Determination of heavy metals in flavored e-liquids using ICP-OES Spectrometry

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■ Overview

Between 2013 and 2015, the number of electronic cigarettes users increased by 86%. Excluding USA and China, seven countries including France, Germany, Poland, Italy and Russia; represent more than 75% of the e-cigarettes world market.

Figure 1: electronic cigarette: safe pleasure or heavy metals poison ?

In order to prevent European consumers health, the European Council included some regulations for this kind of product in the Tobacco Products Directive (TPD) 2014/40/EU. Concerning heavy metals contamination in e-liquids, European Commission directive 88/388/CEE is applied. This regulation sets maximum concentration values for 5 toxic elements : arsenic, cadmium, mercury, lead and tin.

Element	As	Cd	Hg	Pb	Sb
Maximum authorized Value (mg/L)	3	1	1	10	5

Table 1: Heavy metals maximum authorized values in e-liquids according directive 88/388/CEE.

A new French experimental standard XP D90-300-2 was recently developed, forcing the e-liquids producer to quantify this five elements in their products. Moreover, recent studies show that aluminum, copper, iron, chromium and nickel could also be found in e-liquids and e-vapor.

Then a fast and easy to use method for simultaneous analysis of 10 elements (Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb) in e-liquids has been developed using the Shimadzu ICPE-9820. This method is also able to quantify the 10 elements in e-liquids raw materials (polypropylene-glycol PG and Vegetable Glycerin VG) and e-vapors.

■ Shimadzu ICPE-9820: performance, simplicity and reduced costs.

The combination of a large CCD detector (1 inch) and an efficient vacuum optical system in ICPE-9820 results in high sensitivity and resolution (5 pm at 200 nm). The Shimadzu exclusive vertical Minitorch limits memory effects and drastically reduce Argon consumption during analysis run (12 L/min). Moreover, the new Shimadzu RF solid state generator insure a great stability for plasma generation and measurement. At the same time, this device enables an “eco mode” which reduces Argon total consumption at less than 4 L/min between measurement run. For each sample, the easy to use ICPESolution software saves all the wavelength between 167 nm and 800 nm, thereby facilitating the data processing.

■ Samples preparation and method parameters

Four different flavored e-liquids, called ELiQ1 to ELiQ4 are analyzed. One of them, ELiQ2, is studied with two different nicotine level (3 and 18 mg/L). Tow raw materials, vegetable glycerine (VG) and propylene glycol (PG) are also studied. Finally, e-vapors from ELiQ4 are analyzed, thanks to a smocking machine (50 and 180 puffs).

Thanks to ICPE-9820 robustness and performance, only easy sample dilution is used. Only 1.5 mL of nitric acid 15% are added at 2 g of sample. Then, the resulting solution is completed at 25 mL with distillated water before ICP analysis.

Parameter	Setting
RF generator power	1.2 kW
Plasma gas	10 L/min
Auxilliary gas	0.6 L/min
Carrier gas	0.7 L/min
Nebulizer type	*Concentric 10*
Spray chamber	*Cyclonic*
Plasma torch	*Minitorch*
View	axiale
Exposure time	30 s

Table 2: ICPE-9820 relevant parameters

■ Calibration

For each studied element, calibration curves including 4 or 6 points in the targeted concentration range are realized in 2% nitric acid solutions.

All samples are measured in triplicate and one of them, ELiQ1 is spiked with known concentration values (50 ppb) in order to check the method accuracy.

A 1 ppm Yttrium internal standard solution in 2% nitric acid was mixed using online mixing with sample, before it is aspirated.

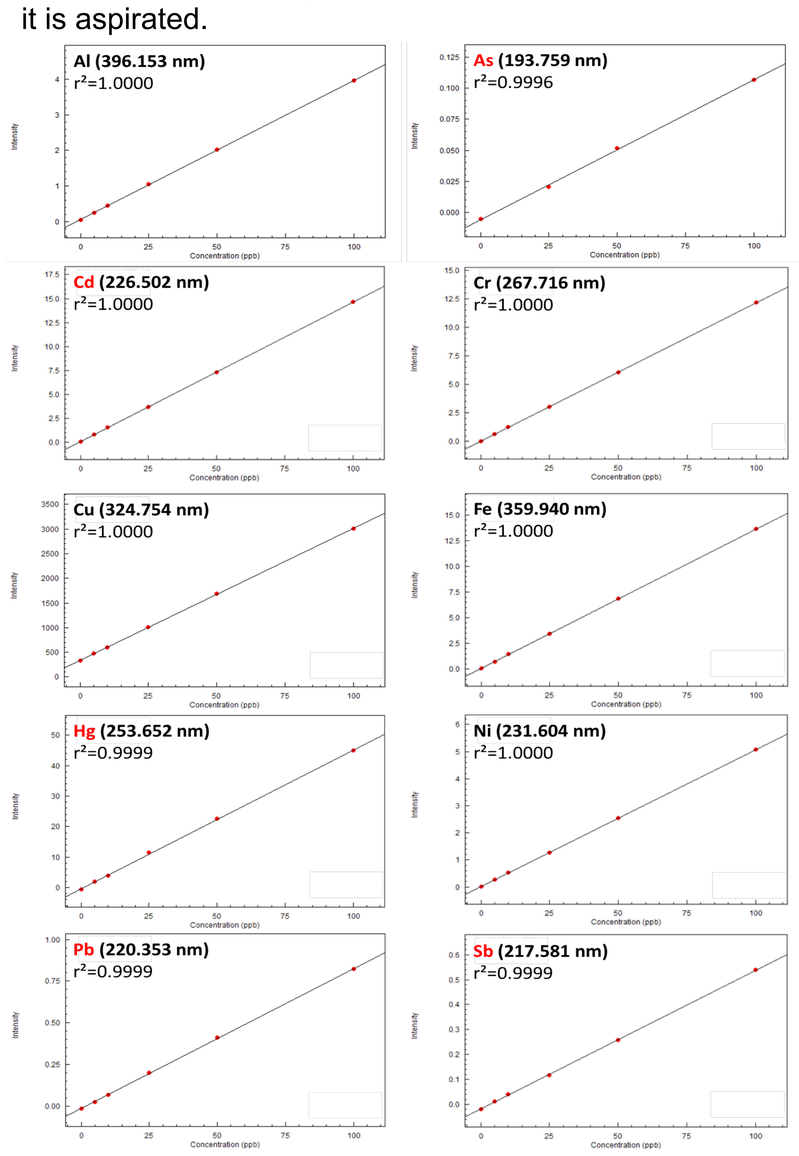


Figure 2: Calibration curves obtained using 2% HNO_3. Red elements are specifically targeted by 88/388/CEE.

The different curves in Figure 2, show all correlation coefficients r² achieving a 0.9999 level.

■ Detection limits calculation

Detection limits (LD) are calculated automatically by *ICPESolution* software with 3σ method. All LD shown in table 3 below are reported in e-liquids sample.

Element	As	Cd	Hg	Pb	Sb
LD (ppb)	150	1	75	33	54
Element	Al	Cr	Cu	Fe	Ni
LD (ppb)	7.5	2.5	2.5	6.3	6.3

Table 3: LD values for e-liquids sample.

As shown in Table 3, all the LD obtained values are far lower than the maximum authorized contents in e-liquids required by the European regulation. It demonstrates ICPE-9820 ability to check the safety of this kind of product.

■ Results

The results of five studied e-liquids are collected in Table 4. Table 5 refers to element values in raw materials and e-vapors.

	ELiQ1	ELiQ2 (3mg)	ELiQ2 (18 mg)	ELiQ3	ELiQ4
Al (ppm)	0.062	0.091	0.097	0.051	< LD
As (ppm)	0.025	0.020	0.012	0.080	0.069
Cd (ppm)	< LD	< LD	< LD	$3.7.10^{-3}$	$7.2.10^{-3}$
Cr (ppm)	< LD	< LD	< LD	$3.0.10^{-3}$	$2.6.10^{-3}$
Cu (ppm)	$7.5.10^{-3}$	0.046	0.049	< LD	0.020
Fe (ppm)	0.105	0.094	0.035	< LD	0.366
Hg (ppm)	< LD	< LD	< LD	< LD	< LD
Ni (ppm)	< LD	< LD	< LD	< LD	$5.3.10^{-3}$
Pb (ppm)	0.076	0.244	0.256	0.275	0.265
Sb (ppm)	0.109	0.363	0.394	0.346	0.410

Table 4: Elements concentration in studied e-liquids.

The quantitation results in table 4 demonstrate that ICPE-9820 is able to quantify simultaneously the various target elements present in e-liquid samples whatever the flavor or the nicotine level.

	PG	VG	ELiQ4 vapor 50 puffs	ELiQ4 vapor 180 puffs
Al (ppm)	0.097	0.086	0.028	0.043
As (ppm)	<LD	0.055	0.02	<LD
Cd (ppm)	0.012	0.017	<LD	<LD
Cr (ppm)	0.012	0.014	$1.6.10^{-3}$	$1.7.10^{-3}$
Cu (ppm)	<LD	<LD	0.020	0.011
Fe (ppm)	0.151	0.014	0.035	0.078
Hg (ppm)	<LD	<LD	<LD	<LD
Ni (ppm)	$7.7.10^{-3}$	0.016	$3.0.10^{-3}$	$3.5.10^{-3}$
Pb (ppm)	0.268	0.219	0.01	0.049
Sb (ppm)	0.384	0.324	0.028	0.038

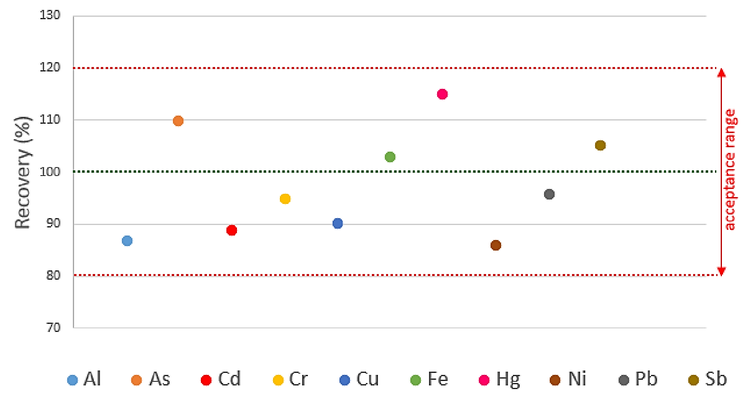
Table 5: Elements concentration in studied e-liquids raw materials and ELiQ4 vapours.

As demonstrated by the values in Table 5, the ICPE-9820 using the developed method is also able to quantify element concentrations in e-liquids raw materials and vapors.

■ Method accuracy

In order to demonstrate the method accuracy, some spike of each element is done in e-liquid ELiQ1. The achieved results are mentioned in graph 1 and calculated according to:

$$recovery(\%) = \frac{value\ after\ spike - initial\ value}{initial\ \ value} \times 100$$



Graph 1: recovery values for each element in ELiQ1.

The recovery rate for all the elements are between 80% and 120% (min. 87%, max. 115%) indicating the suitability of the developed method from point of accuracy, independent from initial element concentration.

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