

**DETECTION OF LEAD, CADMIUM AND NICKEL
IN CHILDREN'S PLASTIC TOYS USING ATOMIC
ABSORPTION SPECTROSCOPY (AAS)**

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DETECTION OF LEAD, CADMIUM AND NICKEL IN CHILDREN'S PLASTIC TOYS USING ATOMIC ABSORPTION SPECTROSCOPY (AAS)

by

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**Dissertation submitted in partial fulfilment of the requirements
for the degree of
Bachelor of Science in Forensic Science with Honours**

February 2025

CERTIFICATE

This is to certify that the dissertation entitled “Detection of Lead, Cadmium and Nickel in Children’s Plastic Toys Using Atomic Absorption Spectroscopy (AAS)” is the bona fide record of research work done by Hazirah binti Hashim during the period from October 2024 to February 2025 under my supervision. I have read this dissertation and that in my opinion it conforms to acceptable standards of scholarly presentation and it fully adequate, in scope and quality, as a dissertation to be submitted in partial fulfilment for the degree of Bachelor of Science in Forensic Science with Honours.

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DECLARATION

I hereby declare that this dissertation is the result of my own investigations, except where otherwise stated and duly acknowledged. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at Universiti Sains Malaysia or other institutions. I grant Universiti Sains Malaysia the right to use the dissertation for teaching, research and promotional purposes.



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Date: 26/2/2025

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LIST OF ABBREVIATIONS AND SYMBOLS

%	Percentage
&	And
°C	Degree Celsius
>	More than
<	Less than
-	to
±	Plus-minus sign
=	Equal
x	Multiplication
µg/L	micrograms per litre
As	Arsenic
AAS	Atomic absorption spectroscopy
ACD	Allergic contact dermatitis
ADHD	Attention deficit hyperactive disorder
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
Ba	Barium
BDL	Below detection limit
BPA	Bisphenol A
Cd	Cadmium
CDC	Centers for Disease Control and Prevention
Cl	Chlorine
Co	Cobalt
CPA	Consumer Protection Act
CPSC	Consumer Product Safety Commission
Cr	Chromium
Cu	Copper
et al	and others
EN71	European Union Toy Safety Standard
EU	European Union
FAAS	Flame atomic absorption spectroscopy

Fe	Iron
FTIR	Fourier transform infrared spectroscopy
g	gram
H ₂ O ₂	Hydrogen peroxide
Hg	Mercury
HCl	Hydrochloric acid
HNO ₃	Nitric Acid
HPLC	High-performance liquid chromatography
IARC	International Agency for Research on Cancer
ICP-MS	Inductively coupled plasma mass spectrometry
IQ	Intelligence coefficient
kg	kilogram
KPDN	Ministry of Domestic Trade and Cost of Living
L	litre
LOD	Limit of detection
LOQ	Limit of quantification
mg/kg	milligrams per kilogram
mg/L	milligrams per litre
mL	millilitre
Mn	Manganese
ng/L	nanogram per litre
Ni	Nickel
Pb	Lead
PFT	Plastic food toy
pH	Measure of acidity or alkalinity
ppt	parts per trillion
PVC	Polyvinyl chloride
R ²	Coefficient of determination
RSD	Relative standard deviation
RoHS	Restriction of Hazardous Substances
Sb	Antimony
Se	Selenium
Si	Silicon
Sn	Tin

Sr	Strontium
WHO	World Health Organization
XRF	X-ray fluorescence
Zn	Zinc

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**PENGESANAN PLUMBUM, KADMIUM DAN NIKEL DALAM
MAINAN PLASTIK KANAK-KANAK MENGGUNAKAN SPEKTROSKOPI
PENYERAPAN ATOM (AAS)**

ABSTRAK

Pendedahan kepada logam berat yang terdapat dalam mainan plastik yang boleh menimbulkan risiko kesihatan yang ketara kepada kanak-kanak, menjadi kebimbangan yang semakin meningkat, terutamanya melalui tingkah laku memasukkan ke dalam mulut seperti mengunyah, menjilat dan menghisap. Tiga logam berat (Pb, Cd, dan Ni) dianalisis dalam enam sampel mainan plastik kanak-kanak menggunakan Spektroskopi Penyerapan Atom (AAS). Sampel mainan plastik disediakan menggunakan kaedah pengabuan kering dan dicernakan dengan asid nitrik dan hidrogen peroksida. Analisis menunjukkan bahawa semua enam sampel mainan plastik mengandungi Cd (0.2026 - 3.5519 mg/kg), lima daripada enam sampel mengandungi Ni (0.5581 - 6.8927 mg/kg), dan hanya satu sampel mengandungi Pb (3.4529 mg/kg). Semua kepekatan logam berat adalah di bawah had yang dibenarkan seperti yang ditetapkan dalam EN71-3:2019 oleh Kesatuan Eropah (EU). Kajian larut resap Pb, Cd, dan Ni dari sampel mainan plastik dijalankan di bawah dua keadaan suhu yang berbeza: suhu bilik dan 50°C. Sampel yang terdedah kepada suhu 50°C selama empat jam menunjukkan peningkatan tahap Pb, Cd, dan Ni berbanding sampel yang tidak dipanaskan, membuktikan bahawa suhu tinggi mempercepatkan perlepasan logam berat daripada mainan plastik. Walaupun begitu, kadar larut resap tersebut masih berada dalam had yang ditetapkan oleh EU. Penemuan ini menekankan risiko potensi penyimpanan mainan plastik dalam persekitaran bersuhu tinggi, seperti di dalam kenderaan di bawah cahaya matahari secara langsung untuk tempoh yang lama.

Walaupun mainan yang diuji dianggap selamat untuk kanak-kanak, amalan penyimpanan yang betul amat disarankan.

DETECTION OF LEAD, CADMIUM AND NICKEL IN CHILDREN'S PLASTIC TOYS USING ATOMIC ABSORPTION SPECTROSCOPY (AAS)

ABSTRACT

Exposure to heavy metals present in plastic toys which can pose significant health risks to children is a growing concern particularly through mouthing behaviours like chewing, licking and sucking. The contents of three heavy metals (Pb, Cd and Ni) were analysed in six children's plastic toys samples by using atomic absorption spectroscopy (AAS). The plastic toy samples were prepared using dry ashing method and digested with nitric acid and hydrogen peroxide. The analysis showed that all six plastic toy samples contained Cd (0.2026 - 3.5519 mg/kg), five out of six samples contained Ni (0.5581 - 6.8927 mg/kg) and only one sample contained Pb (3.4529 mg/kg). All heavy metal concentrations were below the permissible limits specified in the EN71-3:2019 set by the European Union (EU). Leaching of Pb, Cd and Ni from plastic toy samples was conducted on the plastic toy samples under two different temperature conditions: room temperature and 50°C. Samples exposed to 50°C for four hours exhibited increased levels of Pb, Cd and Ni compared to unheated samples, demonstrating that elevated temperatures facilitated heavy metal leaching from plastic toys. Despite this, the leaching rates remained within the EU limits. These findings emphasised the potential risks of storing plastic toys in high-temperature environments, such as inside vehicles under direct sunlight for extended periods. While the tested toys were deemed safe for children, proper storage practices were strongly recommended.

CHAPTER 1

INTRODUCTION

1.1 Research Background

In Malaysian Standard 2001, toy is defined as any product designed or clearly intended for use in play by children less under 14 years old (Said *et al.*, 2024). Toys play a vital role in children's development at a young age as they help to develop the physical, intelligence and social abilities of children besides bringing fun, joy and entertainment (Levesque *et al.*, 2022). However, their safety is a growing concern due to the potential of presence of toxic heavy metals such as lead (Pb), cadmium (Cd), and nickel (Ni). These metals frequently incorporated into toys for purposes such as pigments, stabilizers and coatings can pose significant health risks to children who are more vulnerable to their toxic effects due to their developing physiological systems. This includes neurological disorders, kidney complications and cancers (Akimzhanova & Guney, 2022; Igweze *et al.*, 2020).

Each age group interacts and handles toys in different ways, therefore it can lead to various exposure pathways for heavy metals such as direct ingestion or mouthing behaviour like licking, sucking, chewing or hand-to-mouth behaviour which can result in metals leaching from the toys through saliva (Gul *et al.*, 2022). In 2007, the Consumer Product Safety Commission (CPSC) issued a total of 448 recalls, and 231 or 52% of those were for toys and other children's products, leading to the year being dubbed as "Year of the Recall" (Ismail *et al.*, 2020). To make matters worse, world's renowned toy companies, Mattel Inc, recalled 436,000 toy cars alone for violations of Pb paint standards (Teagarden & Hinrichs, 2009). By the end of 2007, nearly 6 million toys were recalled due to excessive Pb levels (Schmidt, 2008).

The presence of heavy metals in toys is prevalent around the world with studies consistently detecting them at varying concentration. Cui *et al.* (2015) analysed 45 children's toys and jewelry in China including metallic, plastic and paper/wood, brittle/pliable and paint coating using inductively coupled plasma mass spectrometry (ICP-MS). Their findings showed that the total concentrations of arsenic (As), Cd, antimony (Sb), chromium (Cr), Ni and Pb were in the range of 0.22 -19 mg/kg, 0.01 - 139 mg/kg, 0.1 - 189 mg/kg, 0.06 - 846 mg/kg, 0.14 - 2,894 mg/kg and 0.08 - 860,000 mg/kg, respectively. In Nigeria, Kamara *et al.* (2023) revealed that the concentration of Pb, Cd, Cr, Ni and manganese (Mn) in 22 imported low-cost plastic toys using AAS ranged from below detection limit (BDL) - 4,838 mg/kg, BDL - 44.9 mg/kg, 0.331 - 79.8 mg/kg, 0.273 - 59.1 mg/kg and 0.205 - 31.0 mg/kg, respectively. Both studies highlighted that the levels of certain heavy metals exceeded the permissible limits established by international toy safety standards such as the EN71-3 standard set by the European Union (EU).

According to Haniff *et al.* (2022), toy safety has been a major concern in Malaysia since 2009. To address this, Malaysia has introduced its own toy safety regulations, known as the Consumer Protection (Safety Standards for Toys) Regulations 2009 (Regulation 2009) which officially came into effect on 30 January 2010. In particular, Malaysia has implemented 13 international safety standards including EU's toy safety standard regulation starting 1 January 2018 (Praveena *et al.*, 2021). With this amendment, all toys available in the Malaysian market must undergo testing for the presence of selected chemicals including heavy metals and phthalates, especially when it comes to toys intended for oral contact.

Thus, this study aimed to assess the concentration of Pb, Cd and Ni in children's plastic toys available on the Malaysian market and compare them with the international standard, the EU's EN 71-3:2019. This is because Pb and Cd are the most frequently detected heavy metals detected in plastic toys and often exceed the permissible limits. While Ni is less studied, recent research has reported concerning concentration of Ni, thereby making it important to include in this study. Additionally, the effect of temperature on leaching of heavy metals from plastic toys was explored. It is important to ensure that the concentration of heavy metals present in plastic toys remain below the safe limit as addressed by the regulation to ensure toy safety in Malaysia.

1.2 Problem Statement

In Malaysia, the market for children's toys is heavily influenced by the availability of affordable plastic toys which makes them an accessible option for many families. Although Malaysia has adopted the EN 71-3:2019 toy safety standard to ensure toy safety, non-compliance remains an issue as some manufacturers continues to use unsafe chemicals levels in plastic toys including heavy metals such as Pb, Cd and Ni. The use of contaminated recycled plastics in toy production may also result in presence of heavy metals in the plastic toys (Kang & Zhu, 2013). This situation highlights a critical gap in regulatory enforcement and compliance monitoring which compromises the safety of toys available in the Malaysian market.

The situation is further compounded by the limited availability of studies in Malaysia assessing the safety of these toys particularly in terms of heavy metals concentration. To date, one study has been conducted in Malaysia by Syed Ismail *et al.* (2017), in which they analysed Sb, As, Ba, Cd, Cr, cobalt (Co), copper (Cu), Pb,

Mn, Hg, Ni, Se, strontium (Sr), tin (Sn) and zinc (Zn) in 42 toy samples using X-ray fluorescence (XRF). However, XRF is primarily a screening tool and lacks sensitivity to detect heavy metals with very low concentration. Additionally, while the presence of heavy metals in plastic toys is well documented across the world, there is no mention of the potential impact of temperature on the leaching of these heavy metals. This represents a knowledge gap in current research as heavy metals in plastic toys can leach into the saliva of children who are more likely to place toys in their mouths, therefore increasing the risk of heavy metals to children safety and health.

1.3 Objectives

1.3.1 General Objective

The general objective of this study was to determine the presence of Pb, Cd and Ni in children's plastic toys using atomic absorption spectroscopy (AAS).

1.3.2 Specific Objectives

1. To analyse the presence and concentration of Pb, Cd and Ni in children's plastic toys using atomic absorption spectroscopy (AAS).
2. To analyse the leaching of Pb, Cd and Ni from children's plastic toys at two conditions: heated and unheated.
3. To compare the concentration of Pb, Cd and Ni in children's plastic toys with toy safety standard EN 71-3: 2019 set by European Union's Toy Safety Directive.

1.4 Significance of Study

This research is significant in assessing whether plastic toys are safe for children to play with. This is because it can provide useful information regarding the concentration of heavy metals such as Pb, Cd and Ni in the children's plastic toys, given the potential health risks associated with heavy metal exposure. Additionally, this research contributes to raising public awareness, particularly among parents, about the risks of heavy metals in children's plastic toys. This can lead parents to make purchasing choices when selecting not only entertaining but also safe toys for their children.

Furthermore, this study emphasises the importance of proper storage practices of plastic toys such as avoiding leaving toys in cars or under direct sunlight for extended periods. This promotes safer use of plastic toys and reduces potential health risks to children. In addition to its public health implications, this research also helps to ensure that the heavy metals content in children's plastic toy complies with toys safety standard and permissible limits in Malaysia. If the concentration of heavy metals in the children's plastic toys is found to exceed permissible limits, appropriate action can be taken by the Malaysian regulatory body which is Ministry of Domestic Trade and Cost of Living (KPDN) in cases of noncompliance or offences.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metal in Plastic Toys

Since the invention of plastics, they have revolutionised the manufacture of children's toys and are now becoming the primary material in the children's toys production (Jung *et al.*, 2022). Plastics toys are highly valued for their controllable flexibility, processability, durability, safety, affordability and relatively simple mass production compared to the conventional materials such as wood, metals, ceramic or natural fibres (Kundu *et al.*, 2021). These qualities have contributed to the mass production of plastic toys at lower cost which facilitates the widespread distribution and availability of plastic toys in the market worldwide. This ultimately benefits consumers particularly parents across various socioeconomic groups, as they can purchase a wider variety of plastic toys at a more affordable price for their children.

However, the increasing use of plastic in the toy manufacturing has also introduced potential health hazards to children, primarily due to the presence of heavy metals. Previous studies around the world have reported about the levels of heavy metals found in plastic toys (Al-Qutob *et al.*, 2014; Cui *et al.*, 2015; Gati *et al.*, 2014; Kang & Zhu, 2015; Igweze *et al.*, 2020; Oyeyiola *et al.*, 2017). In Pakistan, for example, Gul *et al.* (2022) found high total metal concentrations in children's plastic toys, with 83% exceeding EU permissible limits for Pb and 65% for Cd. Other toxic elements such as Cr and Ni were also detected, posing health risks. Similarly, Syed Ismail *et al.* (2017) investigated low priced toys sold in Malaysia and confirmed findings of heavy metals with different concentrations in their samples such as As (23.4 ppm), Cd (26.1 ppm), Cr (94.4 ppm), Pb (109.9 ppm) and Hg (7.1 ppm).

This is because these toxic heavy metals can enter the production process through additives or pigments used to enhance the properties and aesthetics of plastic toys such as colours, material hardness or elasticity. Another possible explanation is that some toys are manufactured using recycled waste plastic that has been contaminated with heavy metals as mentioned by Aurisano *et al.* (2021). Akimzhanova and Guney (2022) supported this, arguing that in some instances, in order to reduce production expenses, some manufactures use recycled materials from old batteries and electronic waste in the creation of new consumer products including children's toys. Kang and Zhu (2015) also highlighted how the lack of adequate supervision and the use of outdated technology in the recycling process contributed to the unsafe handling of waste materials. If this is indeed the case, the recycling process as it is currently conducted could unintentionally introduce harmful heavy metals into new plastic toys for children.

2.2 The Unique Vulnerability of Infants and Children to Heavy Metals Toxicity

Children are particularly susceptible to the adverse health effects of heavy metal exposure. Infants and children have unique developmental stages and patterns of exposure that differ significantly from those of adults, therefore this generally increases their risk of toxicity since the first years of life are a sensitive period in the human development (Pandelova *et al.*, 2012; Pereira *et al.*, 2020). As children undergo rapid growth and development of organs and tissues, their highly complex developmental processes are more sensitive to disturbed cellular processes. These organs systems are not yet fully matured and the barrier functions are not completely formed, so their bodies may be unable to repair the damage caused by toxic heavy metals (Carroquino *et al.*, 2012).

More important, the body of children is not yet capable in metabolising and excreting chemicals including heavy metals properly, keeping these chemicals or residues in their body longer (Landrigan & Goldman, 2004). Slow metabolism prolongs the exposure of emerging chemicals in their bodies which makes them more susceptible to accumulation and toxicity (Zhou & Ma, 2019). The high degree of vulnerability of children to heavy metal toxicity is also linked to higher gastrointestinal absorption than adult (Ahamed & Siddiqui, 2007). For instance, a child's gastrointestinal tract can absorb about 40% to 50% of the Pb they ingest, while adults only absorb about 10% to 15% (Sample, 2024). Additionally, children have more future years of life than most adults, thus they will have a longer life span to develop chronic diseases triggered by early exposure (Amran *et al.*, 2022).

Furthermore, children are very prone to heavy metal toxicity due to play behaviour and increased hand-to-mouth activities (Jan *et al.*, 2015). Mouthing behaviours such as licking, sucking and chewing also creates a direct exposure pathway for heavy metals from plastic toys (Shahzad *et al.*, 2022). According to Karaś and Frankowski (2018), infants (6–12 months) and toddlers (1–3 years) exhibit particularly high mouthing frequency and duration. What is noteworthy here is that, when children suck or chew on plastic toys containing heavy metals, these toxic substances can leach from the plastic toys upon contact with saliva (Guney & Zagury, 2014). Therefore, this is an area of great concern as children typically spend a high amount of time playing with plastic toys and may thus increasing their risk of exposure to heavy metals.

2.3 Law and Regulation in Malaysia

Malaysia regulates the safety of toys through Consumer Protection (Safety Standards for Toys) Regulations 2009 and its subsequent amendments. These regulations fall under Consumer Protection Act of 1999 (CPA 1999) and are overseen by KPDN to ensure that toys supplied in Malaysia market comply with the acceptable safety standard for toys (SGS, 2017). In 2016, Malaysia updated its toy safety regulations by publishing the Consumer Protection (Safety Standards for Toys) (Amendment) Regulations 2016 in the Federal Government Gazette. This amendment expanded the list of recognised international safety standards in the First Schedule, including EN71 Part 3 (Migration of Certain Elements) which has been in force since 1 January 2018 (Karpudewan, 2024).

2.3.1 Toy Safety Standard EN71-3:2019

EN71 standard is the European standard for toy safety that was first introduced in 1988. It falls under the Toy Safety Directive 2009/48/EC which is the main legislation regulating the safety of toys in the EU (Guney *et al.*, 2020) . EN71 standard sets safety criteria that toys must meet before they can be sold in any EU country. The updated EN71-3:2019 (Migration of Certain Elements) specifies permissible limits of 19 elements, including Pb, Cd and Ni (European Council, 2019). The limits are aimed to minimise children's exposure to certain potentially toxic elements. Table 2.1 outlines the permissible limit Pb, Cd and Ni in toys, expressed in in milligram per kilogram (mg/kg) toy material.

Table 2.1: Permissible limit of Pb, Cd and Ni in toys set by EU in EN71-3:2019

Element	Permissible limit (mg/kg)
Pb	23
Cd	17
Ni	930

2.4 Lead (Pb)

Pb is a bluish-gray metal that naturally occurs in the Earth's crust and non-degradable in nature. Unlike other metals such as iron (Fe) and Zn, Pb is non-essential element and has no known benefits to human body (Swaringen *et al.*, 2022). However, because of its valuable chemical and physical properties such as softness, malleability, ductility, poor conductivity and resistance to corrosion, its uses can be retraced to historical times (Wani *et al.*, 2015). The ancient Romans were the first to use Pb extensively in the production of pipes for water supply, tableware, kitchen utensils, facial powders, ointments and even as pigment. They also used Pb pots to brew grape juice syrup as sweetener for wine and cider causing such a high quantity of Pb to leach into the liquid during the brewing process, with just one teaspoonful was more than sufficient to cause chronic lead poisoning (Nadakavukaren, 2006). The extensive use of Pb has led to the belief that Pb poisoning contributed significantly to the decline and fall of the Roman empire (Cilliers & Retief, 2019).

During the 16th to 19th centuries, lead poisoning became a significant concern due to its widespread use in pottery, plumbing, boat building, windows manufacturing, weapon production, pigments and book printing (García-Lestón *et al.*, 2010). The

harmful effects of Pb on human health have been known for thousands of years yet modern uses of Pb continue to put humans in danger of exposure. Luby *et al.* (2024) pointed out in their writing that despite the phase-out of Pb from most gasoline, paint, plumbing and other consumer products by the year 2000, the market for Pb is growing due to increasing demand for low-priced Pb-acid batteries. In addition, Pb is still widely used as components in various products including pigments, cosmetics, radiation shielding, cable sheathing and solders of cans of food or beverages (Alissa *et al.*, 2024; Haniff *et al.*, 2020).

In the toy industry, Pb is often used as the most cost-effective thermal stabilizer especially for polyvinyl chloride (PVC) toys. PVC is the world's third-most widely produced synthetic polymer of plastic and it is made by combining vinyl chloride monomers units (Mohan *et al.*, 2022). One of its main problems is that chlorine radicals within its structure reacts with free hydrogen radicals to form hydrochloric acid (HCl). As a result, this reaction degrades plastic and may even damage the manufacturing equipment (Omolaoye *et al.*, 2010). Pb is hence added as it effectively stabilizes bound chlorine, therefore keeping the plastic strong, durable and resistant to degradation. However, the problem is aggravated when Pb-based paints are used to paint PVC toys (Njati & Maguta, 2019).

Despite its widespread application, Pb is toxic which contains neurotoxin, carcinogenic and has been classified by the Agency for Toxic Substances and Diseases Registry (ATSDR) as the second most toxic heavy metal after As because of its ubiquity (Zulfiqar *et al.*, 2019). Moreover, the World Health Organization (WHO) includes Pb as one of the 10 chemicals of public health concern (WHO, 2020). Once Pb enters the body, it can accumulate in bones, blood and soft tissue causing long damage. The

problem with Pb is that its toxic effects on children are quite profound as it can hinder development in a child's brain capacity, where Pb disrupts normal neurotransmitter functions (Malavika *et al.*, 2021). As explained by Heidari *et al.* (2022), Pb poisoning at low concentration can cause cognitive impairment which then leads to lower intelligence quotient (IQ) levels, increased behavioural problems including attention deficit hyperactive disorder (ADHD) and antisocial behaviour, poor attention span and learning deficiencies.

In contrast to adults, the effects of chronic exposure to Pb in children are irreversible, even after a decrease in blood levels. In other words, children who survive severe Pb poisoning may be left with permanent intellectual disability and behavioural disorders (WHO, 2024), which persist into adulthood. When Pb toxicity has reached larger amounts, it also affects the kidney particularly by damaging the proximal tubules which play crucial role in filtering waste from the body (Naranjo *et al.*, 2020; Zheng *et al.*, 2017). According to Wani *et al.* (2015), severe damage to the brain and kidney can lead to coma, convulsions and even death. And yet, the Centers for Disease Control and Prevention (CDC) has published that there is no safe level of Pb exposure for children due to the absence of a clear threshold below which adverse effects do not occur for fetuses, infants and children (Min *et al.*, 2022). Therefore, this highlights the urgency of addressing Pb exposure as a serious public health issue especially to children.

Even with strict regulation on Pb use due to its severe toxicity to children, recent research still indicates ongoing high levels of Pb in plastic toys. A total of 145 plastic toys were gathered from wholesale shops, retail shops and roadside stalls in Sri Lanka to assess for Pb contamination. In this study, it was revealed that the plastic toys contain high levels of Pb from 30.34 mg/kg to 4,469.09 mg/kg (Ratnakumar *et al.*, 2018). In a

separate study, Pb levels in 22 plastic toys in Nigeria was found as high as 4,838 mg/kg with 18% of samples exceeded the EU limit (Kamara *et al.*, 2023). These findings underscore the critical regulatory gap as high Pb levels persist in children's toys despite existing safety standard, emphasizing the urgent need for stricter enforcement.

2.5 Cadmium (Cd)

Cd is a malleable metal in the form of a blueish or silvery-white powder. However, it is a highly toxic, non-essential and non-biodegradable heavy metal with an estimated half-life of around 20 years (Khan *et al.*, 2022). Like Pb, Cd is listed as chemicals of major public health concern by the WHO. While Pb is second on ATSDR's list of harmful environmental substances, Cd is the fourth heavy metal on ATSDR's list of harmful environmental substances, but it ranks at number seven on ATSDR's list overall (Bair, 2022). Additionally, Kim *et al.* (2015) stated that Cd is considered a class 1 carcinogen by the International Agency for Research on Cancer (IARC). Despite such serious toxicity, Cd has found wide applications in various industries such as metal finishing, ceramics, fabrication of Ni-Cd batteries, neutron-absorber in nuclear power plants as well as in glass manufacturing and galvanic industry (Charkiewicz *et al.*, 2023; Godt *et al.*, 2006).

Following the increased scrutiny and stricter restrictions on the use of Pb in children's products, the manufacturers have partly switched to Cd as plastic stabilizer (Becker *et al.*, 2010). This substitution is largely due to Cd's ability to prevent the formation of HCl which can degrade plastic polymers. Furthermore, Turner (2019) noted that Cd is commonly used as an inorganic pigment in various consumer plastics because it can endure extremely high temperatures during the manufacturing process. Besides, Cd-based pigments are highly durable and produce vibrant, long-lasting colors

such as yellow, orange, red, and maroon (Tworek *et al.*, 2021). These properties make Cd pigments particularly valuable for plastics requiring superior color stability and longevity, which organic pigments may not effectively provide. However, the incorporation of Cd in plastic toy poses serious health risks for children.

One of the primary concerns regarding Cd exposure in children is its implications for kidney function in children. As the primary storage organ of poisonous substances, the kidney is always the critical target organ that exhibits initial signs of Cd toxicity causing renal tubular dysfunction and proteinuria (excess protein in urine) which may lead to kidney failure in later stages (Satarug *et al.*, 2022). Following suit with Pb, cognitive development is another critical area affected by Cd exposure. Evidence suggests that Cd can induce neurotoxic effects, leading to cognitive deficits and behavioural issues (Chandravanshi *et al.*, 2021). This includes reduced IQ, learning difficulties, attention deficits and emotional instability. Moreover, Lee *et al.* (2018) reported that Cd exposure is also associated with susceptibility to ADHD and symptom severity in school-age children.

Chandravanshi *et al.* (2021) further explained that even at low exposure levels, Cd can enhance oxidative stress with DNA damage and protein modification in early life. In addition, the detrimental impact of Cd exposure is an increased risk of developing cardiovascular diseases such as heart failure, stroke, and coronary heart disease, in addition to cancers development (Al Osman *et al.*, 2019). Moreover, Cd is recognized as an endocrine disruptor, meaning it can interfere with normal hormone function. It has been shown to influence oestrogens, thyroid and growth hormones which can lead to stunted growth and developmental abnormalities in children (Gardner *et al.*, 2013).

In earlier studies, researchers worldwide have studied Cd in plastic toys and found high concentration of Cd. For instance, Charehsaz *et al.* (2014) reported concentrations ranging from 0.37 mg/kg to 21.11 mg/kg in Turkey, while Oyeyiola *et al.* (2017) found levels between 3.55 mg/kg and 40.7 mg/kg in Nigeria. Additionally, Ratnakumar *et al.* (2018) documented even higher concentrations in Sri Lanka, with values ranging from 15.09 mg/kg to 1,140.73 mg/kg. Given its severe toxicity to children, the continued presence of Cd in high concentrations above the permissible limits raises significant safety concerns regarding the safety of the plastic toys.

2.6 Nickel (Ni)

Ni is one of the most abundant elements in the Earth's crust amounting to roughly 3% of the Earth's composition and ranking as the 24th most prevalent element in the crust of Earth (Singh *et al.*, 2024). Ni is a silver white metal with excellent hardness, malleability and ductility. Additionally, it is resistant to very high temperatures, corrosion and oxidation as well as it alloys readily and is fully recyclable (Genchi *et al.*, 2020). According to Coman *et al.* (2013), the most significant quality of Ni lies in its ability when alloyed with other metals to increase the strength and corrosion resistance of the other metal over a wide temperature range.

Due to its outstanding physicochemical properties, Ni is used in a wide range of industrial and commercial applications such as inexpensive jewellery, keys, paper clips, clothing fasteners including zippers, snap buttons and belt buckles, stainless steel household utensils, electrical equipment, armaments, coins, alloys, metallurgical and food processing industries, pigments and catalysts (Genchi *et al.*, 2020). According to Vo *et al.* (2017), Ni is used as thermal stabilizers to enhance material properties and reduce material costs in plastic.

As for toxicity, nickel is classified by IARC as human carcinogens that primarily affects the initiation processes the lung cancer development (Chiu *et al.*, 2004). Moreover, one of the most significant health concerns related to Ni exposure in children is the development of allergic contact dermatitis (ACD). According to Jacob *et al.* (2015), Ni is recognized as a leading cause of ACD from early childhood through adolescence. As Ni is a well-known skin sensitizer, repeated exposure even at low levels can lead to itchy rashes, redness, swelling and eczema (Jellesen *et al.*, 2006; Silverberg *et al.*, 2020). In 2019, 8% - 10% of children among European population suffered from Ni allergy (Lerma *et al.*, 2023). Additionally, the accumulation of Ni in the body through chronic exposure can lead to cardiovascular system poisoning and kidney disease (Denkhaus & Salnikow, 2002).

Compared to Pb and Cd which are well known for their severe toxicity and strict regulatory control, Ni contamination in plastic toys has received relatively less attention despite its potential health risks to children. Recent studies, however, have detected the presence of Ni in plastic toys at concerning concentration. For example, Wajid *et al.* (2024) reported that 5% of 22 plastic toys samples in Pakistan exceeded the EU safety limits for Ni. Another study also found that Ni was detected at a very high total metal concentrations (TMCs), with 2% of 44 analysed plastic toy samples surpassing the EU limits (Gul *et al.*, 2022). These findings suggest that while the prevalence of Ni contamination is lower compared to Pb and Cd, its presence in children's plastic toys still raises health concerns for children and cannot be dismissed as negligible.

2.7 Sample Preparation: Dry Ashing Method

Prior to analysis of analytical techniques, sample preparation methods that allow for complete decomposition of the samples and effective extraction are required for the monitoring of heavy metal content in plastic toys. Hoenig and de Kersabiec (1996) stressed these steps as the most critical part of analysis because they are responsible for the most important errors. Among the various methods available, dry ashing is frequently applied for the determination of heavy metals in various matrices, including plastic toys.

Dry ashing is a sample preparation technique that removes organic matter by heating samples in a muffle furnace capable of maintaining temperature, typically ranging from 450°C to 600°C. During this process, water and other volatile materials are vaporised while the organic components of plastics are converted into carbon dioxide and water in the presence of oxygen from the air (Barnes *et al.*, 2014). This leaves behind an inorganic residue or ash containing the targeted analytes, such as heavy metals for further analysis. This ash residue is dissolved in acids such as nitric acid (HNO₃), hydrochloric acid (HCl) or combination of acids with hydrogen peroxide (H₂O₂), which is then diluted with deionised water for quantitative determination of heavy metals using spectroscopic methods like ICP-MS or AAS (Kailasa & Wu, 2012).

One of the key advantages of dry ashing is its simplicity and cost effectiveness. This is because muffle furnaces are relatively inexpensive, and crucibles made of porcelain, quartz or platinum are easily handled (Barnes *et al.*, 2014). Compared with wet digestion methods which require large volumes of hazardous chemical reagents, dry ashing on the other hand simplifies the process by dissolving the resulting ash in a small volume of acid. This not only minimises chemical usage and expensive reagents

but also making it an environmentally friendlier option. Additionally, dry ashing is highly efficient for high-throughput analysis as it allows multiple samples to be ashed simultaneously. This method also permits the preconcentration of trace elements in the final solution, which is useful for detecting very low concentrations (Hoenig & de Kersabiec, 1996; Kailasa & Wu, 2012).

Multiple studies have utilised dry ashing method for sample preparation for plastic toys prior to analysis of heavy metal. For instance, a total of 18 plastic children's toy and baby item samples were prepared using dry ashing at 550-600°C followed by acid digestion with 70% HNO₃ (Mohammed *et al.*, 2020). In a study by Kamara *et al.* (2023), 22 low-cost plastic toy samples commonly sold in Nigeria were dried ash in a muffle furnace at 480°C and then digested with 69% HNO₃. Additionally, Gul *et al.* (2022) prepared 44 plastic toy samples using dry ashing method, followed by acid digestion with a mixture of 65% HNO₃ and 30% H₂O₂.

While the method is straightforward, one must also accept several drawbacks to dry ashing procedures such as potential loss of volatile elements and time consuming. In summary, the practicality, cost-effectiveness and simplicity of dry ashing have made it the most appropriate choice. Besides, the selection of the dry ashing method in this study was based on its demonstrated effectiveness and suitability for the determination of heavy metals in plastic toys.

2.8 Analytical Techniques for Detection of Heavy Metal in Plastic Toys

A wide range of factors were worth considering when evaluating the suitability of a technique for heavy metals detection in plastic toys. AAS is a well-established and valuable analytical technique for the detection and quantification of heavy metals in diverse matrices, including plastic toys. AAS relies on the principle of measuring the absorption of light by free atoms at specific wavelengths when in the gaseous state (Tasneem *et al.*, 2020). When analysing heavy metals using AAS, the fundamental question arises as to the sub-techniques. Flame atomic absorption spectroscopy (FAAS) and graphite furnace atomic absorption spectroscopy (GFAAS) are available which differ in their manner of atomization (Krüger *et al.*, 2024). In FAAS, the sample undergoes atomization process in a flame, with typical FAAS detection limits in the parts per million (ppm) range (Soodan *et al.*, 2014).

In contrast, the atomization process in GFAAS occurs inside small graphite furnace tube which undergoes longer heating cycle. This allows atoms to retain in the light path for an extended period of time. As a result, sensitivity and detection limits of GFAAS are significantly improved in the parts per billion (ppb) range over FAAS (Butcher, 2017). Despite the higher sensitivity of GFAAS, FAAS remains a widely preferred technique as it is faster, more cost-effective and easier to operate. The utilization of FAAS for detecting heavy metals in plastic toys has been well documented in previous research.

A study by Igweze *et al.* (2020) examined Pb, Cd and As in 30 low-cost plastic toys purchased from supermarket and street vendor in Nigeria using FAAS. Their results showed that Pb, Cd and As were present in all plastic toys with concentrations of 4.16 - 9.747 mg/kg, 1.942 - 6.5 mg/kg and 1.499 - 6.318 mg/kg, respectively. While

Mohammed *et al.* (2020) analysed six heavy metals (Pb, Mn, Ni, Cr, Cd and Cu) in 18 plastic children's toys and baby items sold in Trinidad and Tobago, Yazdanfar *et al.* (2022) examined eight heavy metals (As, Ba, Cd, Cr, Hg, Pb, Sb and Se) in 150 popular cheap priced plastic toys in Iran by using FAAS. Both studies reported wide concentrations of heavy metals in the range of mg/kg.

In addition to AAS, there are several other analytical techniques which are well suited to the determination of heavy metals in plastic toy samples such as inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XFR) spectrometry. ICP-MS is a remarkably powerful technique for investigating a variety of heavy metals in highly complex samples with very few interferences (Chen *et al.*, 2022). The principle of ICP-MS involves ionizing the sample using an argon plasma generated by an inductively coupled plasma and then analysing the ions with a mass spectrometer to determine their mass-to-charge ratios. According to Verma *et al.* (2024), interest in this technique undoubtedly related to the excellent detection power which provides extremely low detection limit, often down to parts per trillion (ppt).

Recent study by Alsaigh *et al.* (2024) reported that low-cost plastic children's toys in Riyadh were highly contaminated with chemical elements particularly Ba, Cd, Cr, Pb, As, Co, Cu, Mn, Ni, Se, Sr, Zn and Hg. The ICP-MS method used in this study demonstrated excellent performance, achieving limit of detection (LOD) of 0.001 - 14.89 µg/L and limit of quantification (LOQ) of 0.003 - 45.12 µg/L with relative standard deviation values (RSD) of 0.70 - 4.98 %. Besides highly matrixed sample, they highlighted that ICP-MS reliably determined minor and major element levels following a very simple digestion step using 65% HNO₃ and 35% H₂O₂.

Additionally, ICP-MS is capable of simultaneously analysing multiple elements, making it much more efficient for samples containing a variety of heavy metals. Al-Qutob *et al.* (2014) utilized ICP-MS to simultaneously analyse eight heavy metals (Pb, Cd, Cr, Hg, As, Se, Ba, Zn) in 50 plastic toys from Palestinian markets and 17 plastic toys from Israeli markets. This simultaneous analysis significantly reduces the time required for testing compared to AAS, which typically measures one element at a time. In this study, results indicated that 40% of the Palestinian plastic toy samples contained Pb levels exceeding permissible limits, 30% for Cd, 34% for Cr, 6% for Hg, 42% for As, 32% for Se, 20% for Ba and 40% for Zn. In contrast, 95% of Israeli plastic toy samples were safe and within the permissible limits.

In another study conducted in Hanoi, the heavy metal content in 31 imported plastic toy samples was successfully determined using ICP-MS (Vo *et al.*, 2017). The analysis revealed As, Cd, Pb, Cu, Zn, Mn, Ni and Cr was detected in all imported plastic with concentrations in a range of 0.2026 - 3.5519 mg/kg, 1.84 - 30 mg/kg, 0.27 - 86.48 mg/kg, 0.86 - 440.45 mg/kg, 2.35 - 642.69 mg/kg, 22.71 - 7,752.69 mg/kg, 9.68 - 188.33 mg/kg, 9.11 - 210.09 mg/kg and 17.45 - 303.04 mg/kg, respectively. Even so, the expensive cost and complex operational of ICP-MS due to advanced technique that requires specialized training and expertise to operate effectively have been described as its drawbacks compared to AAS (Wilschefski & Baxter, 2019).

While both AAS and ICP-MS are destructive techniques that require aqueous samples for heavy metal analyses and thus heavy metals from solid samples (i.e., plastic toys) are extracted into solutions using acids, XRF is a non-destructive technique which allows multi-element analysis without sample pretreatment (i.e., no acid digestion) in various solid samples. Therefore, it can save time in the analysis and may serve as a

rapid screening tool (Hillyer *et al.*, 2014). For instance, a total of 145 plastic toys in Sri Lanka were screened on-site for heavy metals using handheld XFR as it provided fast results, making it suitable for large scale testing of toys (Ratnakumar *et al.*, 2018). The analysis detected significant concentrations of Pb (30.34 - 4,469.09 mg/kg), Cd (15.09 - 1,140.73 mg/kg), As (15.53 - 46.02 mg/kg), Cr (15.21 - 247.78 mg/kg) and Hg (28.12 - 94.92 mg/kg) in plastic toys.

In another study, Ahmid *et al.* (2022) used a portable XRF to assess 197 plastic food toys (PFTs) from a childcare center in Boston for Pb contamination. Their findings showed concerning levels of Pb, with 8.63% of the tested PFTs exceeding the United State CPSC's regulatory threshold of 100 ppm for Pb in children's products. Unfortunately, the lack of calibration standards in the XRF analysis of plastic toys can reduce the accuracy of the measurements resulting in higher method detection limit (Lehtimäki & Väisänen, 2017). Similarly, Syed Ismail *et al.* (2017) pointed out the limitation of XRF in their study, noting its lack of sensitivity for detecting trace elements in plastic toys at very low concentrations.

The continuous reports of Pb, Cd and Ni contamination in plastic toys worldwide highlight unresolved public health concern and regulatory issues. To best of our knowledge, only one study has been conducted in Malaysia, revealing violations of existing regulatory standard. However, this study utilized XRF, which while effective, it lacks the precision of more sensitive quantitative techniques. To bridge this methodological gap, FAAS was chosen for this study as it provides fast analysis with only 10 to 15 seconds per sample, very easy to use due to its simplicity and it is cost-effective. More important, FAAS has detection limits in the parts per million (ppm) range, therefore it is highly effective and reliable. Given that permissible limits for

heavy metals in toys typically fall within this range, FAAS provides sufficient sensitivity without the need for more expensive and complex techniques such as GFAAS or ICP-MS.

In addition, this study was intended to fill a gap in existing literature by examining the effect of temperature on the leaching of Pb, Cd and Ni from plastic toys which has been overlooked in previous research. This can provide valuable insight into proper storage conditions for plastic toys. Overall, this study aimed to provide critical data for authorities to strengthen safety standards, raise public awareness and well as ensure safe plastic toys for children.

CHAPTER 3

METHODOLOGY

3.1 Sample Collection

This study complemented a previous study conducted by Nurul Farhana binti Pead in 2018 which focused on the determination of bisphenol A (BPA) in six plastic toys using high-performance liquid chromatography (HPLC). Expanding on that research, the present study aimed to further investigate the same plastic toy samples by determining the presence of heavy metals using AAS. These samples were originally purchased from supermarkets around area of Kubang Kerian, Kelantan. Plastic toys intended for children were specifically selected with a focus on toys that likely to be chewed, sucked or licked by children.

The toys were chosen to be representative for the main exposure pathway as object mouthing is a common behaviour for children less than five years old. The collected toys were predominantly made from hard and soft plastics/polymers, and the price was between low and moderate considering accessibility to children from middle- and low-income households. During sample collection, information on packaging of plastic toys was documented to assess for any misleading or contradictory claims about their safety. The details of the plastic toy samples are given in Table 3.1 and Figure 3.1 shows the plastic toy samples used in this study.