Desolvating Introduction System Temperature Optimization for Linear Zinc, Cadmium, and Tin Calibrations with Triple Quad ICP-MS for E-cigarette Aerosol Analysis

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BACKGROUND

- Metals in e-cigarette aerosols are almost entirely from device components.
- Inhalation of metals can cause health effects. Examples: zinc (Zn)-irritant; cadmium (Cd)-carcinogen; tin (Sn)-inflammation.
- Metals in aerosol were analyzed by Triple Quad-Inductively Coupled Plasma-Mass Spectrometry (QQQ-ICP-MS) with Apex desolvating system.
- The Apex is designed with a heated cyclonic spray chamber followed by a peltier-cooled condenser to reduce solvent load and plasma interferences which increase sensitivity.
- Occasional zinc, cadmium, and tin calibration curve linearity issues were observed at Apex default temperature settings.
- The Apex temperature was adjusted to below boiling points of Zn, Cd, and Sn species and e-cigarette aerosol samples were analyzed.

METHOD

Used previously validated toxic metals in e-aerosol method[1]

E-aerosol Generation & Collection

- 55 mL puff volume, 3 sec. puff, 30 sec. interval, square profile, 50 puffs
- Fluorinated Ethylene Propylene (FEP) tubing to collect aerosol

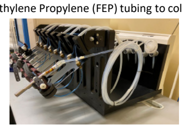

Figure 1: Cerulean CETI-8 Aerosol Machine with FEP fluoropolymer tubing trap

ICP-MS Analysis

- Agilent 8800 QQQ-ICP-MS (Santa Clara, CA) with Elemental Scientific Apex™ HF 2 desolvating introduction system (Omaha, NE)

  Default temperature: 140 °C; Custom temperature: 100 °C
- Calibration standards (2% v/v nitric acid, 1% v/v hydrochloric acid, and 0.25% v/v hydrofluoric acid)

Table 1: Analytes with instrument modes, quantitated ions, and internal standards

Analyte	Gas Mode	Mode	Quad 1	Quad 2	Internal Standard
Chromium (Cr)	Ammonia	Mass Shift	52	86	Rh: 103->171
Nickel (Ni)	Oxygen	Mass Shift	60	76	Rh: 103->119
Copper (Cu)	Ammonia	Mass Shift	63	97	Rh: 103->171
Zinc (Zn)	Ammonia	Mass Shift	66	117	Rh: 103->171
Cadmium (Cd)	Oxygen	On Mass	111	111	Rh: 103->119
Tin (Sn)	No Gas	Single Quad	118	n/a	Rh: 103
Lead (Pb)	No Gas	Single Quad	206+207+208	n/a	Rh: 103

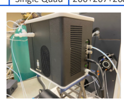

Figure 2: Apex desolvating system

RESULTS & DISCUSSION

Linearity

- The decrease in Apex heating temperature improved Zn, Cd, and Sn linearity.
- Figures 3 and 4 show examples of tin calibration curves. Figure 3 was with Apex default temperature showing a calibration that has a downward curve. Figure 4 was with lower custom Apex temperature showing an improvement with linearity.
- Similar results were seen for Zn and Cd with improvements in linearity at 100 °C Apex temperature.
- The default Apex temperature of 140 °C is above the boiling point of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$; 105-131°C), cadmium nitrate tetrahydrate (Cd(NO3)2·4H2O; 132°C), and tin(IV) chloride ($SnCl_4$; 114°C) species which could occur in the presence of nitrate and chloride anions in the dilute acid solvents.
- The adjusted temperature of 100 °C is below the boiling point of the zinc, cadmium, and tin species.

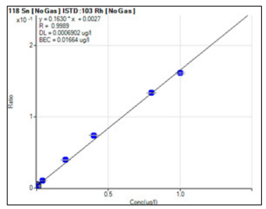

Figure 3: Tin calibration curve using default Apex heating temperature (140 °C).

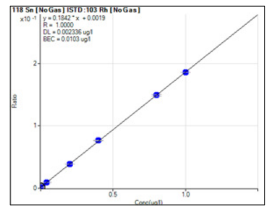

Figure 4: Tin calibration curve using decreased Apex heating temperature (100 °C).

Aerosol Results from Vaping Devices

- Table 2 shows aerosol results from 3 different vaping devices for all method analytes chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), tin (Sn), and lead (Pb). Analyte limits of detection (LOD) and lowest reportable levels (LRL) are also included.
- Custom Apex temperature settings were used.
- For this small subset of devices, relatively low metals results were obtained, including for the analytes with improved linearity from Apex changes. The majority of metals were below or near lowest standards or detection limits.
- Figures 5-7 show internal components, including metal components, that may be in contact with the liquid.

Table 2: Toxic metals in aerosol results for 3 vaping devices (ng/10 puffs) using custom Apex temperature settings, n=5

	Cr	Ni	Cu	Zn	Cd	Sn	Pb
Limit of Detection (LOD)	0.125	0.250	0.200	5.00	0.050	0.100	0.050
Lowest Reportable Limit (LRL)	0.500	0.500	1.00	10.0	0.200	0.200	0.500
bidiStick® Gold Fresh Mango, 6% nicotine; disposable	1.38 ± 1.48	20.4 ± 11.8	<LRL	16.3 ± 14.6	<LOD	5.59 ± 6.47	<LRL
Brez® Tobacco, 5% nicotine; pod	<LOD	3.58 ± 2.74	6.12 ± 8.46	<LRL	<LOD	<LOD	1.75 ± 3.48
glas® Signature Tobacco, 5% nicotine; pod	1.56 ± 0.52	4.38 ± 2.63	3.37 ± 2.19	<LOD	<LOD	<LOD	<LRL

Figure 5: bidiStick® internal components

Figure 6: Brez® internal components

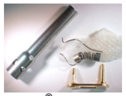

Figure 7: glas® internal components

CONCLUSIONS

- Metals in e-aerosol are present from device components, such as wires, solder, and battery connections seen in Figures 5, 6, and 7.
- Metal concentrations in e-cigarette aerosol are often low, particularly for metals that are not major components of the device. A method with high sensitivity is necessary to accurately report these metals. The Apex desolvating system along with ICP-MS is used for our current analytical method to achieve this.
- The default Apex heating temperature of 140 °C is above boiling points of some zinc, cadmium, and tin species. This caused occasional calibration curve linearity issues with inconsistent analyte loss from boiling.
- Decreasing the Apex heating temperature to 100 °C improved linearity for zinc, cadmium, and tin calibration curves. The lower temperature is below the boiling point of analyte species.
- The aerosol from this small subset of three vaping devices show relatively low metal concentrations. Metal components in some contact with the e-liquid are shown for each sample (Figures 5-7). Of particular interest for this study, zinc was <LRL for two samples and near LRL for one sample; cadmium was <LOD in all samples; and tin was <LOD for two samples and at low concentration in one sample.
- A method for analyzing metals in aerosol should be suitable for a wide variety of e-cigarettes. Different designs and liquid formulations in e-cigarettes will impact the metal concentrations in the aerosols. Inhalation of metals in e-cigarette aerosol, even in devices with low concentrations, is a health concern. For example, nickel, cadmium, and lead are all classified as carcinogens.
- When developing a method, particularly with the use of an additional desolvating system, analyte species boiling points should be considered.

REFERENCES

1.) Halstead, M.; Gray, N.; Gonzalez-Jimenez, N.; Fresquez, M.; Valentin Blasini, L.;Watson, C.; Pappas, R.S. Analysis of Toxic Metals in Electronic Cigarette Aerosols Using a Novel Trap Design. J. Anal. Toxicol. 2020, 44, 149–155.

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