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Detection of Heavy Metals in Disposable Face Masks by Inductively Coupled Plasma-Mass Spectrometry

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Abstract

The SARS CoV-2 pandemic has caused an increase in face mask wearing in order to mitigate the spread of the coronavirus disease (Covid-19). However, there is growing concern around the environmental fate and indirect pollution potential of these masks as they may contain leachable chemical dyes associated with heavy metals. As there is little data on the potential health and environmental risks caused by disposable face masks, it is important to determine whether theses masks release hazardous heavy metals. In this study, the presence and amounts of 9 heavy metals in various face mask samples were determined using inductively coupled plasma-mass spectrometry, or ICP-MS. In addition, the leaching time of the masks was investigated to determine whether time had any effect. The elements analyzed were, chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), antimony (Sb), thallium (Tl), and lead (Pb). ICP-MS is the preferred technique for elemental determination due to its low detection limits, high precision, and short analysis time. It was found that disposable face masks were observed to have higher concentrations of heavy metals than both cloth (washable) and surgical face masks. Copper was detected in all leachates and had the highest concentrations of any metals ranging from 5.1480 *u*g/L to 52.3797 *u*g/L. Additionally, it was observed that the longer the face masks were submerged in water, the higher the concentrations of heavy metals were detected in the leachates. Findings of this research provide insight into the detection of heavy metals associated with face masks and information for further studies on their environmental impact as well as for regulating strict manufacturing and recycling laws.

1. Introduction

The World Health Organization (WHO) detected the emergence of the coronavirus (Covid-19), caused by the SARS CoV-2 virus, in Wuhan, China in late 2019 (Agaraw 2020; Fadare and Okoffo 2020). Since its declaration as a pandemic, multiple safety measures have been put in place to contain the virus (Agaraw 2020). These have included lockdowns, social distancing, good hand hygiene, travel restrictions and the mass wearing of disposable face masks (Wilder-Smith and Freedman 2020). The introduction of face masks as a precautionary measure to reduce the spread of the virus has caused a significant generation of waste (Jung et al. 2021). This rise in disposable face mask (DFM) waste is regarded as a new source of pollution, as there is no reliable disposal process for masks, with a large portion ending up in water reserves and subsequently the ocean. However, there is still very little data on the effect of the pollution caused by DFMs on the environment (Sullivan et al. 2020).

Figure 1. Image of disposable face mask litter at TRU.

Most disposable face masks are manufactured from plastic fibers and polymeric materials, such as polypropylene, polyethylene, polycarbonate, polystyrene, and nylon (Agaraw 2020; Jung et al. 2021). Additionally, chemical dyes are added in the manufacturing process to add color and patterns (Pranaitytė et al. 2008). Part of the environmental concern surrounding face mask waste is that the major chemical pollutant in dyes and textiles is toxic heavy metals (Sunger and Gülmez 2015; Jung et al. 2021). Heavy metals are referred to as groups of metals and metalloids (semimetals) that may have harmful ecological effects or are expected to be toxic (Bánfalvi 2011). Metals such as chromium, copper, and antimony can be used as catalysts in the dyeing process and can leave behind residues in the textiles (Sullivan et al. 2020). Additionally, some reactive dyes contain heavy metal complexes with nickel and cobalt, and copper (Jung et al. 2021). These dyes, in disposable face masks, are leachable chemicals and can therefore readily release heavy metals and other organic pollutants when submerged in water (Sullivan et al. 2020). Many of these harmful pollutants have bioaccumulative properties when released into the environment and it is apparent that DFMs could be a main source of environmental contaminants (Sullivan et al. 2020). Therefore, there is a need for sensitively detecting and quantifying low levels of heavy metals in textiles, such as DFMs, in order to reduce any potential risks to environmental and human health. This will allow a better understanding of heavy metals associated with face masks and may impact the regulation of manufacturing and recycling laws.

Several analytical techniques, including atomic absorption spectrometry, inductively coupled plasma-optical emission spectrometry, and X-ray fluorescence spectrometry have been proposed for the determination of heavy metals concentrations. However, these methods are often time-consuming, laborious, and less selective (Pranaitytė et al. 2008). Inductively coupled plasma-mass spectrometry (ICP-MS) is a powerful, multi-element technique for determining the elemental composition of a wide range of sample types (Pranaitytė et al. 2008; Voica et al. 2009). Outstanding properties such as high sensitivity and selectivity as well as low background signals which give very low detection limits make ICP-MS an efficient tool for detecting, identifying, and quantifying trace elements (Ammann 2007).

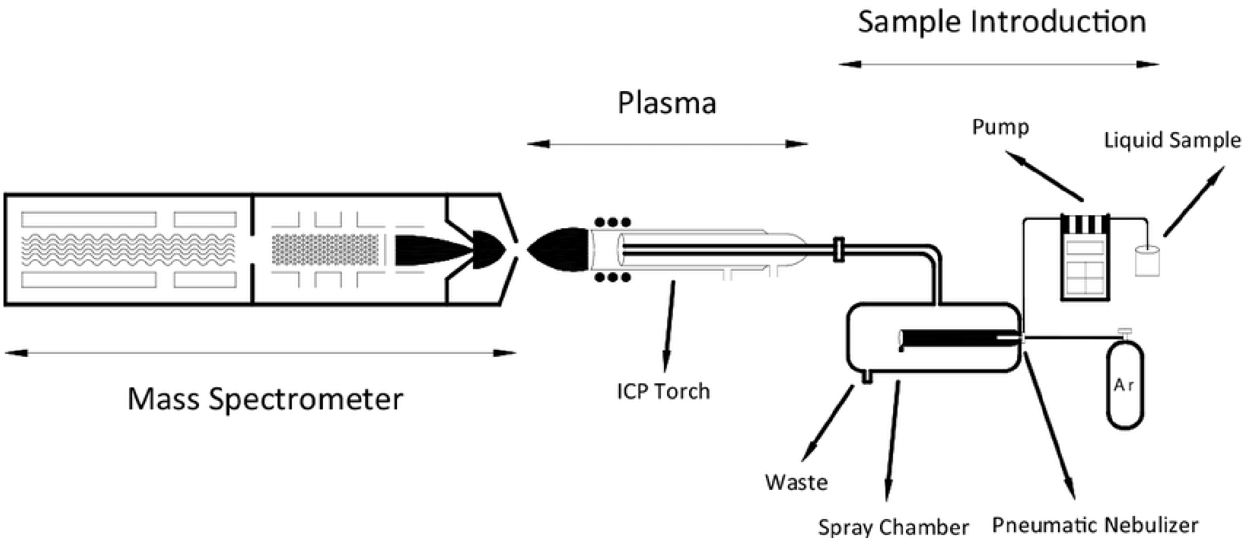

Figure 2. Schematic of major components of ICP-MS (Kashani and Mostaghimi 2010).

In this study, we proposed submerging the center pieces of various face masks in separate beakers of deionized water to recreate environmental conditions. This enabled accurate, total multi-element identification and quantification using ICP-MS based on multi-element standards and certified reference materials (CRMs).

The aim of this work is to determine the presence or absence of heavy metals in various face masks, using ICP-MS, and to identify any potential environmental risks they might pose when disposed of improperly. In addition, the study investigated whether varying the time spent submerged in water affected the concentrations of elements leached out from the masks.

2. Methods and Materials

2.1 Chemicals and Masks

Chemicals used for the preparation of mask samples were environmental grade concentrated nitric acid (VWR International Co., ON, Canada), and concentrated hydrochloric acid (VWR International Co., ON, Canada). Internal standard solutions were made from Agilent Technologies ICP-MS Internal Standard Mix (Santa Clara, CA, USA), which had a concentration of 100 μg/mL. Furthermore, calibration standards were made from Agilent Technologies Environmental Calibration Standard, which had a concentration of 1000 μg/mL for Ca, Fe, K, Mg, and Na, and a concentration of 10 μg/mL for Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V, and Zn. All other reagents were of analytical grade, including 18MΩ water, which was used to prepare both the standard solutions and mask leachates. The matrix used for sample and standard solution preparation was 2.5% HNO_3 and 0.5% HCl. The calibration curve had a range of 0 to 100 ppb.

Masks were selected and purchased from various stores in Kamloops, BC and online platforms, including London Drugs and Amazon. The selection included the typical blue and black disposable face masks, various cloth and multi-colour masks and surgical masks, as listed in Table 1. A total of 9 face masks were collected and then classified into three categories: Disposable (1), Cloth/Washable (2) and Surgical (3). Images of selected samples are shown in Figure 3.

Table 1. Main characteristics of selected face masks under investigation.

Sample ID	Description	Size	Brand
Face mask 1a	Black	Adult	Medicom Connections
Face mask 1b	Light blue	Adult	-
Face mask 1c	Dark blue	Adult	-
Face mask 2a	Blue and pink (50% PBT yarn, 50% polyester)	Adult	Goody comfort
Face mask 2b	Dark blue with flowers (100% polyester)	Adult	Coco & Tashi
Face mask 2c	Green (92% polyester, 8% spandex)	Adult	Coolearth antibacterial
Face mask 2d	Pink (100% cotton)	Child	iTru non-medical kid’s
Face mask 3a	KN95	Adult	Amazon
Face mask 3b	Surgical	Adult	Safe Act

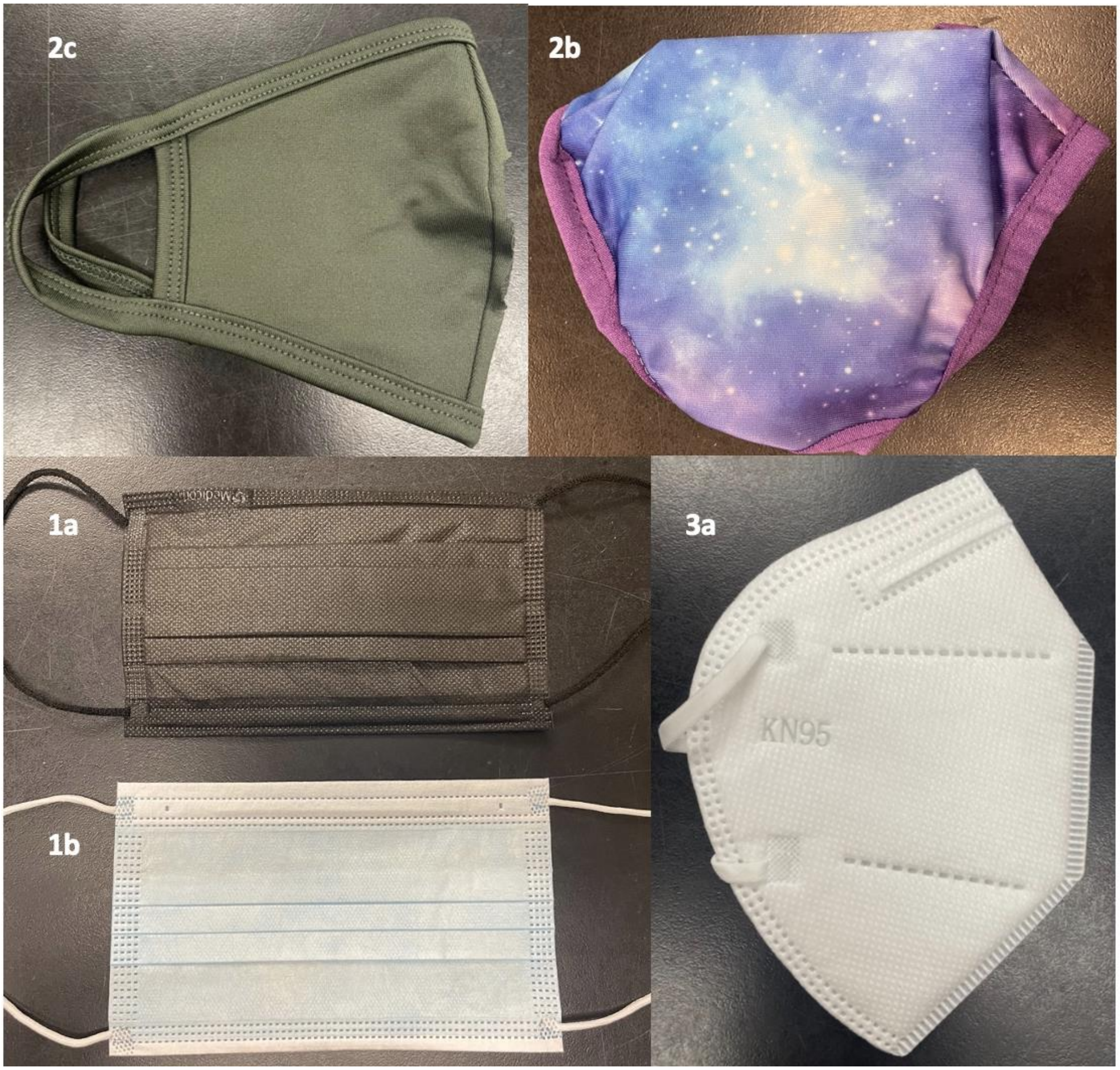

Figure 3. Images of selected face masks used in investigation. Identification corresponds to sample ID in Table 1.

2.2 Leaching and Sample Preparation

The center part of the face masks was cut out, and metal structures and elastics were removed. Approximately 0.5000 g of each sample was weighed and placed into a 250 mL beaker (Figure 4). The masks were submerged in 150 mL of 18MΩ water and left for 24, 48 and 72 h. A watch glass was placed over the beakers to avoid any contamination (Figure 5).

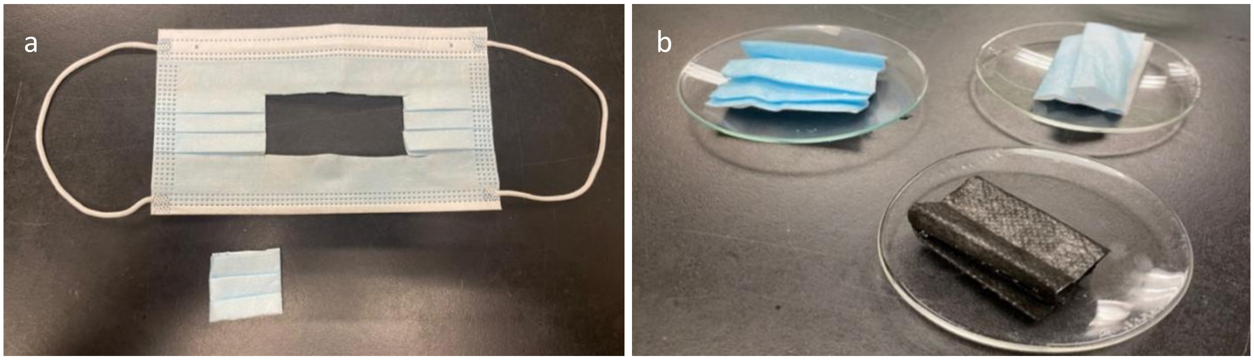

Figure 4. a) Original mask with strip cut out. B) Center part of various masks cut and weighed.

At each time point, 48.75 mL of leachate was subsampled into a centrifuge tube and acidified using 1 mL of 100% nitric acid and 0.25 mL of 100% hydrochloric acid. For ICP-MS analysis, internal standard solutions consisted of 1000 ppb of stock internal standard solution, while verification standards contained 50 ppb of stock environmental solution. A blank control using deionized water and a procedural blank (deionized water taken through procedure) was sampled.

Figure 5. Category 2 face masks submerged in deionized water with watch glass.

2.3 Instrument

Samples were analyzed on an Agilent 7900 model ICP-MS system (Santa Clara, CA, USA) for the detection of Cr, Co, Ni, Cu, Zn, As, Sb, Tl, and Pb. The instrument parameters of the ICP-MS analysis are shown in Table 2.

Table 2. Instrument parameters for Agilent 7900 ICP-MS.

Nebulizer	MicroMist
Spray chamber	Quartz, double pass
RF power	1550 W
Argon flow rate (L/min)	15
Auxiliary gas flow rate (L/min)	0.9
Nebuliser gas flow rate (L/min)	1.0
Sample uptake rate (rps)	0.1
Number of replicates	3
Integration time (s)	0.3-1.0
Autosampler	SPS 4
Probe depth	150 mm
Internal standards	^{72}Ge, ^{74}Ge, ^{103}Rh, ^{115}In, ^{193}Ir, and ^{209}Bi
Isotopes	^{52}Cr, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{123}Sb, ^{205}Tl, and ^{208}Pb

3. Results and Discussion

3.1 Elemental concentrations in face mask leachates

Due to the variety of face mask types investigated, each mask leachate will not have a uniform distribution of elements. A full external calibration was performed to determine analyte concentration, and procedural blanks were used prior and post analysis of samples to avoid potential carryover. All quality control determinants for ^{52}Cr, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{123}Sb, ^{205}Tl, and ^{208}Pb passed acceptance criteria. Calibration curves for investigated elements were performed and had a R value range of 0.8116-1.000 (see appendix).

Table 3 shows the concentrations of leachable heavy metals from the face masks. After 24 h, all mask samples were observed to contain traceable levels of heavy metals (Figure 6). Copper showed the highest levels detected, ranging from 5.1480 *u*g/L (face mask 3a) to 52.3797 *u*g/L (face mask 2c). Copper is a known environmental pollutant, which can cause toxic effects on all organisms (Sullivan et al. 2020). Excessive exposure to copper has been linked to cellular damage as well as tissue damage leading to adverse effects and human disease, such as Wilson disease (Tchounwou et al. 2012). A study conducted by Sullivan and colleagues found similar findings, with all masks releasing copper (2020).

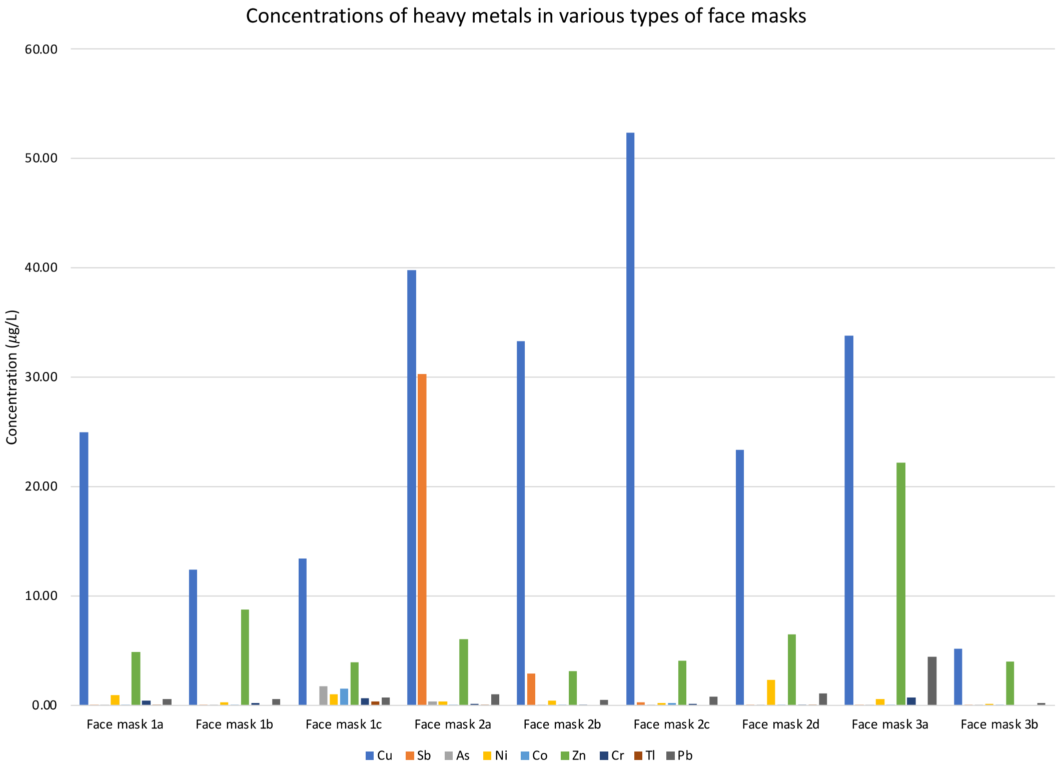

Figure 6. Levels of traceable heavy metals in various types of face masks after 24 hours.

Leachable zinc was present at the second highest concentration, with a range of 3.0956 – 22.2059 *u*g/L. Zinc is an essential trace element required for the maintenance of health, however, excess exposure can cause respiratory tract problems, such as metal fume fever (Bussan et al. 2021). While antimony was present at low levels in most masks (0.00572-0.2573 *u*g/L), concerning levels were released from the category 2 face masks, ranging from 2.8875 *u*g/L (face mask 2b) to 30.2987 *u*g/L (face mask 2a). Sullivan et al. reported similar values in some face masks, ranging from 1.06 *u*g/L to 3.07 *u*g/L, however festive face masks were reported to have released a highest concentration of 393 *u*g/L (2020). This demonstrates the diversity in the types and manufacturing of face masks and their corresponding metal concentrations. Figure 7 illustrates the differences in heavy metal concentrations between the three categories of disposable face masks.

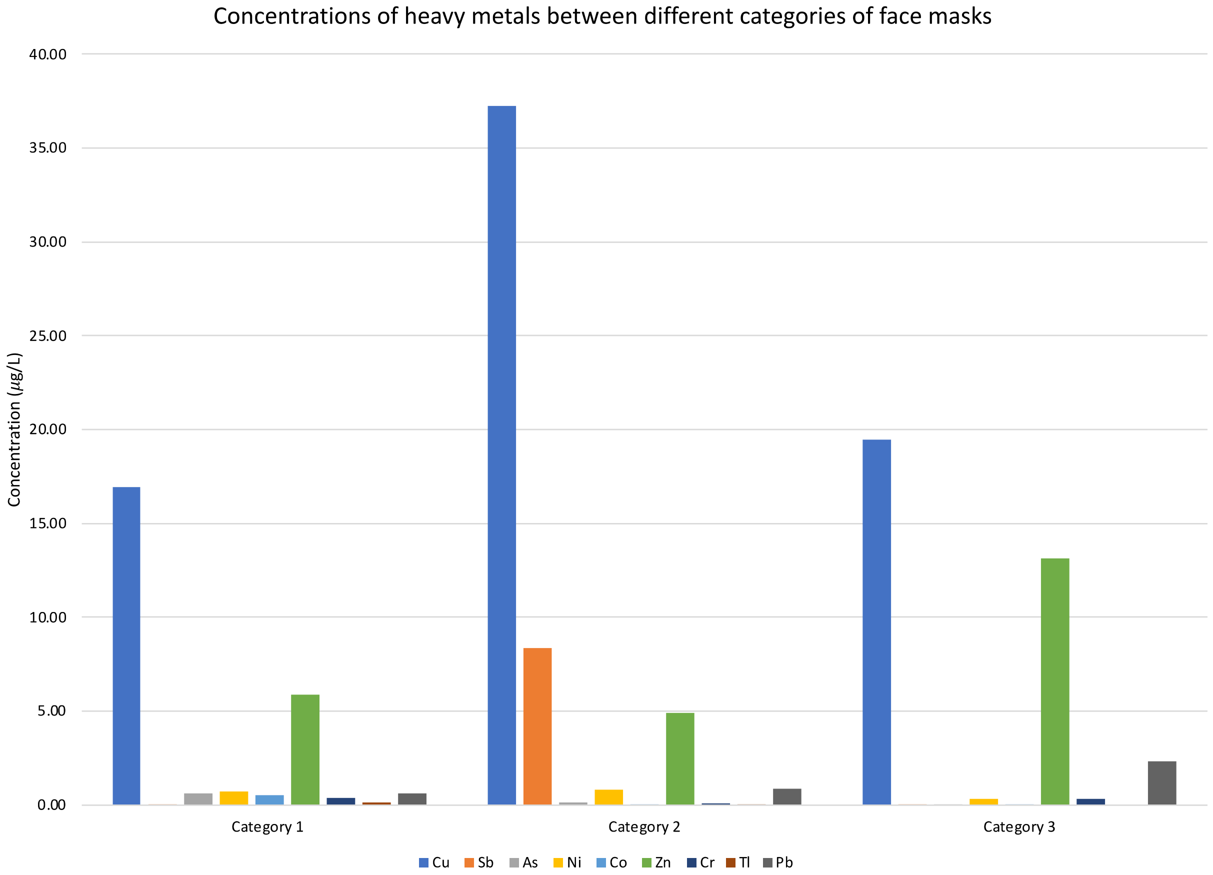

Figure 7. Comparison of the levels of heavy metals in face mask leachates, after 24 h, between the three face mask categories.

Category 2 face masks, representing the colourful cloth masks, showed the highest levels of heavy metals leached out. This is most likely as a result of the manufacturing process and the use of dyes to create the colours and patterns. Although all concentrations of elements were below allowable values, detectable levels of toxic and hazardous elements were still observed. In addition, the findings of this study are only reflective of a single mask. The environmental impact of heavy metals leached from face masks can be deemed significant as the production, usage, and disposal of face masks has reached unprecedented levels. Heavy metals in littered face masks may eventually find their way into the oceans, and an accumulation of face masks in the environment could be cause for even greater concern.

Table 3. Concentrations of heavy metals detected in face mask leachates after 24 h (*u*g/L).

Sample ID	**Cr**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Sb**	**Tl**	**Pb**
Face mask 1a	0.3857	0.0735	0.9407	24.9710	4.8610	0.0335	0.0248	0.0226	0.6018
Face mask 1b	0.1657	0.0176	0.2724	12.4298	8.7570	0.0617	0.0131	0.0021	0.5992
Face mask 1c	0.6113	1.5237	0.9932	13.3901	3.9621	1.7746	N.D.	0.3698	0.7203
Face mask 2a	0.1014	0.0342	0.3469	39.8191	6.0197	0.3245	30.2987	0.0203	1.0115
Face mask 2b	0.0284	0.0091	0.4005	33.3199	3.0956	0.0726	2.8875	0.0037	0.5204
Face mask 2c	0.1131	0.1714	0.2236	52.3797	4.0669	0.0069	0.2573	0.0007	0.8142
Face mask 2d	0.0726	0.0418	2.3122	23.3300	6.5179	0.0507	0.0057	0.0146	1.0726
Face mask 3a	0.6845	0.0686	0.5587	33.8144	22.2059	0.0618	0.0527	0.0004	4.4319
Face mask 3b	N.D.	0.0280	0.1271	5.1480	4.0348	0.0277	0.0438	0.0001	0.2316

N.D. = Not Detected

3.2 Effect of varying leaching time

The masks were left submerged for 24, 48 and 72 h to determine whether this increased the amount of heavy metal leached out. The trend that was observed suggests that the longer the masks were submerged in water, the higher the concentrations of heavy metals detected. Figures 8 and 9 depict the heavy metals leached out of the three categories of masks spanning 24, 48 and 72 h. For the disposable masks, the highest concentration for each metal was detected at 72 h. The exception being copper, which had a concentration of 16.9303 *u*g/L at 24 h. Most noticeable was thallium, which showed an increase from 0.1315 *u*g/L to 2.4895 *u*g/L, while there was only a minute concentration detected in the cloth and surgical masks. Chromium had the highest concentration, 0.3424 *u*g/L, at 24 h in the surgical mask leachates, then proceeded to decrease over time. Similarly, the concentration of copper in the cloth masks decreased. Additionally, cobalt and arsenic showed very little change in concentration in the cloth and surgical masks, while concentration increased exponentially in the disposable face mask leachates. These findings suggest that some heavy metals leached out more than others and at different rates. For each of the masks, there was not enough leachate to sample at the 72-h mark, so a smaller volume was sampled and acidified accordingly. A possible explanation is that the masks expanded when submerged and may have taken up some of the deionized water, resulting in less than the required volume of 48.75 mL.

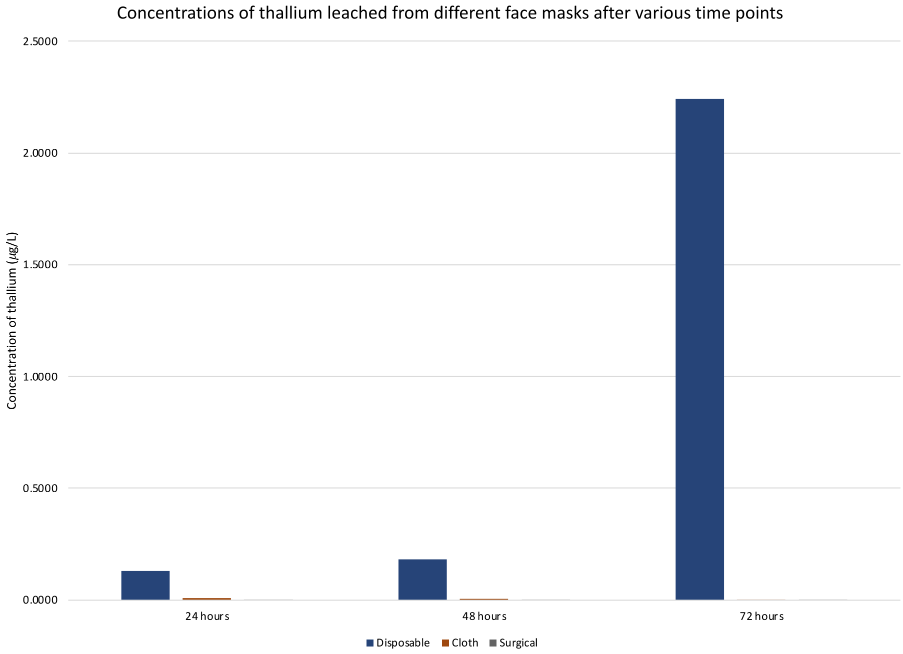

Figure 8. Amount of thallium (Tl) leached out after 24, 48 and 72 h.

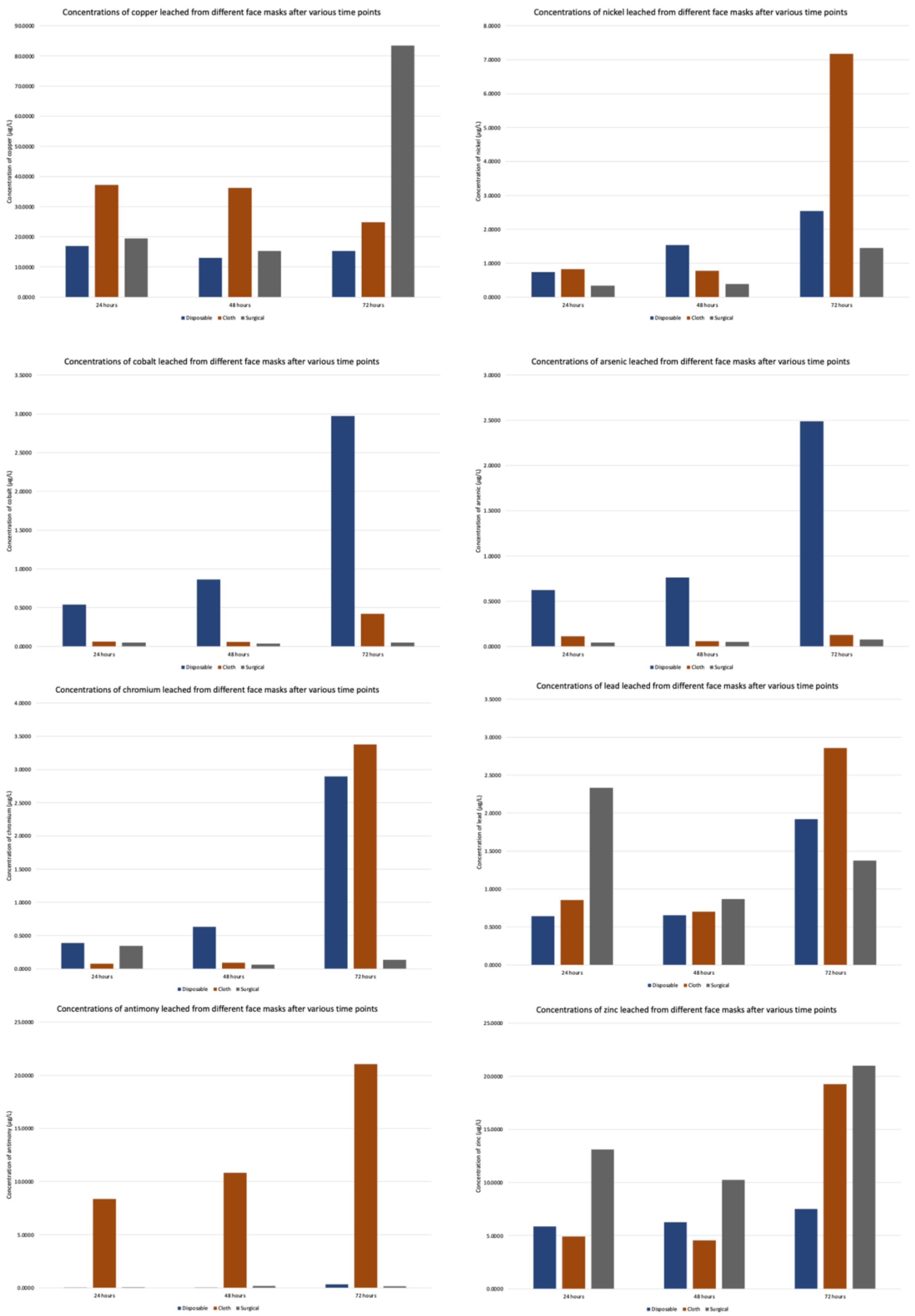

Figure 9. Concentrations of heavy metals leached out from various face masks after 24, 48 and 72 h.

3.3 Future work

This research addressed the possible environmental impact face masks may have by stimulating environmental conditions if the masks were littered. These face masks were brand new and never worn before submerging in water. This was to study the leaching of heavy metals from the masks. For future work, analyzing masks worn in various locations, such as classrooms, community centers (gym) or public hangouts (mall), could be done to investigate whether the use of the masks increases the concentrations of metals observed in comparison to brand new masks (metals from dyes and chemicals in manufacturing process). Additionally, leaving the masks submerged for longer periods of time may indicate the maximum leaching capability of the various masks. Future work could also entail testing the efficiency of the method against other methods, including microwave digestion or ultrasonic probe extraction of the masks. Lastly, only 9 face masks were analyzed, therefore, further investigation of different types of face masks could be done to detect the elemental concentrations present in face masks and gain a more accurate understanding of the consequences of their disposal into the environment

4. Conclusion

In this study, 9 face mask leachates were analyzed for their elemental concentrations to determine whether face masks present an environmental concern. The elements analyzed were ^{52}Cr, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{123}Sb, ^{205}Tl, and ^{208}Pb. It was found that all leachate samples contained traceable levels of heavy metals, however they were lower than allowable levels. Copper and zinc were present in high concentrations relative to the other elements analyzed for. Additionally, colourful cloth face masks showed higher levels of heavy metals in comparison to the disposable and surgical type face masks. A reason for this is the difference in the manufacturing process and composition of the masks as no dyes are used. Furthermore, it was observed that the trend for most heavy metals was the longer the mask was left submerged in water, the higher the concentration of metals leached out. Although, the elemental concentrations observed in each leachate were within established limits, this is only reflective of a single mask. Accumulation of face masks in the environment may still present concern when disposed of incorrectly.

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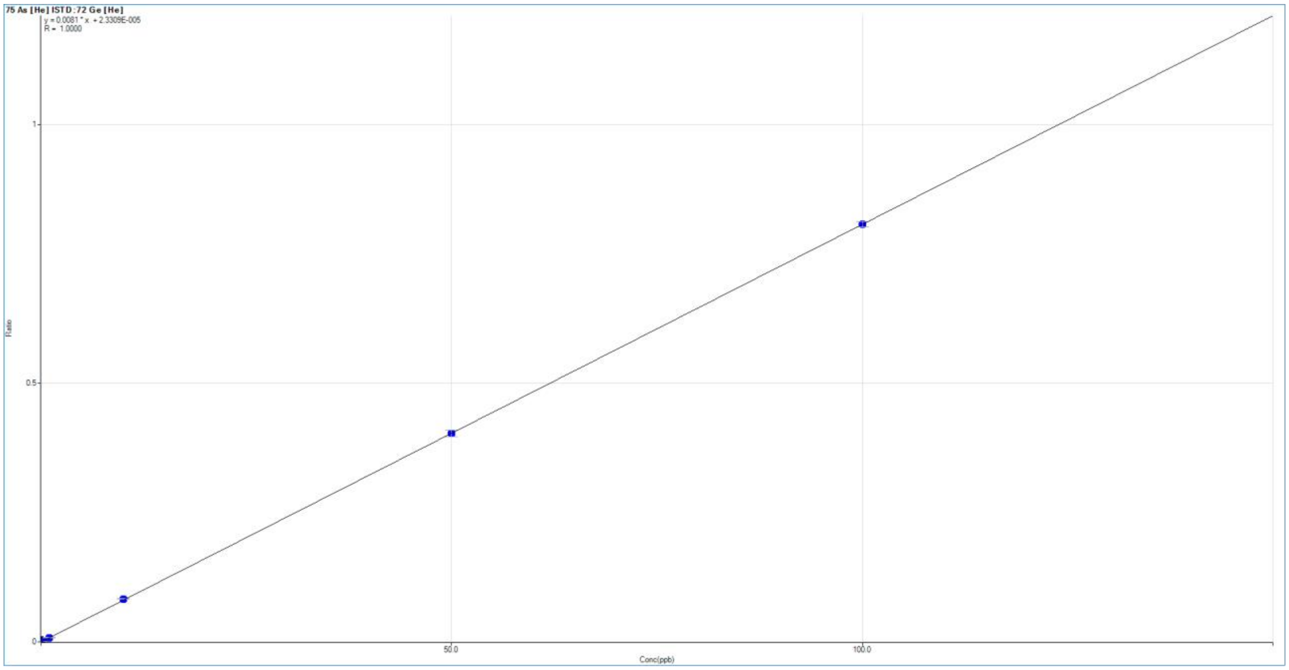
Appendix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0
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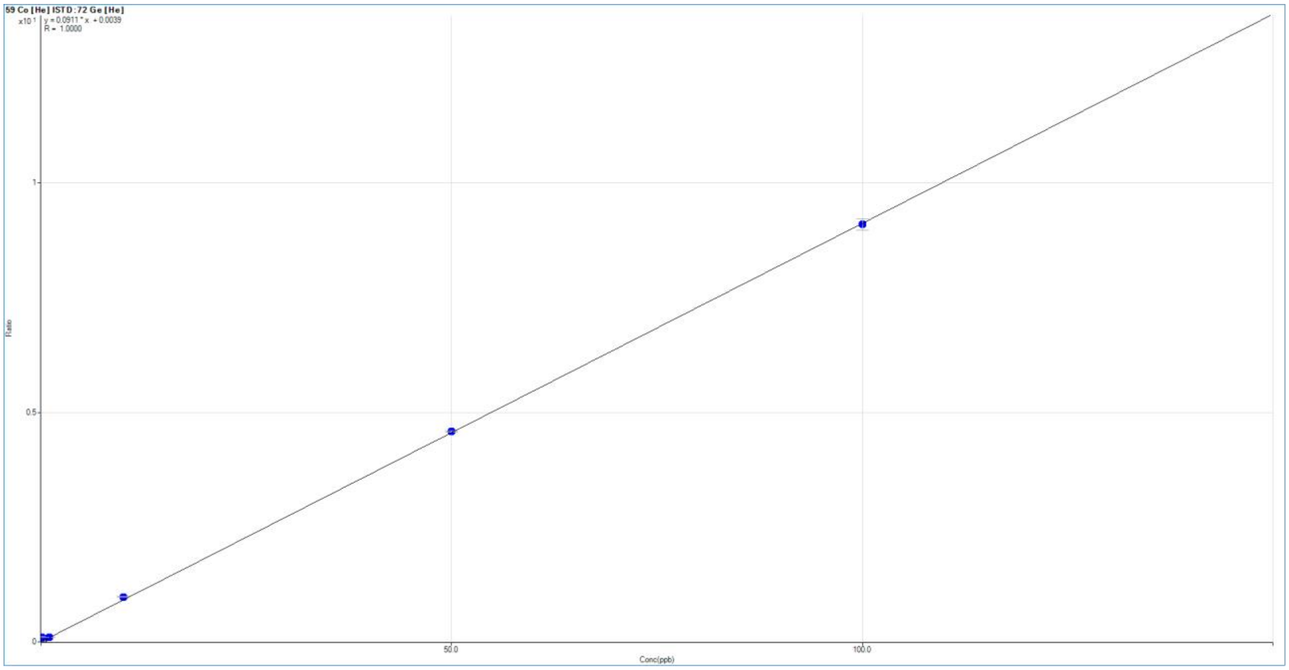
Conc(ppb)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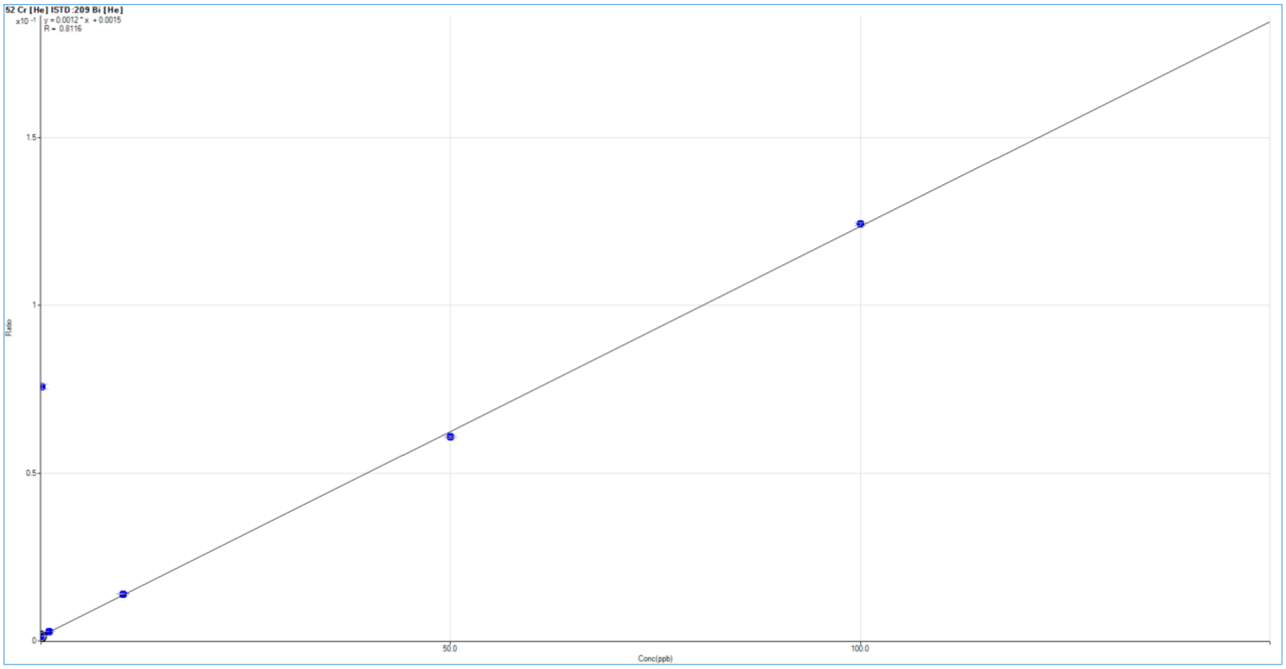
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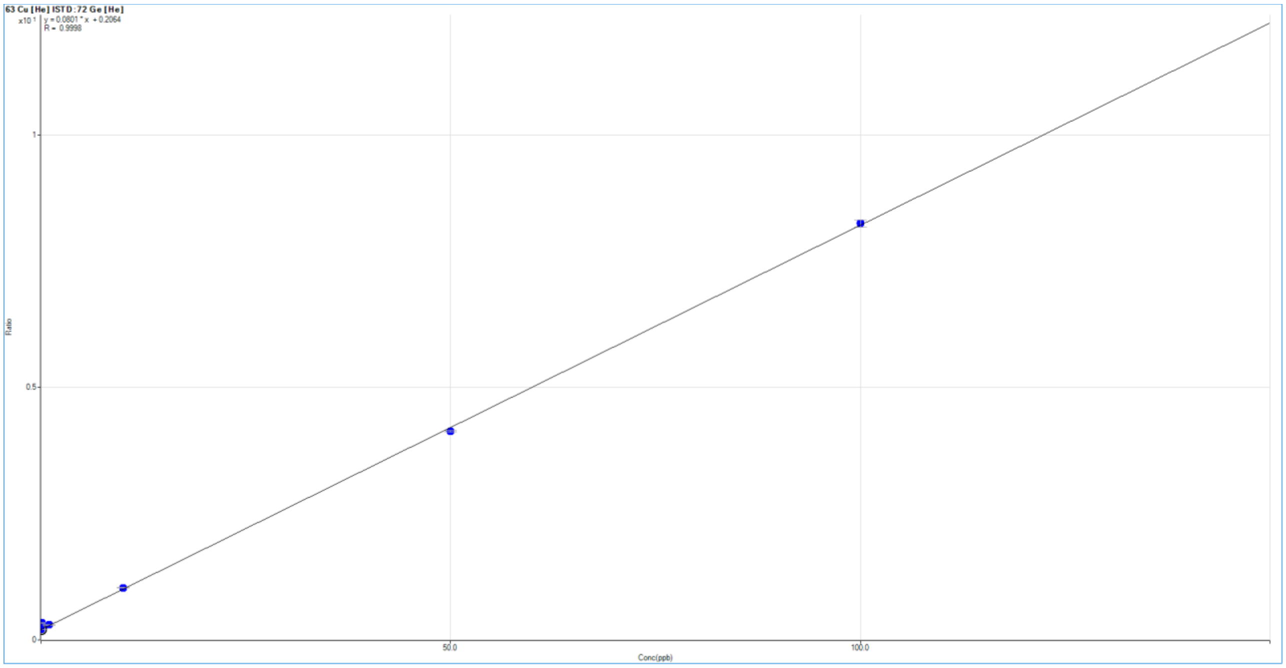
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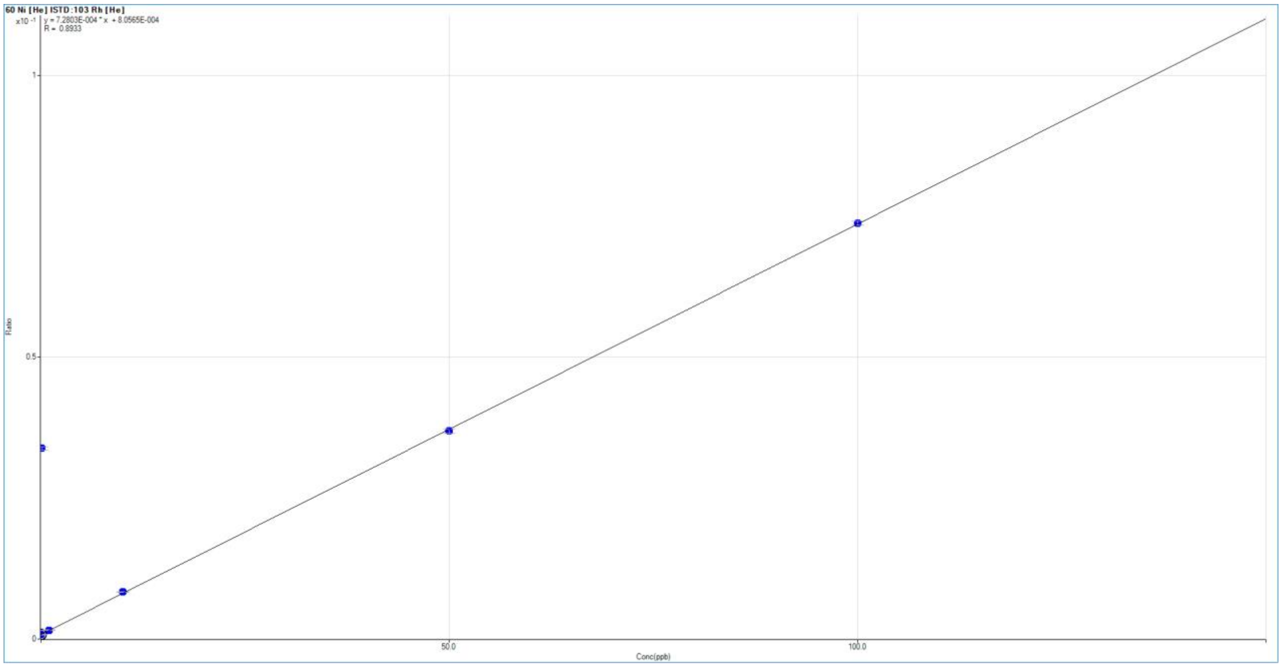

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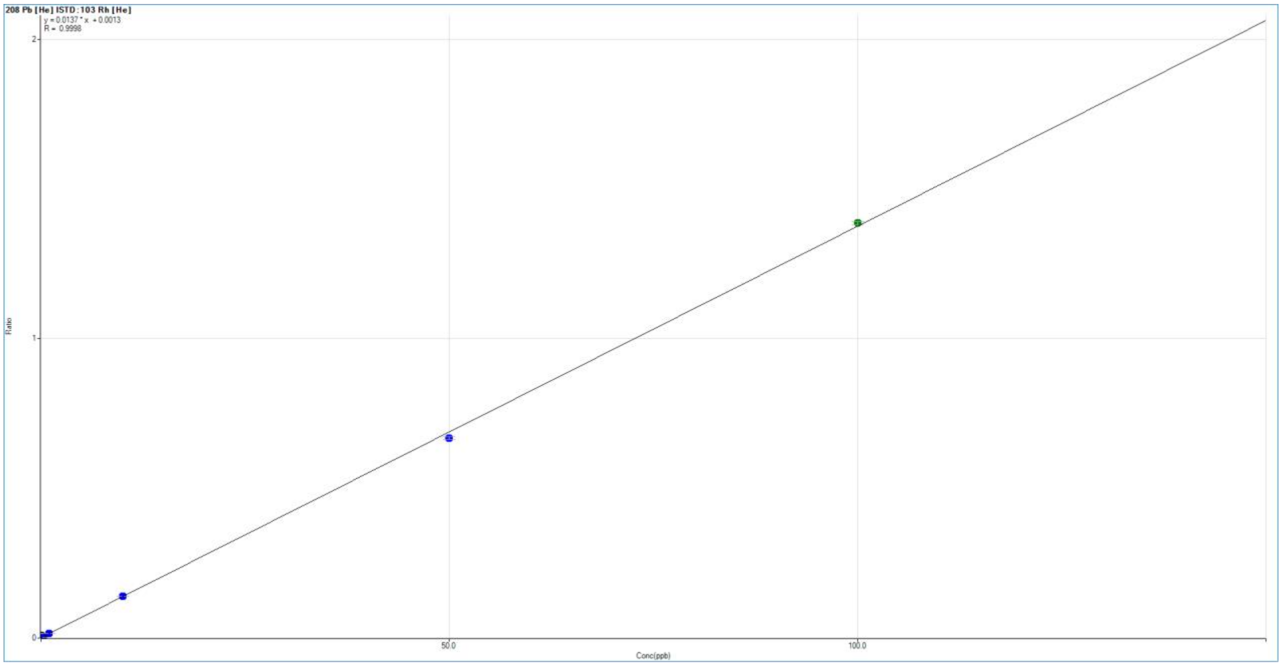

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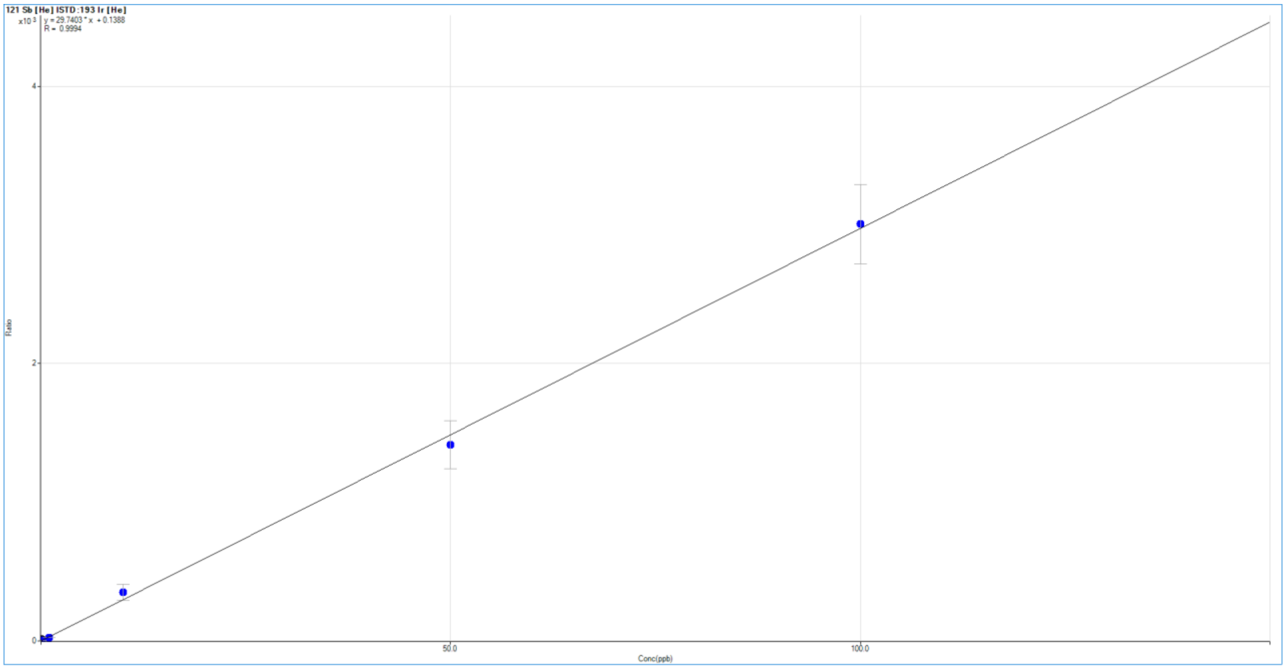
Conc(ppb)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4
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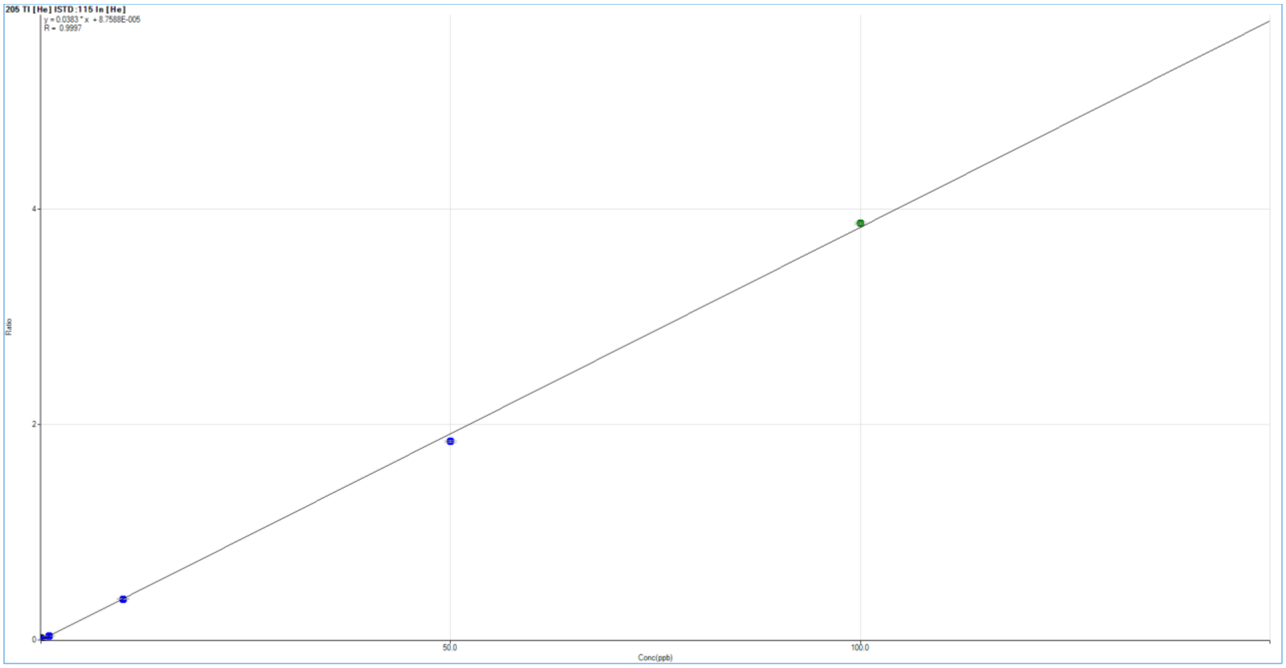
Conc(ppb)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2
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Ratio
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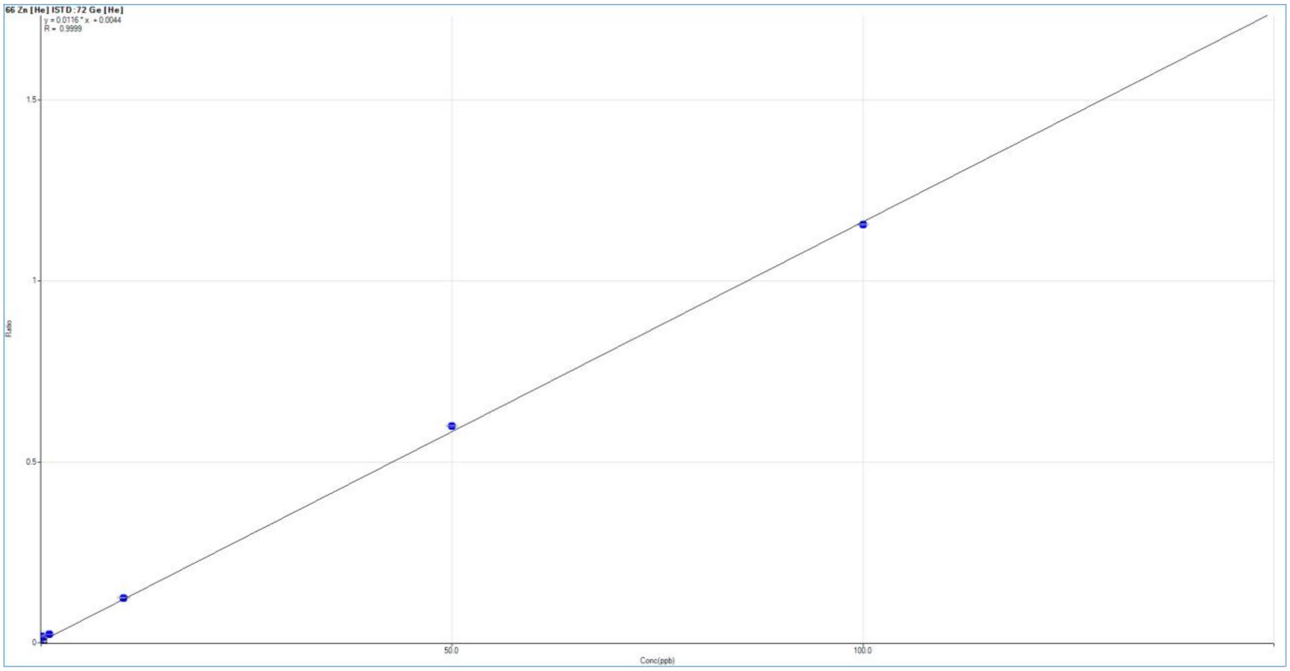
Conc(ppb)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R = 0.9999
Ratio
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1
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Conc(ppb)