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GHANA

DEPARTMENT OF BIOCHEMISTRY AND BIOTECHNOLOGY

ANALYSIS OF METAL CONTENT OF SEIZED COCAINE IN GHANA

By

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A thesis Submitted to the Department of Biochemistry and Biotechnology, College of Science, in partial fulfillment of the requirement for the degree of

MPHIL. FORENSIC SCIENCE

NOVEMBER , 2018

DECLARATION

I hereby declare that this submission is my own work towards the MPHIL and that, to the best of my knowledge; it contains no material previously published by another person, nor material which has been accepted for the award of any other degree of the university, except where due acknowledgement has been made in the text.

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ACKNOWLEDGEMENT

My utmost gratitude goes to the Almighty God for his strength and guidance throughout my studies. I am most grateful to my wife, Mrs. Bianca Bentil for the encouragement she gave me and also to my parent, Mr. and Mrs. Joseph A. Bentil and the family for their advice throughout the duration of my studies.

My sincere gratitude also goes to my supervisors Dr. Nana Asiedu (Department of Chemical Engineering, KNUST) and Mr. James Ataki (Visiting Lecturer, Department of Biochemistry and Biotechnology, KNUST) for the consistent guidance and advice, which made it possible for the completion of this thesis. I thank the entire staff of the Department of Biochemistry and Biotechnology, KNUST and Forensic Science tutors for their encouragement. My gratitude also goes to the immediate past Executive Secretary of Narcotic Control Board, Mr. Akrasi Sarpong and Mr. Martin Sotoro and Mr. John Dankwah of Ghana Standards Authority for providing samples and assistance in the data analysis.

The support provided by my employer, the Managing Director of Aspee Pharmaceuticals Limited, Mr. Aboasu Amponsah-Kodua is also much appreciated.

Big thanks also go to my course mates for their contributions in diverse ways to the success of this work.

ABSTRACT

The trafficking of cocaine has become a global challenge now and Ghana is no exception. Cocaine is a whitish powder, which is, produced both from natural and synthetic means. The aim of the project was to study the metal content of seized cocaine in Ghana and the data used for batch identification. Ten metals namely Pb, Cu, Mg, Mn, Cr, As, Ni, Fe, Co and Ca were analyzed in 37 cocaine samples which were sampled from seizures made from 2010 to 2014 and samples selected based on within-seizure and between-seizure classifications. Seized cocaine samples were obtained from Ghana Standards Authority by the help of Narcotic Control Board of Ghana. All seized illicit cocaine samples used were classified under natural cocaine. Analyses of the metals were done using ICP-MS and data analysis done using ANOVA at 95% confidence level. The results showed that, Calcium recorded the highest amount in all the samples with a mean ppm value of 64.94±54.60 with Magnesium, Zinc and Iron recording moderate amounts. All the samples analyzed contained Calcium since lime is known to be used as one of the additives in the production of cocaine. All the cocaine samples, which were sampled, based on within-seizure classification under class A showed no significant differences between each pair. With three sample pairs under class B in the within-seizure classification, one of the pairs, 10_{3A} and 10_{5B} showed no significant differences between them even though they were sampled from two different packages from the same seizure. Five samples from five different seizures also showed significant difference among them showing that they came from different batches or origin. It could be confirmed that seized cocaine contained some poisonous heavy metals like Lead, Arsenic and Chromium, which had amount that could affect the user. Based on the data gathered from the within-seizure class A group, it could be proposed that a missing cocaine could be identified by its metal content if no adulterants were added during the time it could not be found. With the information on the metal content of cocaine, the identity of seized cocaine can be achieved with the purity during forensic screening in order to protect the cocaine during investigations.

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1.0 INTRODUCTION

Illicit drug trafficking has become a global problem in recent years. Cocaine is one of major concerns because most of the seized cocaine samples are classified under illicit natural cocaine because it is produced from the coca plant (UNODC, 2012). According to UNODC and Interpol recent publications, Colombia, Bolivia and Peru are the leading producers of illicit cocaine because the coca plant strives very well in these countries.

Coca plant grown by South American countries like Argentina, Bolivia, Colombia, Ecuador and Peru falls in the Erythroxylaceae family. It has so many medicinal uses including pure cocaine, which is often referred to as pharmaceutical cocaine with purity of 99.5% used for medical treatment. On the contrary, coca plant is the starting material for the production of cocaine. Cocaine as an illicit drug is one of the most commonly abused illicit drugs in the United States as documented by the National Institute on Drug Abuse., (2012) and gradually Africa is becoming a victim.

West Africa is often used, as a transiting point to transport illicit cocaine to Europe and Ghana happens to be part. In Ghana, aside battling with the issue of illicit cocaine trafficking to and from our harbours and airports, missing of seized cocaine in police custody has become the new challenge. On April 28, 2017, it was reported by The Finder, one of Ghana's news agencies that, 10 bags of suspected cocaine, each weighing 50 kg hidden in a consignment of rice have vanished from the Tema port under mysterious circumstances. This is just one of the numerous cases that are reported concerning missing cocaine in Ghana.

It is useful to know if an illicit drug sample comes from the same batch as a drug whose origin is already known in order to determine the source of illicit drug supply and thus to discover drug trafficking routes. The parameters for determining the origin of illicit cocaine can be based on the fact that the cocaine sold on the market comes with different kind of constituents, which can be classified as contaminants, adulterants, impurities and additives (Bermejo-Barrera *et al*., 1999).

Investigations on organic substances i.e. impurities, additives and adulterants have been conducted to establish the origin and batch of illicit cocaine. Cocaine seized in Madrid during the period from September 1985 to May 1987 contained about 52% of lidocaine as adulterants (Gomez and Rodriguez, 1989). Also in 1997 in Sao Paulo, Brazil, several adulterants and additives were identified in 389 cocaine samples analyzed (Carvalho and Midio, 2003). Several analytical methods such as Gas chromatography (GC) and Ultra Violet (UV) spectrophotometry have been used in identifying adulterants in illicit drugs (Campanella *et al*., 1996).

Quite recently attention has been shifted on contaminants in illicit cocaine as a form of identifying its origin. Contaminants are present in cocaine as a consequence of contamination during the preparation of the final product from the coca leaves. The contaminants are usually classified into two groups namely biotic and abiotic contaminants. Microorganisms such as fungus and bacteria are classified under biotic contaminants whereas metals or inorganic elements often make the abiotic contaminants (Bermejo-Barrera *et al*., 1999).

Elements are found everywhere so in drug profiling, an elemental profile is only one the various methods to be used in distinguishing one sample from another. An analytical pilot

study conducted by Violante *et al*. (1992), the authors proposed that traced abiotic contaminants in cocaine and heroin could be used in characterizing illicit drugs. Electrothermal atomic absorption spectrometry (Bermejo-Barrera, 1996) and flameless atomic absorption spectrometry (Bermejo-Barrera, 1999) as techniques have been used to account for the amount of lead and chromium in illicit drugs respectively.

The use of atomic absorption spectroscopy (AAS) in identifying and quantifying metal content in illicit drugs was employed but the operation of the instrument was tedious since metals had to be determined one after the other. Due to this problem, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has been known to demonstrate powerful resolution and also analyse lot of metals in a single run. This technique of ICP-MS was recently employed in identifying 16 inorganic elements in a total of 96 heroin samples seized in 2013-2014 in Malaysia (Kar-Weng *et al*., 2016).

1.1 PROBLEM STATEMENT

Big seizures of cocaine been made in Ghana according to data from Narcotic Control Board has lead to loud public outcry. To make matters worse some of the seizures got missing leading to the set up of two Committees of Inquiry by the Government of Ghana to establish the whereabouts of the exhibits. Due to lack of data on seized illicit cocaine samples, it has become very difficult tracing missing cocaine samples. Up to date, purity is the only analysis done on the seized cocaine, which is not enough marker for identification of batch. The purity of cocaine changes in event where there is adulteration. Purity is the amount of pure cocaine in the cocaine sample or batch. Substances like lactose and baking soda are sometimes added to either increase the amount of cocaine for more money or to

change the identity of the cocaine. Due to this problem another method of identifying cocaine is necessary thus the metal content approach which may increase the chances of identification of particular cocaine sample.

1.2 OBJECTIVE

To study the levels of trace and heavy metals in seized illicit cocaine in Ghana from 2010 to 2014.

1.3 SPECIFIC OBJECTIVES

- To quantify the metal content as a model of batch identification for illicit cocaine.
- To propose a model for the identification of missing cocaine using the metal profile.

1.4 JUSTIFICATION

It is important to know if illicit cocaine comes from the same batch if the origin is already known in determining the source of illicit drug supply. Production of illicit cocaine allows the introduction of metallic contaminants, which is important in determining the source and the trafficking routes of the illicit cocaine sample in question (Tanner-Smith, 2006). Metal content has also been used in identifying seized cocaine samples from the same manufacturing bulk or batch using pattern recognition techniques (Bermejo-Barrera *et al*., 1999). In Ghana no such work has been done on the seized illicit cocaine samples so this experiment can help in solving some of the missing cocaine sagas in the future if it may happen.

CHAPTER TWO

2 LITERATURE REVIEW

2.1 WHAT IS A NARCOTIC DRUG?

Narcotics are drugs that are very addictive and reduce one's perception of pain by inducing euphoria. Narcotics can be defined as any drug that has a silent sensation or better still produces insensibility. Narcotics often refer to opioids considering all natural or synthetic drugs with morphine like similarities (Beers and Berkow, 2002).

Narcotics are the oldest strongest analgesics known to the world. Opium poppy (*Papaver somniferum*) has been mentioned by Ancient Sumerian and Egyptian medical texts as early as 4000 B.C. as the source of milky fluid known as opium latex. The opium latex was given to people to relieve them of coughs and insomnia and also easing pain. Purified form of opium latex comes as a whitish powder that is crystalline having a bitter taste. It was thought to contain about between 10 - 20% morphine (Beers and Berkow, 2002).

Narcotics are known to be central nervous system depressants. These drugs are powerful additives and often induce euphoria state. In few days, considering the use of narcotics, the human body develops tolerance; in effect higher doses are required to arrive at the same effect. Until recently, countries have strict laws about the cultivation and the distribution of narcotic drugs because of their addictive effect (Beers and Berkow, 2002).

2.1.1 CLASSIFICATION OF NARCOTICS

Narcotics are classified into three main groups with reference to their origin:

- Natural derivatives of opium including morphine and codeine.

- Partially synthetic drugs with morphine as the base.
- Synthetic compounds that resemble morphine in their chemical structure: These include fentanyl (Duragesic), levorphanol (Levo-Dromoran), meperidine (Demerol), methadone, and propoxyphene (Darvon) (Beers and Berkow, 2002).

2.2 THE COCA PLANT

Coca belongs to the family Erythroxylaceae, which is native to the western South America. Coca, which is produced from the coca plant, is a world known plant for its psychoactive alkaloid. This alkaloid is known as cocaine. The coca leaves has an alkaloid content estimated between 0.25% and 0.77%. The indigenes of South America utilize coca plant as a form stimulant, as found in a beverage like coffee, as a source of energy (Plowman, 1979). The plant grows to a height of 2 to 3m. The coca plant has straight branches, with thin, opaque and oval leaves, which taper at the extremities. The coca plant has small flowers on a short stalks. It also has colourful petals often yellow or white. The flowers develop in red berries at maturity. The larvae of the butterfly usually feed on the leaves of the coca plant (Plowman, 1979).

The coca plant is sometimes chewed which has a very good after taste in the mouth and gives a sweet scent. The chewing is often done with the addition of some substances like soda aiding the release of the content of the leaves. The extraction of cocaine from the coca plant requires a number of solvents. Acid/base extraction is often the chemical process.

2.2.1 IMPORTANCE OF THE COCA PLANT

2.2.1.1 Medicine

Coca plant has traditional uses. They are used to manage fatigue. It is also effective against what is known as altitude sickness (Blickman, 2014). The coca leaves were also considered to alleviate pain as known for anesthetics and analgesics. The coca plant has high calcium content which often make it suitable for the treatment of bone fractures (Blickman, 2014).

2.2.1.2 Nutrition

Coca leaves may have some nutritional properties. It contains essential minerals such as Potassium, Phosphorus, Vitamin, and Calcium. It also contains protein and fiber that are also very essential for the development of the body. Traditionally people were chewing the leaves raw to get these nutrients (Plowman, 1979).

2.2.1.3 Religion

Among some people of Peru, Bolivia, Ecuador, Colombia, northern Argentina, and Chile, Coca plant has been vital part of their religious activities. Moreover, there has been documentation of the use of coca in shamanic rituals whenever the local native population cultivates the plant (Blickman, 2014).

2.2.1.4 Commercial and industrial uses

Coca is used in the cosmetic and food industries. In the food industries, it is often used in the manufacture of coca teas, cookies, granola bars and hard candies, just to mention a

few. Also in the production of Coca-Cola, coca leaf is used in their processes as a form of flavour.

2.3 COCAINE

Cocaine, also known as benzoylmethyl ecgonine, is a crystalline tropane alkaloid obtained from coca plant leaves.

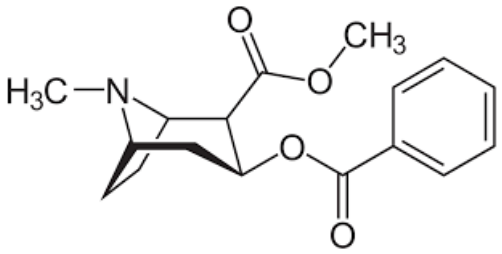

Figure 2.1 Structure of cocaine (source: UNODC, 2012)

Synonyms: [1R-(*exo*,*exo*)]-3-(Benzoyloxy)-8-methyl-8-azabicyclo[3.2.1]octane-2-carboxylic acid methyl ester

3β-Hydroxy-1αH, 5αH-tropane-2β-carboxylic acid methyl ester benzoate

Ecgonine methyl ester benzoate

l-Cocaine

β-Cocaine

Benzoylmethylecgonine

$C_{17}H_{21}NO_4$

Molecular Weight = 303.4 (base), 339.8 (hydrochloride)

Melting point: 98°C (base), 195°C (hydrochloride)

Table 2.1 Solubilities of cocaine in various solvents (1g/ml)

Solvent	Cocaine base	Cocaine hydrochloride
Water	Slightly soluble (1 in 600)	Soluble (1 in 0.4)
Ethanol	Soluble (1 in 6.5)	Soluble (1 in 3.2)
Diethyl ether	Soluble (1 in 3.5)	Practically insoluble
Chloroform	Soluble (1 in 0.7)	Soluble (1 in 12.5)

(Source: UNODC, 2012)

Cocaine is known as an appetite suppressant and a stimulant of the central nervous system. Cocaine comes in the form of a crystalline powder and has a white or off-white colour. It is often fine, and rarely showing dampness (UNODC, 2012).

Internationally trafficked cocaine is rare in adulteration with purity often around 80-90%. For international trafficking purposes, adulteration and transformation of cocaine usually mean the addition of powders or look alike substances, which are often uncontrolled. Most of the commonly used ones are sugars, procaine, lidocaine and caffeine. The process of adulteration does little to the physical appearance of the cocaine. This is so because almost all known adulterants are white powders similar to the cocaine (UNODC, 2012).

2.4 TYPES OF COCAINE

There are two types of cocaine namely licit and illicit and according to The United Nations Office on Drugs and Crime (UNODC) the distinction between licit and illicit cocaine is only attributed to the use.

2.4.1 Licit cocaine

This is also known as pharmaceutical cocaine. Licit cocaine has purity around 99.5% and has very little or no impurity content.

2.4.2 Illicit cocaine

The term illicit cocaine is used to describe cocaine, which is controlled internationally and may or may not have any medicinal properties but are still produced, trafficked or illicitly used.

Illicit cocaine can be classified into two groups' namely natural and synthetic cocaine.

2.4.2.1 Illicit Natural cocaine

It is produced from the coca plant. It accounts for more than 99.99% of all seized exhibit (Casale and Klein, 1993).

2.4.2.2 Illicit Synthetic cocaine

It is produced from synthetic materials other than the coca plant. E.g. production of 2-carbomethoxytropinone (Casale and Klein, 1993).

2.5 PRODUCTION OF COCAINE

2.6 2.5.1 Illicit Cocaine Production

2.7 2.5.1.1 Illicit Natural Cocaine Production

Below are the three major steps employed in the production of illicit cocaine form natural source:

1. The coca paste extraction.
2. Purification process of changing Coca paste to coke base.
3. Coke base conversation to cocaine hydrochloride

The three production steps outlined above is completed in separate laboratories. The production of the three end products from the three steps above (coca paste, coke base and cocaine HCl) can be achieved from various production methods with variations from one laboratory to the other. For the production of illicit cocaine there are no static method or process. Since the inception of the manufacture of cocaine there has been a lot of evolvement of the method, which gives the same final product. It should be noted that the process of achieving the illicit cocaine is no more a secret procedure as widely known before.

2.5.1.1.1 Production of Coca Paste

For the production of coca paste from the coca leaf, there are two generally known methods employed. These methods are solvent extraction and acid extraction. The solvent extraction method is an old methodology, which was used in the early 20th century and was employed commercially in Colombia, Peru and Ecuador, which are the countries with the early history of cocaine production. Acid extraction method is a more recent method but yet a robot and labour intensive procedure which uses less organic solvent in the manufacturing procedure.

2.5.1.1.1.1 The Solvent Extraction Technique

The coca plant leaves are cut and soaked with lime or carbonate salt, which are inorganic base. With very small amount of water, the content is placed in a large barrel usually plastic. The inorganic base is added to produce the free base form of the cocaine. Another inorganic solvent especially kerosene or to a larger extent gasoline which is added afterwards to dampen the slurry of the coca leaf. It is then left to stand for three days amidst intermittent stirring, thus resulting in the extraction of the cocaine base.

The efficiency of the cocaine base extraction is based on two important factors. These factors are; the time it takes for the leaves to be in the extraction solvent and how small the leaves were chopped. The most common machines used for these two processes are leaf mulchers for the maceration or chopping and cement mixers for the extraction. Filtration, pressing, and siphoning are some of the procedures employed to remove the solvent from the system after the extraction procedures. The solution obtained after the extraction procedure is often organic which may contain some amount of small vegetable matter, which can be further removed through filtration.

Back extraction is performed on the large volumes of the solvent obtained from the leaf extraction using a calculated amount of dilute sulfuric acid. The solution is then mixed thoroughly for maximum 10 minutes, which is then allowed to stand for some time to resettle. There is then conversion of the free base cocaine to the sulfate form by the sulfuric acid, thus dissolving in what is known as the aqueous layer. After this the known residual organic solvent is then carefully separated. The cocaine sulfate solution is an

often yellowish-brown mixture, which is often known in the industry as agua rica (Casale and Klein, 1993).

Lime, carbonate or caustic soda is used reaching the final phase of the coca paste isolation. The basic solution is added into the mixture containing the agua rica slowly while stirring. In this process there is the neutralization of the sulfuric acid left in the mixture containing the cocaine sulfate that changes the cocaine sulfate into its free base form, which then precipitate out of mixture as a yellow coloured product. The final product is known as coca paste (Casale and Klein, 1993).

The coca paste contains other components especially alkaloids which are not cocaine. This makes the purity of the cocaine from 30% to 80%. Carbonate salts are normally and widely used to neutralize the agua rica solution. They are used because they have their own endpoint as indicators. The carbonate salts addition to the mixture of the cocaine sulfate and sulfuric acid causes vigorous foaming and discharge of a gas often carbon dioxide, which normally shows the endpoint. The endpoint is the point where the addition of more carbonate salt does not cause foaming of the mixture.

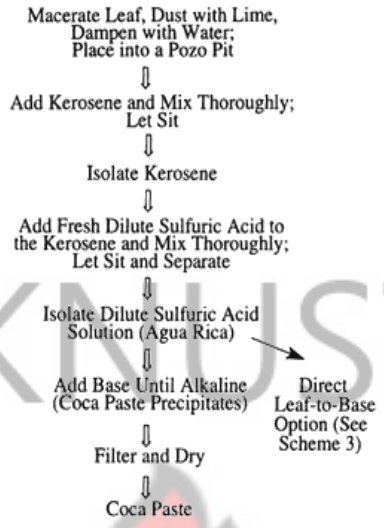

Figure 2.2 Production of coca paste through solvent extraction technique (Source: Casale and Klein, 1993)

2.5.1.1.1.2 The Acid Extraction Technique

In this technique, the leaves from the coca plant are chopped and put in a pit containing dilute sulfuric acid enough to cover the leaves. People getting inside the pit to step on the coca leaves for about 1 – 2 hours sometimes do the maceration in a pit. As a result, the free base cocaine form that is trapped in the leaves is converted to the sulfate form of the cocaine by the acid, which ends up dissolving in the aqueous medium. The acid extraction depends on two important steps namely; how long the leaves were in contact with the acid i.e. sulfuric acid and the force used by the people who stomped the leaves in the pit (Casale and Klein, 1993).

After the stomping the coca juice is brought out and filtered to remove all leaves. As it is done in the solvent extraction process, excess carbonate is added for the neutralization of the remaining acid in the mixture and the cocaine sulfate in order to set the coca paste. As

in the solvent extraction process, end point is also monitored in this technique. It is checked through spot testing using very small amount of the solution with an ethanolic solution of phenolphthalein (Casale and Klein, 1993).

Kerosene is still used on the residual coca paste through back extraction. The mixture with kerosene is mixed for roughly 10 minutes and left to stand till separation. The kerosene layer is then processed just like the solvent extraction technique. The acid extraction technique goes through about 3-5 extractions of the leaves. This is done after stomping of the leaves in the pit with fresh sulfuric acid. The final product agua rica is then handled the same way as the solvent extraction technique.

The generation of coca paste using the acid technique is the same as the solvent technique with the purity of 30 – 80%. The acid technique has some advantage over the solvent extraction technique due to the fact that, it uses less amount of organic solvent but the disadvantage is that it is more labour intensive.

The two main extraction procedures i.e. solvent extraction and acid extraction produce coca paste, which chemically has a gummy consistency and short shelf life. It is broken down into a liquid with an unpleasant odor normally oily when it is continuously exposed to excessive heat and humidity. The clandestine operators know this problem so they quickly process the coca paste into coke base possibly storing it in agua rica form for further production processing (Casale and Klein, 1993).

Figure 2.3 Production of coca paste through the acid extraction method (Source: Casale and Klein, 1993)

2.5.1.1.2 Coke Base

A purification process is employed in obtaining coke base through the chemical conversion of coca paste. After production, the by products consist of inorganic and alkaloids/ impurities which are normally *cis*- and *trans*-cinnamoylcocaine, obtained from the leaves through extraction. The cocaine content tends to have a poor quality with respect to colour and appearance if the impurities are not carefully removed from the final product.

Re-dissolving in a calculated amount of sulfuric acid, which is diluted, makes a fresh reconstituted agua rica solution, thus some of the coca paste as noted previously which has a yellowish brown colour similar to beer. The pH of the solution is sometimes increased by carefully adding a base with the use of a powerful oxidizing agent like potassium

permanganate; the solution obtained is then titrated. The solution gives an intensely purple colour in water due to the potassium permanganate as the oxidizable impurities which are alkaloids in the coca paste reacts with it reducing it to obtain manganese dioxide which is brown-black in colour and insoluble which is normally seen as a precipitates in the mixture.

After the titration with the permanganate, filtration of the manganese dioxide precipitate is performed. The resulting solution, which is colourless and slightly acidic known as oxidized agua rica is treated with dilute ammonia, which is a base amid stirring. With some remaining cocaine sulfate and sulfuric acid in the solution, the ammonia neutralizes them in effect, precipitating the coke base, which is then filtered and after that drying takes place.

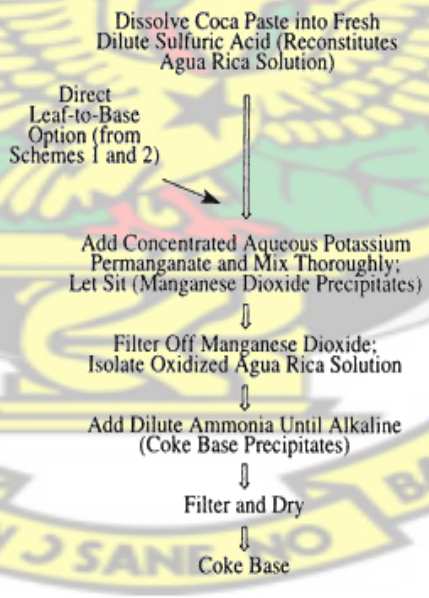

Figure 2.4. Production of the coca base (Source: Casale and Klein, 1993

2.5.1.1.3 Cocaine Hydrochloride

The quality of the final product produced from the previous methods reflects the quality of the coke base. As a result, the coke base is always double checked before converting it into cocaine hydrochloride. As a result of its illegality the illicit cocaine hydrochloride production is always done in large amounts of small batches instead of big batches. A lot of the production can be achieved in 24 hours running shift. There is no single process validation for the cocaine hydrochloride production since the procedure varies from laboratory to another especially with the solvent use. Nonetheless, a classical production uses diethyl ether to dissolve the coke base, which is then filtered from all possible impurities. Addition of equal amount of acetone in a quantity of concentrated HCl is added to the prepared solution. The HCl reacts with the coke base to resulting in the formation of cocaine hydrochloride, which comes out as a precipitate as white crystals.

Large volumes of the HCl is avoided in the reaction which can result in development of yellowish colour especially acetone affecting the final appearance of the cocaine hydrochloride. Placing it in hot water bath can reduce the total reaction time of the production. A technique, which normally results in a reduced quality of the final cocaine hydrochloride product especially affecting the appearance. When the crystallization process is complete, the cocaine hydrochloride is filtered and dried for the intended use. Due to high cost, the solvents used in the production process are often recycled for use.

With the classical solvent combination discussed earlier, there are some critical factors that need consideration;

1. The coke base solubility in solvent A

2. The level of mixing of solvent B with the concentrated HCl

3. The level of insolubility of the cocaine hydrochloride in the A + B solvent combination.

Some of the common solvent used for chemical productions and also used for illicit cocaine production are methyl ethyl ketone, ethyl acetate, benzene, etc. The purity of the cocaine hydrochloride produced ranges around 80 to 97% with an off-white to white colour as a crystal powder similar to the pharmaceutical cocaine, which is legal or licit.

Figure 2.5 Illicit cocaine hydrochloride production from coke base (Source: Casale and Klein, 1993)

2.5.1.2 Illicit Synthetic Cocaine production

Aside the natural synthesis of cocaine, it can also be produced through synthetic means clandestinely. This is outlined below in three major steps;

1. 2-carbomethoxytropinone production

2. Methyl Ecgonine conversion

3. Cocaine benzoylation.

The synthesis of the cocaine through this process produces racemic diastereomers of which (-) – cocaine is the physiologically active enantiomer. The production of 2-carbomethoxytropinone employs the ring coupling Mannich reaction. The method uses methylalmine succindialdehyde and acetone dicarboxylic acid monomethyl ester. It is then mixed in a buffered aqueous solution at 25°C. The solution is made to stand for 2 days, and then made basic and chloroform extraction is later done to obtain 2-carbomethoxytropinone with tropinone being the major impurity. The enantiomers are then obtained by adding (-) and (+)- tartaric acid.

In the conversion of the 2-carbomethoxytropinone to methyl ecgonine in an ice cold dilute sulfuric acid, the 2-carbomethoxytropinone is dissolved and later reduced to methyl ecgonine with 1.5% Na/Hg combination with pH of 3.5 at 5°C. The pH and temperature are critical conditions in this reaction. Changes may result in decarboxylation of 2-carbomethoxytropinone to tropinone, which reduces to the two products pseudotropine and tropine. Also there is c-2 epimerization of methyl ecgonine to pseudoecgonine methyl ester.

The solution is allowed to stand for several hours, then made basic, chloroform extracted and evaporation done to obtain two components, which are methyl ecgonine and pseudoecgonine methyl ester, which are normally oily in an approximate ratio of 3:1. The pseudoecgonine methyl obtained is precipitated by adding diethyl ether and discarded through filtration. After that the filtrate obtained is carefully evaporated and afterwards

dissolved in an amount of diethyl ether, which then results in the conversion to the hydrochloride.

This is the final step where there is Benzoylation of the methyl ecgonine to cocaine. The Benzoylation is done with pyridine containing benzoyl chloride near 0°C. The solution is allowed to stand for a day then allowed to cool to room temperature of around 25°C. There is precipitation of cocaine hydrochloride/pyridine hydrochloride by diluting the resulting solution with diethyl ether. The complex is further washed with some amount of ether to discard of excess benzoic acid. After that the resulting solution is then changed to basic by adding dilute ammonium hydroxide and further extracting with methylene chloride. After that the extract is evaporated to obtain the cocaine base which is then dissolved in diethyl ether/acetone 1:1 and then converted to the cocaine hydrochloride by adding concentrated HCl.

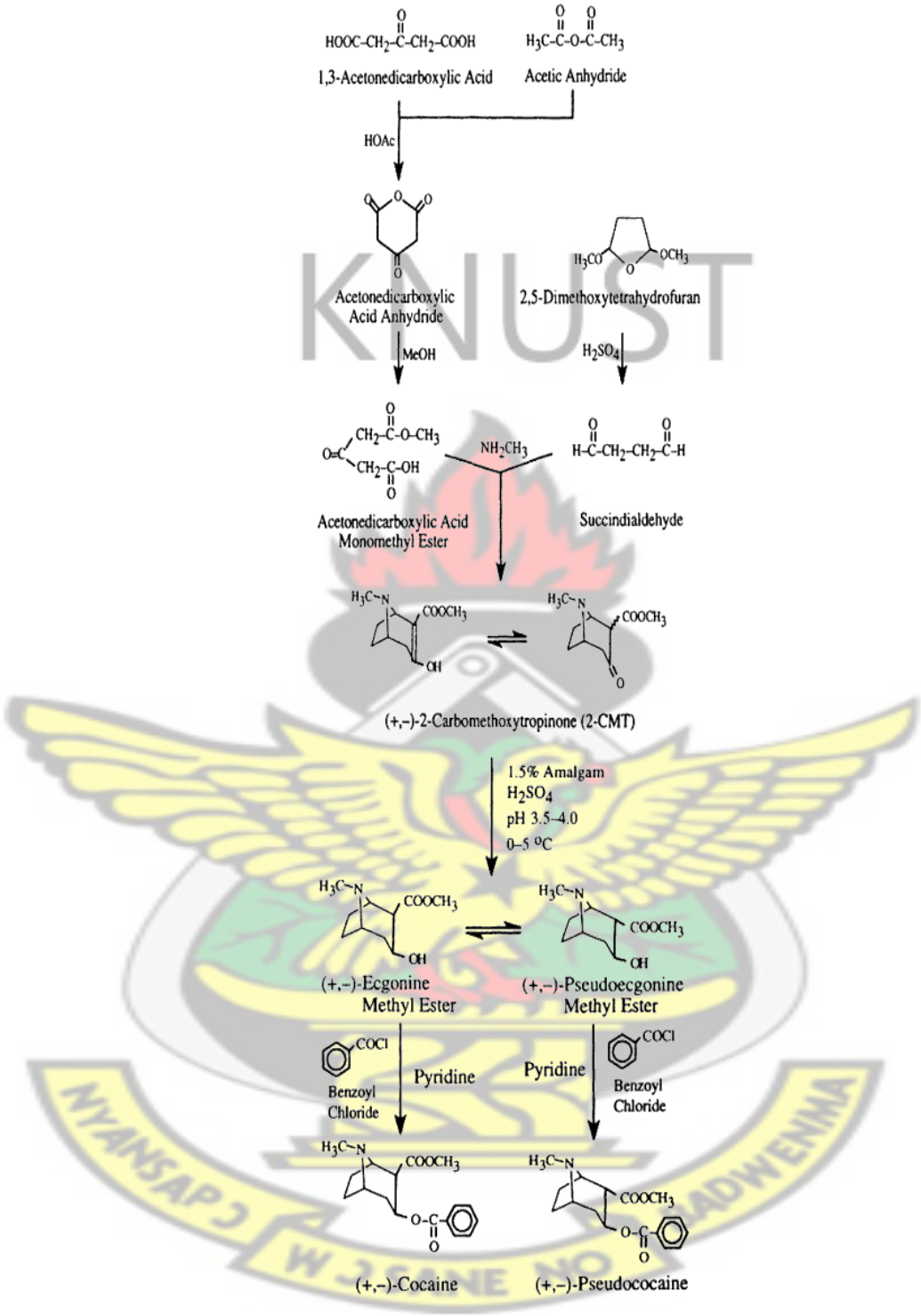

Figure 2.6 Illicit production of synthetic cocaine (Source: Casale and Klein, 1993)

2.5.2 Production of Pharmaceutical Cocaine (Licit cocaine)

Pharmaceutical cocaine production involves a lot of processes mainly involving re-crystallization and purification steps. It is normally the by-product form the extraction of coca industrially often in the soft-drink industries. The purity is around 99.5% (Casale and Klein, 1993).

2.6 DIFFERENTIATION BETWEEN LICIT FROM ILLICIT COCAINE FROM FORENSIC PERSPECTIVE

Illicit cocaine normally from the natural source accounts for about 99% of all the seized cocaine recorded as compared to synthetic cocaine or the pharmaceutical cocaine. The pharmaceutical cocaine often seen is the conversion of the drug in the form of illegal prescriptions. There uniqueness especially with the method of production of both the licit and the illicit cocaine form the forensic point of view. This helps in detailed forensic investigations involving all the forms of cocaine from these sources (UNODC, 2012).

2.7 GLOBAL SOURCE OF COCAINE

The large amount of cocaine globally comes from countries that cultivate high amount of the coca plant. According to reports by UNODC, Colombia, Peru and Bolivia are the countries that have high amount of cocaine production. In 2008, Colombia, which is the world's largest cultivator, reported a significant decrease in coca plant, which brought the total of world's coca cultivation down by approximately 8% (UNODC, 2009).

The world's majority of cocaine seizures were recorded in North and South Americas, nonetheless there was a variable decline in trafficking encountered regarding North

America. In view of this decline the prices of the cocaine on the market rose resulting in low purity levels. In that period USA recorded significant decline in cocaine use by its addicted populace. It was estimated in 2007 worldwide that cocaine users using the product at least once in their lifetime ranged between 16 and 21 million (UNODC, 2009).

2.8 LABORATORY TEST FOR SEIZED COCAINE SAMPLES

Cocaine samples as exhibits are normally powdery form and are known to have adulterants such as lidocaine or sugars such as mannitol and lidocaine known as a medication used to numb tissues in a specific body area. There are several tests used to test for cocaine in seized exhibits. Some of the testing methods are as Scott's colour test, Thin Layer Chromatography (TLC), Fourier-Transform Infrared spectroscopy (FTIR), Gas Chromatography coupled with Mass Spectroscopy (GC-MS) and High Performance Liquid Chromatography (HPLC), which are methods suitable for the positive identification of seized cocaine.

2.8.1 Presumptive tests

They are fast screening procedures to indicate the presence or absence of cocaine in a test sample.

Colour test

Compounds with a particular chemical structure produce colour reactions. Positive results to colour tests are not confirmative result for the presence of cocaine but just a presumptive test. Cocaine may be present or not. The colour test for cocaine is called the Scott's test, which contains a modified cobalt Thiocyanate compound.

2.9 HEAVY METALS

Heavy metals are known to occur naturally in the environment. The earth's ecosystem contains varying amounts of heavy metals in specific distributions. Heavy metals are normally in their elemental form and some are volatile. Some can also be transported in large amounts because they are normally found attached to fine particles (Nriagu and Pacyna, 1988).

Between the years of 1850 and 1990, three metals namely copper, lead and zinc production increased 10-fold, which was as a result of human activities that greatly changed the biochemical cycle and the balance of these metals (CACAR, 2003). The influence of human activities on the environment has become the major source of heavy metals. Some of these activities are but not limited to various industrial processes, mining, foundries, and smelters, combustion of fossil fuel and gasoline, and waste incinerators (Nriagu and Pacyna, 1988).

2.9.1 LEAD

On the periodic table, Lead belongs to group IVA. For metallic characteristics of this group, lead has the most. Lead is considered to be the most abundant transition metal on the periodic table (Greenwood and Earnshaw, 1984). It has 82 as its atomic number and a Molecular Mass of 207. It has two oxidation states (+2 and +4) and four naturally occurring isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb), with isotope ^{208}Pb being the most abundant. It has melting point of 327 ^{0}C, a density at 20 ^{0}C of 11.34g/cm^{3} and boiling point of 1755^{0}C.

Lead is normally common in the environment and found abundantly in soil. People living near hazardous waste sites through drinking water, food or swallowing dirt-containing lead may be exposed to lead and chemicals that contain lead (ATSDR, 1999).

2.9.2 CALCIUM

Calcium has an atomic number of 20 and was discovered in 1808 by Humphry Davy. Ever since, different isotopes of the element have been discovered. Among all the isotopes, the stable ones are ^{40}Ca (96.94%), ^{44}Ca (2.1%), ^{42}Ca (0.64%), and ^{43}Ca (0.145%). The isotope ^{43}Ca is different from the other isotopes by having a nuclear spin, which is different from zero, making it amenable to NMR studies. Isotope ^{45}Ca is important because of its radioactive properties (Weast, 1984).

Calcium is one of the most abundant minerals in body with about 99% of it found in the bones and teeth. The remaining 1% is found in the blood, muscles, and other soft tissues in the body, thus maintaining the integrity of the human body. Calcium also functions in normal muscle contraction and relaxation of the body, clotting of the blood and blood pressure regulation (Weast, 1984).

Calcium ions on the surface of bone act like large ion exchanger by interacting with ions in body fluids. These properties are important in relation to the role of bone as a reserve of calcium to help maintain a constant concentration of blood calcium. Blood calcium also regulate vital body processes such as blood coagulation, muscle contraction, nerve transmission and mediation of some hormonal actions across cell membranes which is a very important role in the body. Consuming too much calcium can cause serious

constipation. In adults, too much calcium often from dietary supplements but not food might increase the risk of getting kidney stones (Weast, 1984).

2.9.3 NICKEL

Nickel has 28 as its atomic number on the periodic table and an atomic mass of 59. Nickel also has two main oxidation states of +2 and +3. It has 5 naturally occurring isotopes namely ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni and ^{64}Ni. Isotope ^{58}Ni out of the rest has 68.3% of the total mass making it the most abundant. Nickel can be described as a hard cubic crystal with a silver white colour. It has malleable and ductile properties and has superior strength and corrosive resistance. Nickel has the property of conducting heat and electricity and also exhibits some magnetic properties. In its metallic form nickel is chemically inert. Based on research, nickel has been proven to be essential for the growth and survival of microorganisms. It has also been thought to help in human metabolism (Reimann and de Caritat, 1998).

Nickel deficiency in the body is known to retard the growth and impairs the uptake of iron. With regards to this, WHO recommends a daily intake of 10µg for humans (WHO, 1996). Source of nickel in the environment may include fuel combustion, fertilizers and detergents (Reimann and de Caritat, 1998).

There are some effects of nickel, which have also been recorded. Several authors have reported kidney malfunction especially through tubular and glomerular lesions. This was concluded after administration of high nickel doses of between 1 and 6 mg/kg of body weight intraperitoneally in both rats and rabbits (IPCS, 1991). Levels of nickel were also attributed to body weight gain, haemoglobin, and plasma alkaline phosphatase which

accounted for significant reduction in weanling rats exposed to nickel (as nickel acetate) at concentrations of 500 or 1000 mg/kg in the diet (equivalent to 25 or 50 mg/kg of body weight per day) for 6 weeks compared with controls (Whanger, 1973).

2.9.4 IRON

Iron has an atomic number 26 on the atomic table with an atomic weight of 55.85. It has a grayish tinge appearance. It has a melting point of 1811K and a density of 7.874g/cm^3. ^{56}Fe is the most abundant isotope with 91.75%. Iron as a mineral is very important in the growth and development of the human body. The body uses iron in the production of haemoglobin, a protein in red blood cells that carries oxygen from the lungs to all parts of the body, and also myoglobin, a protein that provides oxygen to muscles. Iron is also needed in the body to make some hormones and connective tissues (Watson, 2011).

The amount of elemental iron needed in the body everyday is dependent on the age and sex of the individual and also whether the person consumes mostly plant-based diet. Iron is present naturally in many foods and iron fortified food products. Recommended amounts of iron for the human body can be achieved by eating foods, including, lean meat, seafood, and poultry. Iron present in our daily meal comes in two forms namely heme iron and non-heme iron. Non-heme iron is found in plant eaten as food and iron-fortified food products normally contain non-heme iron while normally meat and seafood contains both heme and non-heme iron (Watson, 2011).

Having low amount of iron does not necessarily cause serious symptoms. Normally the body uses iron stored in the muscles, liver, spleen, and bone marrow. Nonetheless when levels of iron stored in the body reaches low levels, its results in iron deficiency anaemia.

Symptoms of iron deficiency anaemia include tiredness and lack of energy, GI upset, poor memory and concentration, and less ability to fight off germs and infections or to control body temperature (Watson, 2011).

2.9.5 MAGNESIUM

Magnesium has an atomic number of 12 on the periodic table with an atomic mass of 24. It has one main oxidation state of +2 and three naturally occurring isotopes of ^{24}Mg, ^{25}Mg and ^{26}Mg. The seventh most abundant element in the Earth's crust is magnesium with average abundance of 2.76%.

Magnesium is one of the abundant mineral elements found in the human body. It is naturally present in lot of foods and food supplements. Magnesium is required as one of the major element employed in couple of important processes. Some of the processes are glycolysis, oxidative phosphorylation and energy production. Magnesium also helps in the development of the human bone. It is also required for the DNA and RNA synthesis. Magnesium in addition plays an important role in the uptake of calcium and potassium ions across the cell membrane through active transport mechanism, which aid in muscle contraction and rhythm of the heart (Rude *et al*., 2010).

Symptoms associated with magnesium deficiency due to low dietary intake in healthy people are not common because of how the kidneys limit urinary excretion of this mineral. In spite of this, habitually low intakes or excessive losses of magnesium due to certain health conditions such as chronic alcoholism, and/or the use of certain medications can lead to magnesium deficiency (Rude *et al*., 2010).

2.9.6 ZINC

Zinc has an atomic number of 30 and belongs to group IIB of the periodic table with atomic mass of 65. It has one main oxidation state of +2 and five naturally occurring isotopes namely ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn and ^{70}Zn, of which ^{64}Zn, ^{66}Zn and ^{68}Zn are the most abundant at 48.6%, 27.9% and 18.8% respectively of the total mass. Zinc is one of the elemental nutrients that the body needs to stay healthy and its found in cells throughout the human body. Zinc aids the immune system fight against invading bacteria and viruses. Zinc is also needed by the body to make proteins and DNA. For proper growth of during pregnancy, infancy, and childhood, zinc forms an important part (WHO, 1996).

Zinc is found in a wide variety of foods including oysters, red meat, poultry, and fortified breakfast cereals. Beans, nuts, whole grains, and dairy products, are also rich in zinc. Zinc deficiency affects both children and adults. In children it slows growth, whilst delayed sexual development is exhibited in adolescents. Deficiency in zinc also causes hair loss, eye and skin sores, and loss of appetite. Key benefit of zinc is helping the skin stay healthy and fresh. The World Health Organization and UNICEF recommendation for intake of zinc for children with diarrhea is 20 mg/day, or 10 mg/day for infants under 6 months for 10 – 14 days (WHO, 1996).

2.9.7 CHROMIUM

Chromium has an atomic number of 24. It has ironic radius of 0.520 Å, boiling point of 2672^0C, melting point of 1907^0C and a density at 20^0C of $7.19g/cm^3$ (ATSDR, 1998). Chromium is a brittle, hard metal with known high corrosion resistance. It is used to plate other metals so as to form a protective and attractive covering when it is polished and has

a shiny surface. Chromium is a naturally occurring element in the environment most notably in rocks, soil, and volcanic dust and gases. Chromium occurs in one of two valence states namely trivalent chromium (Cr (III)), which occurs naturally and is an essential nutrient, and hexavalent chromium (Cr (VI)). Trivalent Chromium is essential in processes like normal glucose, protein, and fat metabolism and thus an essential dietary element for the body. The average daily intake is estimated to be around 60 µg, from the environment (ATSDR, 1998).

Exposure to chromium can be dermal or occupational. Dermal exposure may be attributed to the use of products that contain the metal such as wood or leather. Occupational exposure on the other hand can result from encounters during the production of chromate, stainless steel, and tanning industries. Chromium (III) is an essential element found in humans, with a daily-recommended intake of 50 to 200 µg/d for adults.

2.9.8 ARSENIC

Arsenic occurs naturally and has an atomic number of 33 and atomic weight of 74.9. Pure arsenic found rarely in the environment exists in three allotropic forms namely yellow (alpha), black (beta), and gray (gamma) (HSDB, 2009). Arsenic compounds often occur in two important forms namely trivalent and pentavalent. The most usually found trivalent forms are the trioxide of arsenic and sodium arsenite, and the pentoxide of arsenic and arsenates are the commonly found pentavalent forms. The inorganic arsenic compounds often comes in the form of the sulfide combining with minerals like copper, lead and other metals.

Arsenic compounds often occur in three forms; crystalline, powdery, and amorphous forms. Arsenic as an element has a specific gravity of 5.73. When heated at 613°C its sublimes, with low vapour pressure of 1 mm Hg at 373°C. Many of the inorganic arsenic compounds found in nature occur as white, odourless solids with specific gravities ranging from about 1.9 to over 5 (ATSDR, 2007). Arsenic is not soluble in water but arsenate compounds especially calcium arsenate dissolves in water sparingly. The trioxide and pentoxide of arsenate are mostly soluble in water. It should be noted that, when heated to decomposition, arsenic compounds emit toxic arsenic fumes (HSDB, 2009).

Tobacco contains natural inorganic arsenic which smokers of tobacco are often exposed to. Tobacco plants contain arsenic through the process of taking up from the soil. Arsenic compounds normally come in inorganic and organic forms. Inorganic arsenic compounds that are often present in water are the most toxic while organic arsenic compounds found in seafood are less harmful to the health of the consumer. Some known symptoms of acute arsenic poisoning include vomiting, abdominal pain and diarrhoea followed by numbness and tingling of the extremities, muscle cramping and death, in extreme cases (HSDB, 2009).

The immediate symptoms of long-term exposure to extreme levels of inorganic arsenic are usually observed in the skin. This results in pigmentation changes, skin lesions and hard patches on the palms and soles of the feet (hyperkeratosis). These occur after a minimum exposure of approximately five years and may lead to skin cancer. Other adverse health effects that may be associated with long-term ingestion of inorganic arsenic include developmental effects, neurotoxicity, diabetes, pulmonary disease and cardiovascular disease.

Most arsenic compounds find its way into the human system through eating of food or drinking of water. Drinking water contaminated with arsenic is a problem in many countries in the world.

2.10 EFFECTS OF HEAVY METAL POISONING

Heavy metals have been reported to have several effects both on the human body and the environment. In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum and some enzymes involved in metabolism, detoxification and damage repair (Wang and Shi, 2001). Heavy metal ions have been found to interact with cell components such as DNA and nuclear proteins, causing DNA damage and conformational changes that may lead to cell cycle modulation, carcinogenesis or apoptosis (Yedjou and Tchounwou, 2006).

CHAPTER THREE

3 MATERIALS AND METHODS

3.1 MATERIALS

Sample

Cocaine of average purity of 80% was supplied by the Ghana Standard Authority Forensic Department, Accra. The samples corresponded to confiscation carried out in Ghana especially at the airport and harbour over the period of 2009 to 2014. The cocaine seizures normally come in slabs, pellets or powder. The project samples were taken according to the Forensic Department sampling plan.

Chemicals

All chemicals used were of ultrapure grade, using ultrapure water, which was supplied by the Ghana Standards Authority, Accra. Argon Gas for the ICP-MS was obtained from Ghana Gas Company, Accra.

3.2 METHOD

3.2.1 Sampling method for Cocaine samples

Samples were taken into transparent rubbers and properly sealed and labeled. The samples were taken based on the availability of the cocaine sample after test by the forensic department. The cocaine stock samples were kept in a security protected safe under the right temperature and humidity conditions. Table 3.1 shows the sampling process and labeling. The classification in Table 3.1 was done based on Fig. 3.1.

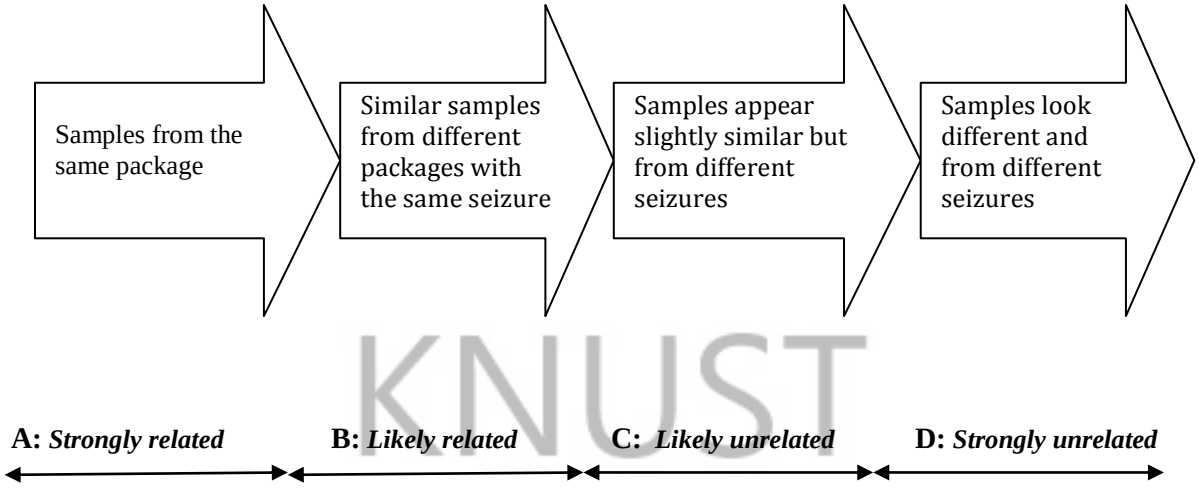

Figure 3.1 Levels of relationship for different kinds of cocaine samples seized (Kar-Weng *et al*., 2016)

For the submission/seizure that contained more packages, individual samples were taken from 2 randomly picked packages to form related samples. The related samples under class A were 13 groups and 3 groups under class B which constituted 16 groups equivalent to 16 seizures, which were used to evaluate within-seizure variability. In the 3 groups, sample 28_2 and 28_3 were from the same seizures but had different signs on the packages, same as $26_{3A}/26_{5B}$ and $10_{A6}/10_{A10}$. Under class C, 5 samples were used equivalent to 5 separate seizures, which were used to evaluate between-seizure variability. The 5 samples were selected because they had slight physical similarities especially the colour and appearance. None of the seizures could be grouped under the class D.

Table 3.1 Sample plan employed for the cocaine samples

Sample Code (Cocaine seizures)	A	B	C
6	6_x, 6_y		-
18	18_3, 18_4		-
7	7_1, 7_6		-
29	29_1, 29_8		-
14	14_1, 14_8		-
23	23_2, 23_5		-
13	13_1, 13_6		-
24	24_4, 24_6		-
28	-	28_2, 28_3	-
32	32_1, 32_4		-
10	-	10_{A6}, 10_{A10}	-
26	-	26_{3A}, 26_{5B}	-
9	9_A, 9_B		-
15	15_{A6}, 15_{A10}		-
19	19_5, 19_8		-
25	25_2, 25_8		-
4	-		4
12	-		12
20	-		20
21	-		21
31	-		31

Total number of samples – 37

– Signifies no sample

3.2.2 Sample weighing

The weighing of the samples was done using an electronic balance (KERN & Sohn GmbH, Germany) and all necessary verification procedures were done on the balance

before use. Amounts of 0.5g of the cocaine samples were weighed into 50ml beaker. The weights were taken in triplicate.

3.2.3 Preparation of Nitric acid (2.0% v/v) as dissolving solution

Approximately 28.60 ml nitric acid was diluted with deionized water to obtain 1-liter solution of HNO_3.

3.2.4 Pretreatment of samples

The samples were dissolved in 1ml of ultrapure water and heated at 40°C to aid complete dissolution. The solution was then transferred into a 100ml volumetric flask, 2ml of 2.0% (v/v) HNO_3 was added to aid in the stabilization of the solution. Afterwards, it was diluted to 30ml with water. After complete mixing of the solution, the volumetric flask was properly sealed and labeled for analysis.

3.2.5 Standard Solution Preparation

An amount of 1ml was withdrawn from the stock solution which contained all known metals and then diluted with 2% HNO_3 to prepare three separate standard solutions in the following listed concentrations: Standard 1; 200ppb, Standard 2; 400ppb and Standard 3; 600ppb. The three prepared standards obtained were then used to perform the standard calibration check.

3.2.6 Blank preparation

A blank solution was prepared as per the same procedure applied to the cocaine samples outlined above.

3.2.7 Quality Control Check

This was done using surface water. Surface water is a solution, which contains multi metals and has a known concentration. It is often preferred because it's eliminating interference from the analyst. The surface water used was prepared into 1000ppb or 1ppm. The percentage recovery obtained is then compared to the reference chart to determine the accuracy of the equipment.

3.2.8 Apparatus

An Agilent model ICP-MS version 7700 with standard nebulization was used. The metals determined were Calcium, Arsenic, Chromium, Iron, Magnesium, Nickel, Zinc, Copper, Manganese and Lead. The metals were picked because they were likely to be found in cocaine according to already reported works. The Operational conditions for the ICP-MS are listed in Table 3.2.

Table 3.2 ICP-MS operational Parameters used

Parameters	Conditions
RF Power	1 kW
Radio frequency	40 mHz
Carrier gas flow rate	0.64L/min
Plasma gas flow rate	15 L/min
Plasma observation	Radial
Pump uptake	1.5 ml/min

Analytical results were calculated using linear calibration graphs. The ICP-MS records the results in two modes namely No Gas mode and Helium mode.

The metal content in ppm is determined by the formula below;

$$\textbf{Content} = \frac{(C - B) \times V}{W}$$

Where

C – Concentration of final solution

B – Concentration of blank solution

V – Final volume of solution

W – Weight of sample

3.2.9 Statistical Analysis

The ICP-MS data were analyzed statistically by means of Excel version 10.0. Each elemental concentration in ppm was considered as the variables for each cocaine sample. After the variables were defined, ANOVA was performed at 95% confidence level. The results were expressed in mean ± SD.

CHAPTER FOUR

4 RESULTS AND DISCUSSIONS

4.1 AMOUNT OF METALS IN COCAINE SAMPLES: DESCRIPTIVE DATA

Table 4.1, displays the descriptive data for the 10 metals found in the cocaine samples seized from 2010 to 2014. As indicated by the standard deviation (SD), the 37 samples analyzed showed wide range of concentrations for most of the metals which were measured in parts per million. The marked difference between the maximum and the third quartile (Q3) indicates the presence of outliers as presented by Calcium and Magnesium in table 4.1. Due to these differences it is much meaningful to use the median to measure the central tendency of the data.

Table 4.1 Descriptive data in ppm of 10 metals in 37 cocaine samples

Element	Mean	SD	Minimum	Q1	Median	Q3	Maximum
Ca	61.94	54.60	13.13	17.39	30.94	34.87	960.43
As	0.32	0.13	0	0.26	0.34	0.42	0.52
Cr	1.66	0.55	0	1.57	1.81	1.99	2.21
Fe	2.65	2.41	0	1.65	2.11	3.42	11.54
Mg	1.75	1.19	0	0.87	1.67	2.49	4.71
Ni	0.093	0.091	0	0.03	0.07	0.13	0.35
Zn	1.51	1.99	0	0	0.59	2.17	6.10
Cu	0.33	0.29	0	0.12	0.26	0.46	1.38
Mn	0.22	0.18	0	0.07	0.15	0.34	0.77
Pb	0.14	0.28	0	0	0.06	0.18	1.56

Q1 – 1st Quartile

Q3 – 3rd Quartile

Calcium was present in extremely high levels with a mean ppm value of 64.94. This high level could be attributed to calcium containing agents, which are added during the illicit cocaine production steps (Kar-Weng *et al*., 2016). At the final phase of the coca paste isolation, excess lime is added to neutralize the sulfuric acid in the solution. Lime is also

known as calcium oxide containing the inorganic element, Calcium, thus the high presence of Calcium. Since the production of illicit heroin involves the addition of lime, Calcium recorded a high amount around 4050 to 14200 μg/g in 44 illicit heroin samples seized in Turkey (Taner-Smith, 2006). It could also have originated from water, which was usually added during the cooking process in cocaine production (Kar-Weng *et al*., 2016).

Magnesium, Zinc, Chromium and Iron had moderate amount in the cocaine samples after Calcium. This could be attributed to the metal pot used in the heating processes in the manufacturing process as reported by Taner-Smith (2006). Furthermore Iron, Magnesium, and calcium may have originated from tap water because it naturally contains these elements in high levels. All the metals with the exception of Calcium were not detected in some of the samples, which accounts for the high levels of Calcium in the environment as earlier reported.

4.2 BATCH IDENTIFICATON USING METAL CONTENT

From the illustration in Figure 3.1, the samples analyzed were grouped into class A, B and C based on the descriptions given. From Table 3.1, 14 pairs of the cocaine samples fell under class A. According to the P-values outlined in Table 4.2 at 95% confidence level ($p \leq 0.05$), it showed that there were no significant differences between the pairs in the samples selected with reference to metals analyzed. This could confirm the fact that the pair of samples was taken from the same package during the seizure from 2010 to 2014.

Only two pairs of the samples were classified under Class B i.e. samples 26 and 28. The p-values showed that there were significant differences between the pairs in the two cocaine

samples with reference to the metals. With sample 26_{3A} and 26_{5B}, 26_{3A} did not record the presence of 8 metals and showed the presence of only Calcium and Manganese as compared to the other pair 26_{5B}. Similarly with 28_2 and 28_3, both did not show the presence of Zinc with 28_3 showing the absence of other metals like Iron, Magnesium, Nickel, Copper, Manganese and Lead. These difference showed between the samples can be attributed to within bulk variety. There are some critical parameters measured during production processes, which can affect the consistency in a bulk batch produced under the same conditions and personnel e.g. mixing speed and time.

Table 4.2 Within-seizure presentation of some metals in cocaine samples in ppm.

Code	Ca	As	Cr	Fe	Mg	Ni	Zn	Cu	Mn	Pb	P-values
$\mathbf{6_v}$	34.52	0.21	1.88	ND	0.83	ND	0.59	0.28	0.04	0.07	**0.3234**
$\mathbf{6_x}$	15.09	0.24	1.89	ND	0.64	ND	ND	0.24	0.03	0.06	
$\mathbf{18_3}$	118.64	0.12	1.41	1.70	1.39	0.06	1.93	0.12	0.38	0.23	**0.4470**
$\mathbf{18_4}$	110.23	0.16	1.27	2.37	1.44	0.32	2.29	0.16	0.37	0.05	
$\mathbf{7_1}$	88.77	0.25	1.53	1.78	2.82	0.13	6.10	0.45	0.32	0.13	**0.3467**
$\mathbf{7_6}$	40.16	0.26	1.58	6.68	2.48	0.09	4.70	0.31	0.22	0.18	
$\mathbf{29_1}$	14.24	0.40	1.98	2.74	1.73	0.07	ND	0.07	0.63	ND	**0.4527**
$\mathbf{29_8}$	17.39	0.29	1.74	1.22	3.04	0.06	ND	0.38	0.58	0.17	
$\mathbf{14_1}$	13.53	0.32	1.57	2.39	0.38	0.06	ND	0.54	0.09	0.06	**0.3846**
$\mathbf{14_8}$	13.13	0.51	1.99	2.45	3.11	0.03	ND	0.26	0.06	ND	
$\mathbf{23_2}$	82.31	0.29	1.64	4.56	2.63	0.15	0.96	0.67	0.21	0.18	**0.2435**
$\mathbf{23_5}$	22.56	0.33	2.05	2.05	1.26	0.05	1.98	0.41	0.07	0.07	
$\mathbf{13_1}$	13.18	0.35	1.71	1.65	0.62	0.03	ND	0.53	0.09	0.06	**0.3371**
$\mathbf{13_6}$	15.17	0.42	1.91	1.91	0.84	0.03	ND	ND	0.06	ND	
$\mathbf{24_4}$	18.59	0.36	2.13	4.88	1.51	0.09	ND	0.16	0.09	0.95	**0.5244**
$\mathbf{24_6}$	16.12	0.51	2.04	5.29	1.75	0.06	ND	0.86	0.06	0.19	
$\mathbf{28_2}$	23.22	0.46	2.07	2.11	0.90	0.05	ND	0.94	0.05	0.12	**0.0154**
$\mathbf{28_3}$	22.36	0.05	0.05	ND	ND	ND	ND	ND	ND	ND	
$\mathbf{32_1}$	15.07	0.28	1.31	0.52	ND	ND	1.01	0.26	0.02	0.02	**0.0752**
$\mathbf{32_4}$	16.18	0.35	1.83	2.03	0.42	0.05	0.59	0.57	0.10	ND	
$\mathbf{10_{A6}}$	33.23	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.2186**
$\mathbf{10_{A10}}$	35.33	0.42	2.04	4.82	1.68	0.18	5.42	2.46	0.15	0.24	
$\mathbf{26_{3A}}$	34.77	ND	ND	ND	ND	ND	ND	ND	0.01	ND	**0.0072**
$\mathbf{26_{5B}}$	34.87	0.39	2.21	3	0.96	0.25	1.82	0.59	0.25	0.10	
$\mathbf{9_A}$	34.81	0.41	1.78	1.83	4.71	0.07	1.19	0.18	0.27	ND	**0.3142**
$\mathbf{9_B}$	31.37	0.42	1.81	2.59	4.70	0.09	ND	0.09	0.30	ND	
$\mathbf{15_{A6}}$	77.08	0.36	1.92	3.42	3.52	0.10	1.02	0.73	0.14	ND	**0.4656**
$\mathbf{15_{A10}}$	111.83	0.52	2.14	7.93	3.33	0.35	2.15	0.17	0.26	0.20	
$\mathbf{19_5}$	29.42	0.31	1.67	4.05	1.56	0.15	4.49	0.23	0.13	0.11	**0.2345**
$\mathbf{19_8}$	22.74	0.42	2.09	2.29	1.54	0.03	0.24	0.08	0.39	ND	
$\mathbf{25_2}$	33.94	0.30	1.90	1.81	2.50	0.17	5.80	0.30	0.78	ND	**0.3410**
$\mathbf{25_8}$	33.44	0.34	1.89	2.61	1.93	0.13	5.19	0.08	0.61	ND	

ND – Not Detected: each value is a mean of three determinations

Five of the samples had slightly similar physical properties (physical inspection) but were from different seizures (class C) encountered from the year in review: 2010 to 2014. The samples were 4, 12, 20, 21 and 31 as shown in Table 3.1. They had different composition with reference to amount of metal elements. Sample 4 did not contain iron, nickel and zinc; whiles sample 21 and 31 did not contain lead and iron respectively. This clearly shows that those samples are probably from different production batches and origin or country as shown in Table 4.3. Nonetheless, these samples could be from the same bulk but having undergone different degrees of contamination after they have been dispersed from the main bulk. Such samples may have had their metal profiles altered. These samples also did not have any correlation with the other others used for this experiment.

Table 4.3 Metal data of selected cocaine samples in ppm from different seizures

Metals	Ca	As	Cr	Fe	Mg	Ni	Zn	Cu	Mn	Pb
4	22.08	0.47	1.48	ND	1.28	ND	ND	0.35	0.08	0.08
12	960.43	0.50	2.05	2.05	2.02	0.08	5.34	0.25	0.19	0.25
20	33.35	0.28	1.80	3.89	2.70	0.34	3.44	0.14	0.18	1.56
21	21.78	0.34	1.79	11.54	1.99	0.07	0.21	0.48	0.41	ND
31	30.94	0.17	1.35	ND	2.42	0.11	0.20	0.28	0.48	0.06

ND – Not Detected; each value is a mean of three determinations

All the samples used for the experiment appeared similar so none of them were grouped under class D. Sample 10 had a unique metal profile between the pair though they had different signs on the packages, the content did not show any significant difference between them. This can mean that they can be from the same production batch but they were packed differently.

4.3 PROPOSED IDENTIFICATION OF MISSING SEIZED COCAINE

The aim of the sampling plan for the seized cocaine was to compare two samples from the same cocaine batch with respect to their metal profile. From Table 4.4, some of the samples from the same batch showed no significant differences between them. Based on the data gathered there can be two proposed ways of identifying missing cocaine looking at their metal profiles. Firstly, confirmation test can be done on missing metals and secondly the amount of each metal can be confirmed. This can produce perfect results if there is no adulteration. The metal content analysis can be preceded by analysis of adulterants.

Assuming sample x was first seized, analyzed for metal content as shown in table 4.5, then got missing from custody. The metal profile for sample y is representing the found sample x that got missing.

Table 4.3 Metal profile of cocaine sample x and y in ppm

	Ca	**As**	**Cr**	**Fe**	**Mg**	**Ni**	**Zn**	**Cu**	**Mn**	**Pb**
Sample x (*First seized*)	18.59	0.36	2.13	4.88	1.51	0.09	0	0.16	0.09	0.95
Sample y (*Found missing sample*)	16.12	0.51	2.04	5.29	1.75	0.06	0	0.86	0.06	0.19

Sample x and y represent samples 24_4 and 24_6 respectively

From the earlier hypothesis, the first metal that would be analyzed for on sample y will be the element Zinc. It can be seen from the analysis conducted on the sample x that, Zn was missing from the metal profiling done. Ideally if nothing was added to the cocaine when it got missing, it is expected that Zinc will also be missing in sample y.

Secondly the amount recorded for each metal in the two samples would also be compared. According to Table 4.4, it can be seen that the two sample x and y almost look the same compared to the amount of metals. There is only a slight change, which is not significant according to the p-value.

4.4 HEAVY METAL CONTENT: HEALTH HAZARDS ON COCAINE USERS

According to Table 4.4, the heavy metal content of seized cocaine with reference to lead, arsenic and chromium were higher than the ones contained in water, animal fats and edible fats and oils as the acceptable limits in ppm outlined in Codex standard 193: 1995.

Table 4.4 Mean ppm values of some heavy metals in cocaine compared to Natural mineral water, animal fats and edible fats and oils.

Elements	Cocaine	Natural Mineral water	Animal fats	Edible fats and oils
Lead (Pb)	0.14	0.01	0.1	0.1
Arsenic (As)	0.32	0.01	0.1	0.1
Chromium (Cr)	1.66	0.003	0.05	0.05

With the amounts recorded for the three metals, it can have an adverse effect on anyone who takes in cocaine contaminated to this level with these metals.

Abernathy *et al.* (1999) indicated that the toxicity of arsenic depends on these factors; exposure dose, frequency and duration, biological species, age and gender as well as on genetic and nutritional factors. Investigations from epidemiological studies have indicated that long-term exposure to arsenic can end up in carcinogenesis (Zhao *et al*., 1997). All the health hazards attributed to arsenic can be related to chromium and lead and with the high levels of these metals; the end user of the illegal powder can have a serious health

consequence on him. Measures should be put in place in other to prevent people from taking in these substances so it will not add up on the small amounts taken through food and water daily.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The study shows that illicit cocaine can be confirmed to contain metals that can be used as a form of identification. The metal profile on the seized cocaine samples using ICP-MS can be used to identify cocaine that comes from the same batch even though they might be from different seizures. Seized illicit cocaine also contains some amount of heavy metals such as Lead, Arsenics and Chromium and they can have serious health implications on the end user.

5.2 RECOMMENDATIONS

In spite of the data gathered, these are some few recommendations for future studies;

a. More metals should be analyzed to aid in less variation between within-batch cocaine samples.

b. To have a sample from missing and found cocaine to compare the changes in metal profile between the multiple samples.

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APPENDICES

Sample 6

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	1079.104	9	119.9004	6.402736	0.005392	3.178893
Columns	20.43838	1	20.43838	1.091419	0.323404	5.117355
Error	168.5379	9	18.72643			
Total	1268.08	19				

Sample 18

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	22964.43	9	2551.604	684.9746	1.14E-11	3.178893
Columns	2.355038	1	2.355038	0.632207	0.447008	5.117355
Error	33.52597	9	3.725107			
Total	23000.32	19				

Sample 7

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	7681.983	9	853.5536	7.101859	0.003727	3.178893
Columns	118.4871	1	118.4871	0.985854	0.346701	5.117355
Error	1081.686	9	120.1873			
Total	8882.156	19				

Sample 29

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	418.0879	9	46.45421	63.12959	4.67E-07	3.178893
Columns	0.453306	1	0.453306	0.616026	0.452692	5.117355
Error	6.622693	9	0.735855			
Total	425.1639	19				

Sample 14

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	298.4433	9	33.16037	82.57644	1.43E-07	3.178893
Columns	0.335405	1	0.335405	0.835231	0.384594	5.117355
Error	3.614146	9	0.401572			
Total	302.3929	19				

Sample 23

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	4695.235	9	521.6928	3.02482	0.057351	3.178893
Columns	268.6005	1	268.6005	1.557369	0.243541	5.117355
Error	1552.236	9	172.4707			
Total	6516.072	19				

Sample 13

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	341.8538	9	37.98375	173.1062	5.37E-09	3.178893
Columns	0.225569	1	0.225569	1.028002	0.337109	5.117355
Error	1.974821	9	0.219425			
Total	344.0541	19				

Sample 24

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	514.701	9	57.189	145.2892	1.17E-08	3.178893
Columns	0.172608	1	0.172608	0.438513	0.524433	5.117355
Error	3.542597	9	0.393622			
Total	518.4162	19				

Sample 28

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	906.9165	9	100.7685	324.8468	3.23E-10	3.178893
Columns	2.755789	1	2.755789	8.88382	0.015435	5.117355
Error	2.791828	9	0.310203			
Total	912.4641	19				

Sample 32

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	415.886	9	46.20955	285.0302	5.79E-10	3.178893
Columns	0.655582	1	0.655582	4.043767	0.075217	5.117355
Error	1.459094	9	0.162122			
Total	418.0007	19				

Sample 9

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	5171.554	9	574.6171	841.538	4.51E-12	3.178893
Columns	0.775786	1	0.775786	1.136154	0.314225	5.117355
Error	6.145359	9	0.682818			
Total	5178.475	19				

Sample 15

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	210176.5	9	23352.94	256.7125	9.25E-10	3.178893
Columns	52.8125	1	52.8125	0.580553	0.465593	5.117355
Error	818.7233	9	90.96926			
Total	211048	19				

Sample 19

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	1748.343	9	194.2603	2.011651	0.156257	3.178893
Columns	156.8224	1	156.8224	1.623965	0.234459	5.117355
Error	869.1082	9	96.56758			
Total	2774.273	19				

Sample 25

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	1919.497	9	213.2775	2574.384	2.96E-14	3.178893
Columns	0.083722	1	0.083722	1.010571	0.341027	5.117355
Error	0.745614	9	0.082846			
Total	1920.327	19				

Sample 10

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	2913.373	9	323.7081	2.332019	0.111584	3.178893
Columns	242.8278	1	242.8278	1.749352	0.218579	5.117355
Error	1249.292	9	138.8102			
Total	4405.492	19				

Sample 26

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	2105.408	9	233.9342	396.9403	1.31E-10	3.178893
Columns	7.041284	1	7.041284	11.94767	0.0072	5.117355
Error	5.304092	9	0.589344			
Total	2117.753	19				