycerol and sample 2 comprised 50% propylene glycol–50% glycerol. Both e-liquid samples were diluted 5x (v/v) in pure water before analysis.

The samples were spiked with 100 ppb of each analyte to test the recoveries of the five heavy metal elements.

Results and Discussion

Calibration linearity

Table 3 summarizes the calibration standard concentration range and correlation coefficients for all five elements. Correlation coefficients were greater than 0.999 in all cases. Representative calibration curves for As and Hg are shown in Figure 1.

Table 3. Correlation coefficients from linear calibration models.

Element	Wavelength (nm)	Calibration range (µg/L)	Correlation coefficient
As	193.696	0–200	0.99980
Cd	226.502	0–200	0.99999
Hg	253.652	0–200	0.99977
Pb	220.353	0–200	0.99995
Sb	217.582	0–200	0.99979

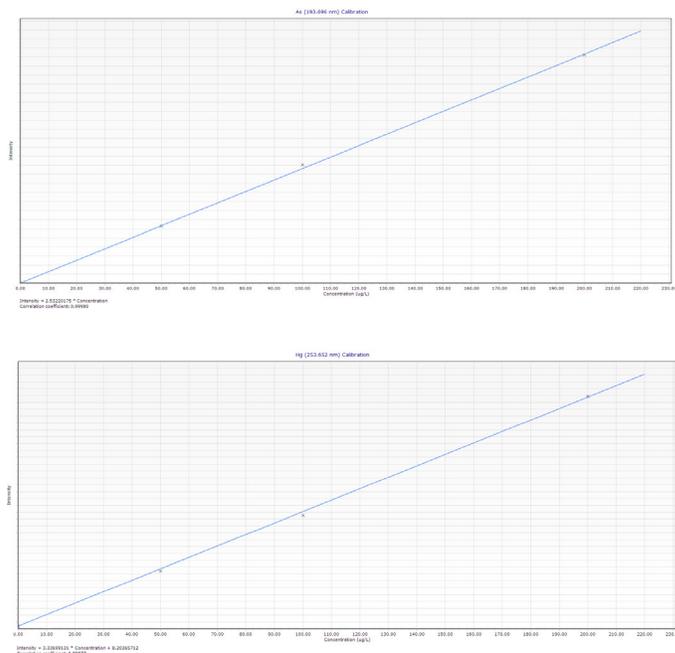


Figure 1. Calibration curves for As 193.696 nm and Hg 253.652 nm, showing excellent linearity across the calibrated range.

Limit of detection and quantification (LOD and LOQ)

Limits of detection (LOD) and limits of quantification (LOQ) of each element were determined based on three and 10 sigma of 10 replicate measurements of the blank solution, respectively.

AFNOR standard method XP D 90-300-2 specifies an upper limit for trace heavy metals in e-liquids, as shown in Table 4. Since the samples were diluted, LOQs in solution are also shown. The LOQs obtained on the 5110 VDV ICP-OES using FACT background correction are all well below the maximum limits specified in the standard method.

Table 4. Comparison of method LOQs for all elements, and specifications for heavy metals in an e-liquid, as outlined in standard method XP D 90-300-2. All units are mg/L (ppm).

Element	Specified maximum concentration in e-liquid	ICP-OES method LOQ in e-liquid	Specified LOQ in 1/5 diluted sample	ICP-OES method LOQ in solution
As	3	0.069	0.6	0.014
Cd	1	0.001	0.2	0.0002
Hg	1	0.051	0.2	0.010
Pb	10	0.032	2	0.006
Sb	5	0.058	1	0.012

Examples of FACT background correction are illustrated in Figure 2 for As, Cd, Pb, and Sb. The different colored peaks show how FACT has deconvoluted the overlapped emission. Blue is the total emission, red is the interference peak, and green is the result of subtracting the interference from the total. For complex matrices, FACT provides lower detection limits, better recoveries, and better precision than other background correction methods.

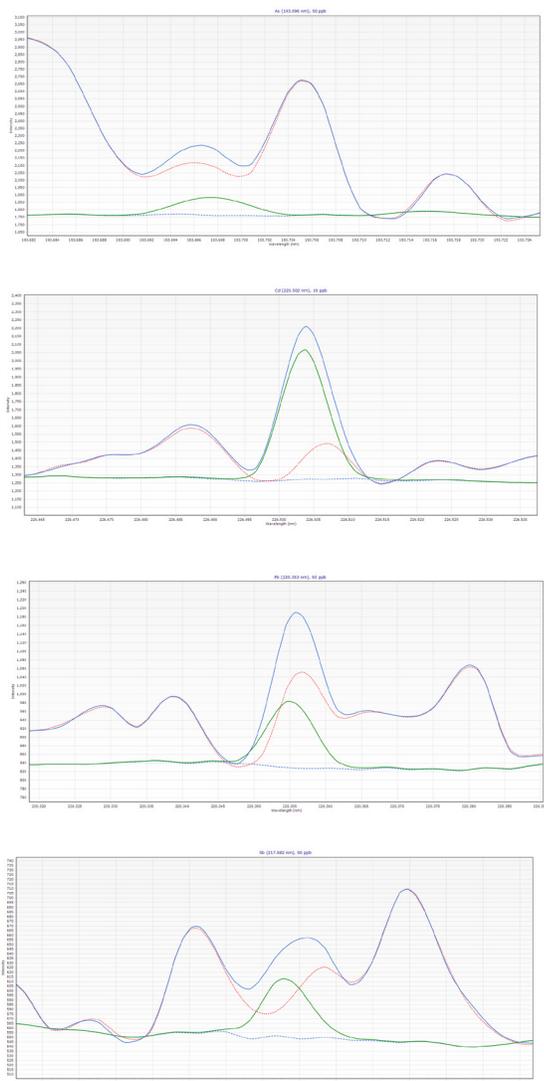


Figure 2. Spectra of 10 µg/L Cd and 50 µg/L As, Pb, and Sb with FACT background correction (analyte in green, interferent in red, and total emission in blue).

Method precision

To test the precision of the method, the five elements were measured multiple times in the 50 µg/L matrix-matched standard. Good precision was achieved with less than 3.5% RSD for all elements. Recoveries were all within ±10% (Table 5).

Table 5. Mean, precision, and recovery of 10 measurements of 50 µg/L.

Element	Wavelength (nm)	Mean of 10 measurements of 50 µg/L standard (µg/L)	%RSD	% Recovery
As	193.696	45	3.3	90
Cd	226.502	48.3	0.5	96.7
Hg	253.652	48.5	3.1	97
Pb	220.353	46.1	2.1	92
Sb	217.582	46.8	3.0	93.5

Spike recoveries

Two different diluted e-liquid samples were spiked with As, Cd, Hg, Pb, and Sb at 0.1 mg/L (equivalent to 0.5 mg/L in the undiluted samples).

All recoveries were within ±10% of the target value, as shown in Table 6. The excellent recoveries demonstrate the ability of the 5110 ICP-OES to accurately determine As, Cd, Hg, Pb, and Sb at the required levels in e-liquid samples comprising 100% glycerol or 50% propylene glycol/50% glycerol. None of the five elements were detected above the LOQ in either of the e-liquid samples.

Table 6. Measured values and spike recoveries (0.5 mg/L) for five elements in e-liquid sample 1 (100% glycerol) and sample 2 (50% propylene glycol/50% glycerol).

Element	Wavelength (nm)	e-liquid sample 1 (mg/L)	Spiked sample 1 (mg/L)	Spike recovery, %	e-liquid sample 2 (mg/L)	Spiked sample 2 (mg/L)	Spike recovery, %
As	193.696	<LOQ	0.46	91.7	<LOQ	0.49	98.4
Cd	226.502	<LOQ	0.49	98.2	<LOQ	0.48	95.8
Hg	253.652	<LOQ	0.52	104.3	<LOQ	0.53	107.0
Pb	220.353	<LOQ	0.47	94.1	<LOQ	0.45	90.4
Sb	217.582	<LOQ	0.46	92.0	<LOQ	0.48	95.8

Conclusions

The Agilent 5110 Vertical Dual View (VDV) ICP-OES can be used for the routine analysis of five heavy metals in e-liquids at the levels required by ANFOR's XP D90-300-2 standard. France is the first country to develop voluntary standardization tools to help improve the safety of e-cigarette users.

By combining the robustness of a vertically oriented torch and plasma with the sensitivity of axial view ICP-OES, excellent detection limits were achieved for all selected wavelengths.

FACT background correction further enhanced the method detection limits in the e-liquid samples. FACT modeling effectively corrects highly complex background structures that cannot otherwise be resolved.

Despite the complex matrix of e-liquid, good accuracy and precision were achieved for the five heavy metals at the concentration levels specified in the XP D90-300-2 standard.

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