Sudan University of Science and Technology

College of Graduate Studies

Determination of Organic and Inorganic Components in Printing Inks

تعيين المكونات العضوية واللاعضوية في أحبار الطباعة

A Thesis submitted in partial fulfillment for the requirements of the M.Sc. degree in chemistry

By:

Amal Salih Hasabelrasoul Abdin

B.sc. (Honor) University of Khartoum

Supervisor: Prof. Elmugdad Ahmed Ali

March 2018

Dedication

This work is dedicated to my big family, parents, brothers, sisters and my small family husband and son.

To my friends and everyone who helped me.

Acknowledgements

First thanks to Allah for giving me the strength to complete this work.

Special and great thanks to my supervisor Prof. Elmugdad Ahmed Ali for his support, patience and follow up during all stages of this research.

Thanks are also extended to all the academic teaching staff of the chemistry department, college of Science (SUST) for their kind help.

Abstract

This work was directed toward the study and analysis of printing inks specially those inks used in the printing of the newspapers.

The goal is to determine the organic, inorganic contents and the additive materials of the ink by methods of analysis and to evaluate its toxicity and effects on the workers or dealers and the effect on the environment is traced.

The samples were collected carefully from printing press in the industrial area – Khartoum. The methods of analysis were performed by atomic absorption and infra-red analysis after the samples preparation using acid digestion which approved existence of heavy metals have negative effects like iron ,lead , cadmium,cupper,cobalt and chromium.

The results obtained from atomic absorption spectroscopy shows that the contents of heavy metals such as Iron $^{(2)}$ in the black ink 3.149 ppm and in red ink 3.026 ppm ,in blue ink2.817ppm ,and in yellow ink 3.561 ppm

lead is not found in any ink, and also cadmium.

Cobalt in black ink 1420 ppm, in the red ink 7050 ppm and in the blue ink 1153 ppm .

Chromium in black ink 1735 ppm red ink 1604 ppm ,in the blue ink 1911 ppm and in the yellow ink 1282 ppm .

copper in black ink 418 ppm red ink 205 ppm ,in the blue ink 416 ppm and in the yellow ink 663 ppm .

And infra red spectroscopy spectra show carbonyls (aldehydes) (1700-1740 cm^{-1}) ,amines(3300-3500 cm^{-1}) and alcohols(3300-3600 cm^{-1}) functional groups.

المستخلص

يقوم هذا العمل بدراسة وتحليل مكونات الأحبار المستخدمة في الطباعة وخاصة الأحبار المستخدمة في طباعة الصحف والهدف الرئيسي من هذا البحث هو تحديد مكونات هذه الأحبار والمواد المضافة إليها بعدة طرق لتحديد المواد العضوية وغير العضوية المكونة لها وبالتالي محاولة تحديد هل إذا ما كانت سامة أم لا وأثرها على الانسان سواء أكان عاملا بها اما متعاملا معها وعلى البيئة أيضا بواسطة أجهزة الامتصاص الذري للعناصر وتحليل الاشعة تحت الحمراء.

تم أخذ عينات من الأحبار ومضافاتها من مطبعة خاصة بطباعة الجرائد بالمنطقة الصناعية بالخرطوم بحذر شديد وتم تحليلها بالطرق السابق ذكرها وكانت النتائج بالنسبة لجهاز الامتصاص الذري للعناصر وجود عناصر ثقيلة ذات أثر سالب وهي الحديد ، الرصاص ، الكادميوم ، الكوبالت ، النحاس والكروم .

وقد وجدت نسب هذه العناصر كالاتي :

نسبة الحديد في الحبر الأسود 3.149ppm ، في الحبر الأحمر 3.026ppm ، في الحبر الأزرق 2.817 ppm وفي الحبر الأصفر 3.561 ppm .

من خلال الفحص لم يتبين وجود كلا من الرصاص والكادميوم.

نسبة الكوبالت في الحبر الاسود 1420 ppm في الحبر الأحمر 7050ppm، في الحبر الأزرق 1153 ppm.

نسبة الكروم في الحبر الاسود 1735ppm في الحبر الأحمر 1604ppm ، في الحبر الأزرق 1911ppm وفي الحبر الأصفر1282ppm .

ونسبة النحاس في الحبر الاسود 418ppm في الحبر الأحمر 205 ppm، في الحبر الأزرق

416 ppmوفي الحبر الأصفر 663 ppm .

أما تحليل الأشعة تحت الحمراء فقد بين وجود مركبات كاربونيلية (ألدهيد) التي أعطت إمتصاص عند (1700-1740 cm^{-1})وأمينات أعطت إمتصاص عند (3300-3500 cm^{-1}) وكحول أعطت إمتصاص عند (3300-3600 cm^{-1})كزمر وظيفية.

List of Contents

List of abbreviations:

A.A.S: atomic absorption spectroscopy.

ppm: part per million.

IR: infra red.

HF: hydrofluoric acid.

Cm $^{-1}$: wave number.

Chapter One

Introduction and Literature Review

1.1 Introduction :

Ink is a liquid or semi –liquid material used for writing printing or drawing. It is colloidal system of fine pigment particles dispersed in solvent. The pigment may or may not be colored and the solvent may be aqueous or organic established with a natural gum or materials like albumen.

May have additional ingredient known as vehicle include PH modifiers, humectants to rated premature drying , polymeric resins to impart binding and allied properties ,deformers /antifoaming agents to regulate foam efficiency-wetting agents such as surfactants to control surface properties , bio acids to inhibit the fungal and bacterial growth and the lead to fouling and thicker or rheology modifiers to control the ink application.

Over 90% of inks are printing inks in which color is imparted by pigments rather than dyes used in writing inks, ink pigments are either organic or inorganic most.

With few exceptions, the composition of modern day printing inks is remarkably complex in an effort to print well onto particular substrate , such as paper by way of given process, such as lithography, inks must have the properties.

If any one of the dozen ink properties is incorrect the ink could:

Fail to dry on the substrate.

Set up or actually dry while still on press.

- Attack the plate material.
- Fail to adhere to the substrate.
- Create a printed image that is unacceptable in appearance in a number of ways.

Far too often, apress operator encounters problems like these because of one of two mistakes:

1. Using the wrong ink in a particular situation.
2. Adding one or more components to an ink without an understanding of the chemistry involved.

In either case, the problem lies in not knowing enough about inks components and their functions.

Clearly, there are several components to any printing ink and they are all necessary for that ink to function at an optimum level on a given substrate when applied by a particular printing process (Finely 1997).

Ink formulas vary, but commonly involve 2 components: colorants and vehicles. and generally fall into 4 classes:

Aqueous, liquid, paste and powder (Kipphan, Helmut 2001)

Printing Ink is manufactured by proper incorporation of dry pigments into the vehicle by grinding. These two ingredients in suitable proportions are mixed with or without modifiers, driers, wetting agents, anti-oxidants, etc. Depending upon the types and quality of the printing ink in a mixer like dough type mills, triple roll mill, and agitator are used.

For Paste Form Ink the ingredients are mixed well in a mixer like charge pan mixer, Rotary mixer. After completion of mixing the mixed ingredients is passed through triple roll mill. 7 to 8 passes are given till required fineness is obtained. For Liquid Ink formulated with pigments, resin, vehicles and solvent are grounded in a ball mill for 36 - 48 hrs. For low viscosity ink such as newsprint ink, gravure ink etc, colloid mills are used. However, after completion of proper mixing and grinding the ink is packed in a suitable container after proper testing in the laboratory. Quality Control and Standards Printing inks have to possess all the physical and chemical properties as per Indian Standard specifications for getting good quality and marketability of the products.

The laboratory is primarily involved in quality control, although in some larger companies it is also involved in designing special ink formulations for unusual printing situations. Inks are tested for a variety of properties during and after manufacture process. Most of the tests are dictated by their end use. Typical tests include:

- Non volatile content
- Viscosity
- Dispersion
- Shade
- Adhesion

• Slip
• Scratch resistance
• Gloss
• Flexibility
• Water resistance
• Heat Resistance
• Opacity

(Kirk-Othmer 1981)

1.1.1 History of ink:

In its most basic level, ink is composed of pigments and vehicle that carries them. Because the pigments provide most of the optical qualities of an ink, their importance is obvious.

However, because pigments are finely ground solid particles ,slice chalk dust they are worthless without a liquid that can carry them to the surface to be printed.

For this reason, modern inks, like the crude inks used 2000 years ago, are fundamentally pigments carried in a vehicle. For several centuries, all inks were black, usually lampblack (soot) dispersed throughout a vehicle derived from the boiling of linseed oil. Just as today's ink markers are able to provide hundreds of colors through a variety of pigments; high-tech printing is only possible because research has provided abroad range of vehicles, each one being well-suited to a particular printing situation.

Many ancient cultures around the world have independently discovered and formulated ink for purposes of writing and drawing. The knowledge of the inks, their recipes and the techniques for their production comes from archaeological analysis.

Although today's ink contain variety of additional ingredients that distinguish one ink from another, the need of a pigment and a vehicle is common to them all (Finely 1997).

1.1.2 Ink pigments:

Ink solid pigments don’t dissolve in the vehicle that carries them .a rough analogy can be drawn between the pigment –vehicle relationship and a container of fruit

gelatin in which the pieces of fruit are dispersed through the liquid and are held in place after the gelatin sets up.

The insolubility of pigments in their vehicle distinguishes from dyes, which do dissolve in their vehicles.

Ink manufacturers obtain their pigments in one or two forms, dry and flushed. Dry pigments are obtained by mixing, in water solution, two relatively colorless chemicals that combine to form pigment crystal. These crystals become part of the solution, which is then rinsed and filtered to remove impurities as well as excess water.

The resulting compound (called press cake) is then baked in an oven until the water or other liquid has evaporated out.

The dried pigment material is then ground into a powder and mixed with the selected vehicle to form a printing ink .however, dry pigments sometimes produce particles that cluster together and are difficult to grind and disperse evenly through an inks vehicle. For this reason, an alternative to removing the water by evaporation is to flush it out and replace it with another liquid. While the press cake still has a moisture content of 30 to 80 percent, it is mixed with a different fluid, often oil. This fluid is selected because of its ability to draw the pigment particles to it and away from the water; the water then separates away from the oil-pigment mixture and can easily be poured off. In this way, the pigments have been flushed from the water and are termed flushed pigments.

They are now ready to be combined with a proper vehicle and other ingredients by the ink manufacturer .Because flushed pigments are easier to work with later on in the ink manufacturing process , the extra time involved in producing flushed pigments is usually a wise investment(Finely 1997).

1.1.3 Ink vehicles:

The ink vehicle is the liquid portion of the ink .Some printing inks are rather simplistic in the composition of their vehicles, while others are an amazingly complex collection of chemicals necessary to impart some desired characteristic to the ink in question. The composition of the vehicle will determine the inks stiffness, drying rate, ability to adhere to particular substrate, degree of gloss, rub

resistance, and appropriateness to lithography. Gravure or any other printing process.

When discussing the components in an inks vehicle , several publications refer to it as varnish , abroad term sometimes said to be the portion of the vehicle that includes an inks solvent , resin , and/or drying oil – but exclude any drier or wax .

It is important to reiterate that, with the exception of its color, all of inks characteristics are determined by the vehicle. For this reason, a brief analysis of what may be found is a given inks vehicle as appropriate (Finely 1997)

1.1.4 Ink resin \ Binder:

Because ink pigments are solid particles that are carried to the substrate by a liquid vehicle, provision must be made to bond these pigments to one another, as well as to the substrate after most of the vehicle has evaporated as part of the drying process. This needed ingredient is a binding agent that ink makers refer to as the inks resin (also known as binder) .Without a resin, the dried ink film would rub or flake from the surface of the substrate.

Several resins are available to the ink maker. the correct one is determined by : the intended substrate (paper , metal , vinyl , etc.) ; the printing process to be used (lithography , screen , flexography ,etc.) the desired gloss level ; the required rub resistance ; and other end user requirements such as resistance to heat or chemicals.

There are two basic classifications for resins: natural and synthetic.

A popular natural resin found in lithographic and letterpress printing is rosins, a natural compound found pine trees. Rosin –based resins are paste inks such as lithographic and letterpress inks, as well as liquid inks such as gravure and flexographic. Another group of natural resins contain cellulosic's, resin derived from cellulose fibers and also resins occurring are cyclized rubber.

Synthetic resins such as vinyl's used in screen inks ;malice (much –LAY –iks) , used in lithographic and flexographic inks ; polyamides (poly –A-mizds) ,used in flexographic and gravure inks ; acrylics used in flexographic , gravure and screen inks ; and epoxies , used offset metal decorating inks (Finely 1997)

1.1.5 Ink solvents:

All ink resins are solid compounds that must be dissolved or nearly dissolved by a liquid before they are useful in printing inks .the liquid that dissolves these resins and maintains them in a solution is the inks solvent.

The selection of the correct solvent is crucial in ink formulation and involves several considerations .First, the solvent must be a liquid that dissolves the resin, but does not cause the pigments color or bleed. Second, it must evaporate at an acceptable rate .Third, it must be compatible with the printing plate material and it must impart the flow and adhesion properties that are desired of the ink film.

Ink makers can select from a number of solvents. For example, flexographic, and gravure inks rely mainly on alcohols, and oil derivatives such as toluene, heptanes, or acetate for their solvents; these solvent inks dominate the publication and packaging industries.

However, many flexographic and gravure inks also use water in their solvent. the formulation are known as water-based inks and they are becoming increasingly popular due to growing concerns over the emission of volatile organic compounds (VOCs) ,which result from the evaporation of many solvent inks(Finely 1997).

1.1.6 Toxicity of ink:

Toxicity is the degree to which a chemical substance or a particular mixture of substances can damage an organism, but toxicology is that effects of toxicant are dose dependent.

There is misconception that ink is non–toxic even it swallowed. Once ingested, ink can be hazardous to one's health. Certain inks such as those found in common pen can be harmful. Though ink does not easily cause death, repeated skin contact or ingestion can effects such as severe headaches, skin irritation, or nervous system damage. These effects can be caused by solvents, or by pigment intergradient such as p.Anisidine which help create some ink's color and shine.

- **Heavy metals:-**

Heavy metals are generally defined as metals with relatively high densities, atomic weights or atomic numbers. Physical and chemical characterizations of heavy metals need to be treated with caution.

The linkage between heavy metals and printing revolves around the presence of heavy metals in certain traditional ink pigments.

Barium red, lead chromate and cadmium sulfide are examples of pigments used to achieve desired ink colors**.** In addition it instances in which the metal is a significant part of the pigment material, small traces of heavy metals also can find their way into inks as contaminants.

Four metals had traditionally been found in printing ink pigments: lead, barium, cadmium and chromium

A concern of the ink industry is that the list of restricted metals will someday swell to include metals like aluminum, copper, lithium, manganese, molybdenum, silver, titanium, and zinc. Such a move would impact the printing industry in several ways

1.1.7 The effect on humans:

1.1.7.1 Inorganic components:

- **Iron**

Iron may cause conductivities, choroiditis, and retinitis if it contacts and remains in tissues. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of benign pneumoconiosis, called siderosis which is observable as an x-ray change. Excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers.

- **Lead**

Lead can cause several unwanted effects such as:

- Disruption of biosynthesis of hemoglobin and anemia.
- A rise in blood pressure
- Kidney damage.

- Miscarriage and subtle abortions.
- Disruption in nervous system and brain damage**.**

➢ **Cadmium**

Cadmium can make severely damage in lungs, this is may even cause death. Cadmium is first transported to the liver cross the blood .there; it is bond to proteins to form complexes that are transported to the kidneys where it damages filtering mechanism .Cd also causes:

- Diarrhea and stomach pain and vomiting.
- Bone fracture and damage central nervous system.
- Damage in immune system and psychological disorder.
- Possibly DNA damage or cancer development.

➢ **Cobalt**

High concentrations of cobalt may cause human health damage when we breathe in too high concentrations of cobalt through air we experience lung effects, such as asthma and pneumonia. This mainly occurs with people that work with cobalt. Health effects that are a result of uptake of high concentrations of cobalt like food contamination are:

- Vomiting and nausea.
- Vision problems.
- Heart problems.
- Thyroid damage.
-

➢ **Copper**

Long term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea.

Internationally high uptakes of copper may cause liver and kidney damage and even death. Whether copper is carcinogenic has not been determined yet.

Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic change in nasal mucous membranes. Chronic copper poisoning

results in Wilson disease characterized by a hepatic cirrhosis, brain damage, demyelization, renal disease, and copper deposition in cornea.

- **Chromium**

People can be exposing to chromium through breathing or drinking and through skin contact .Cr is known to cause various health effects. it can cause allergic reactions , such as skin rash . After breathing it in chromium can cause nose irritation and nosebleeds, other health problems are:

- Upset stomachs and ulcers.
- Respiratory problems.
- Weakened immune systems.
- Kidney and liver damage.
- Alternation of genetic materials.
- Lung cancer
- Death(lenntech)

1.1.7.2 Organic components:

- **Carbonyls:**

The toxicity of metal carbonyls is due to toxicity of carbon monoxide, the metal and because of volatility and instability of the complexes. Exposure occurs by inhalation or for liquid metal carbonyls by ingestion or due to the good fat solubility by skin restoration.

Carbon monoxide poisoning as nausea, cough, headaches, fever and dizziness. After sometime, causes symptoms such as serve pulmonary symptoms such as cough, tachycardia cyanosis or problems in the gastrointestinal tract occur

In addition to pathological alteration of the lung such as by metalation of the alveoli, damage are observed in the brain, liver, kidneys, adrenal glands and spleen (Blumenthal, Ivan, 2001)

- **Alcohols:**

Alcohols are thought to cause harm partly as a result of direct damage to DNA caused by its metabolites (Brooks ,1997).

- **Amines:**

Amines are only weakly toxic but they are skin irritates, especially as some are easily absorbed through the skin.

Amines are abroad class of compounds and more complex members of the class can be extremely bioactive (Eller,2000).

1.1.8 The effect of heavy metal on the environment:-

Chromium, cadmium and lead have the greatest potential to cause harm on account at their extensive use, the toxicity of some of their combined or elemental form. And their wide spread distribution in the environment, Hexa-valent chromium for example is highly toxic as are mercury vapor and many mercury compound, these elements have strong affinity for sulfur, in the human body they usually bird , via thoial groups (- SH), to enzymes responsible for controlling the speed of metabolic reaction. The resulting sulfur – metal bonds inhibit the proper functioning of the enzymes involved; human health deteriorates.

Cadmium strongly adsorb in the soils, so it can be extremely dangerous , as the uptake through food will increased and increase the damage in the animals .

Chromium is carcinogens; and can damage the animal health in respiratory problems and lower ability to fight disease, birth defects, infertility and tumor formation.

Lead is the most prevalent heavy metal. Lead accumulate in the bodies of water organisms and soil organisms, these will experience health effect of lead poisoning

Lead particularly dangerous chemical as it can accumulate in individual organisms, but also in entire food chain.

Cobalt carcinogens and copper is endocrine disruption, congenital disorders or general toxic effects in fish, plants, birds or other aquatic organisms.

Cobalt will accumulate in plants and bodies of animals that eats these plants, but cobalt is not known to bio magnify up the food chain .because of this fruits, vegetables, fish and other animals we eat will usually not contain very high amounts of cobalt.

*Iron (3) may be hazardous to the environment, special attention and should be given to plants, air and water.

It is strangled advisedly not to let the chemicals enter to the environment because it persists in the environment.

Iron usually occurs in soils in tertiary form but in water saturated soils it is converted to binary Iron there by enabling plant iron uptake; plants may take up water insoluble iron compounds by relating it not s causing it to dissolve.

Iron may be harmful to plants at feed concentration of between 5__ 200 ppm. These cannot found in nature in Norma condition, then low amount of soil water are present. A number take up iron particle and convert them to magnetite, and iron compounds cause serious environmental impact than the element itself

Copper can interrupt the activity in soils, as in negatively influences the activity of microorganisms and earthworms, the decomposition of organic matter may seriously slow down because of this. So animal's health will damage also (Stallman, 1998).

1.1.9 Calibration Curves:

A calibration curves is used to deter mine the unknown concentrations of an any element in a solution.

The instrument is calibrated by analyzing the absorbance of several Solutions of knows concentrations these are known as standard Solution.

The absorbance of these Solutions is directly proportional to concentrations, so higher concentrations is higher absorption. The concept is known as Been – Lambert law calibration curves is produced when the absorbance is plotted against the concentration of standard Solutions. The equation of this line can be displaced $y = mx + b$

y = absorbance m = gradient of line x = concentration (mg/l)

b = y intercept

1.1.10 Atomic absorption spectroscopy:

Atomic absorption spectroscopy is spectroanalytical procedure for quantitative determination of chemical element, using the absorption of optical radiation (light) by free atoms in gaseous state and it can be use to determine over 70 different element in solution , or directly in solid sample, via electro thermal vaporization and used in pharmacology , biophysics and toxicology research.

(Robert Bunsen and Gustav Kirchhoff 2018)

In order to analyze as ample for its atomic constituents it has to be atomized the atomizers most commonly are flames and electro thermal electro thermal atomizers. The atoms should then be irradiated by optical radiation, and the radiation source could be an element, specific line radiation source or a continuum radiation source.

The radiation then passes through a monochromator in order to separate the element –specific radiation foam any other radiation emitted by the radiation source, which is finally measured by a detector.

1.1.11 Infra red spectroscopy:

Infra red spectroscopy is certainly one of the most analytical technique available today's scientist. One of the great advantages of IR spectroscopy is that virtually any sample in any state may be studied.

Liquids, solutions, past, powder, films, fibers, gases and surfaces can all be examined with judicious choice by sampling technique.

Infra red spectroscopy is technique based on the vibrations of the atoms of a molecule, an Infar red spectrum is commonly obtained by passing infra – red radiation through as ample and determining what fraction of incident radiation is absorbed at a particular energy.

The energy at which any peak in an absorptions spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule.

(John Wiley and Sonus 2004).

1.2 Properties and quality control:

- Quality control procedures for thin –layer chromatography (TLC) offered increase reproducibility and dependability of results. During preparation of a TLC ink standard library, several types of inconsistencies were observed .observation of more than 100 chromatograms of writing inks indicated the need for institution of quality control procedures. Procedures were developed to ensure proper solvent selection, TLC plate selection and proper photographic recording of TLC plates (Lewis J.A(1996) .
- One of the most important factors underlying the rheological properties of printing inks is the interaction between pigment and vehicle. the complication formulations for the most inks make it difficult to make a detailed study of this factor , and Avery little attention has been given in it in the past .Simple system of calcium carbonate in polybutene oil was chosen for the study reported here .with this system m quantitative information on the nature of the pigment-vehicle interaction has been obtained(Zettlemoyar A.C. ,Lower G.W ,1955)
- The hazards on the workers health dealing directly with printing inks and its necessary to apply the safety measures and make periodical health test to the workers (Farag F.A., 2008).

1.3 Objectives of the study:

The aims of this study are:

a) Determination the organic and inorganic components of the printing inks .
b) Study the effects of these contents on workers, dealers, animals and on the environment in long terms.

Chapter Two

Materials and Methods

2.1 Materials

2.1.1Samples

- Black ink
- Blue ink
- Yellow ink
- Green ink
- Sheet – fed presses.
- Cleaner.
- Solvent.

2.1.2 Chemicals:

- HF solution (48%).
- Distilled water.
- KBr powder.
- Chloroform
- HCl 50%.
- HNO_3.
- $HCLO_4$

2.1.3Apparatus:

- Conical flasks –volumetric flasks.
- Beakers – glass rod.
- Crucibles - filter papers.
- Oven - sensitive balance.
- Atomic absorption (GBC-A7638) made in Australia.
- Infra –red spectrophotometer(FTIR -8400S – SHIMADZU –made in Japan)
- Quartz cell.
- Hot plate.

2.2Methods:

2.2.1Preparation of Standard Solutions:

Chromium: •

3.735 gm of potassium chromate dissolved in electro of water.

Iron:

I gm of Iron wire dissolved in (1:1) nitric acid and then diluted to a liter of water.

Cobalt:

I gm of cobalt element dissolved in (1:1) HCl and completed to I liter with HCl .

Calcium:

I gm of calcium element dissolved in (1:1) HCl acid then completed to I liter.

Lead:

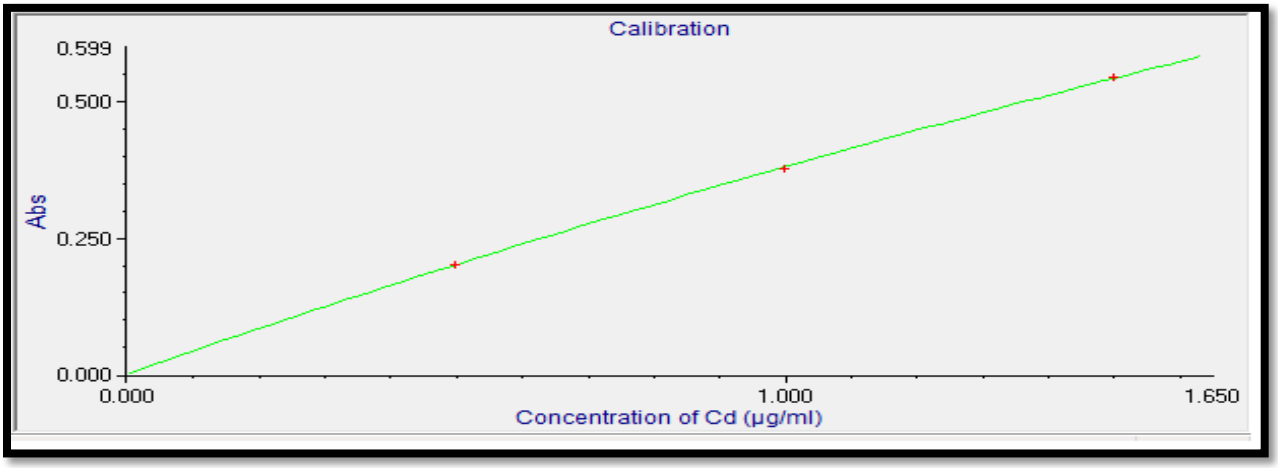
1.598 gm of lead nitrate pb (No3)2 in water and then completed to I liter.

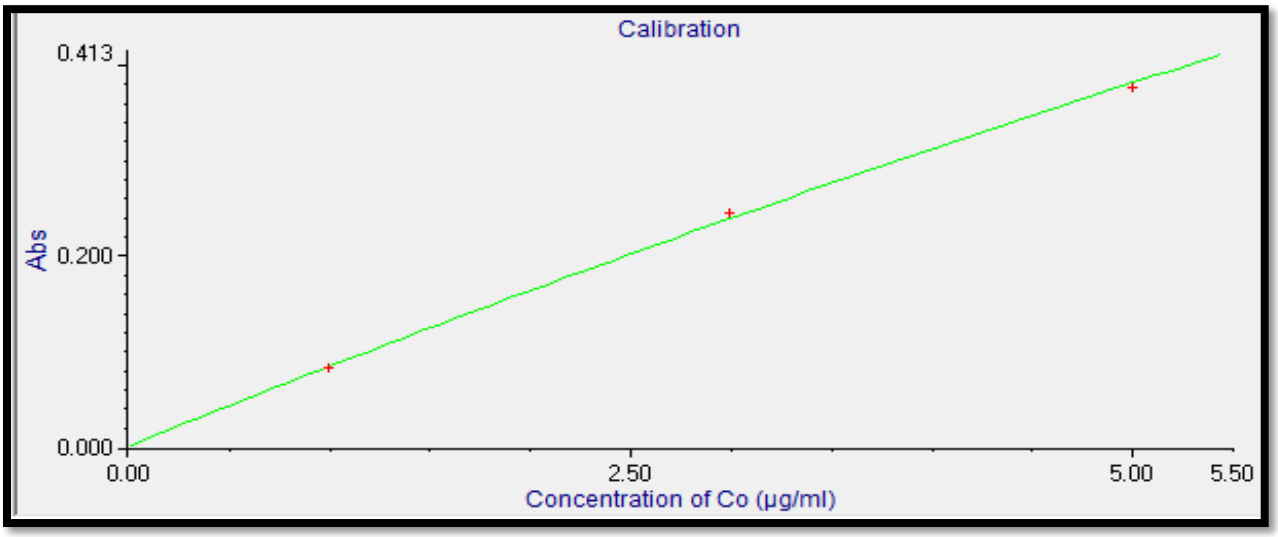
Copper:

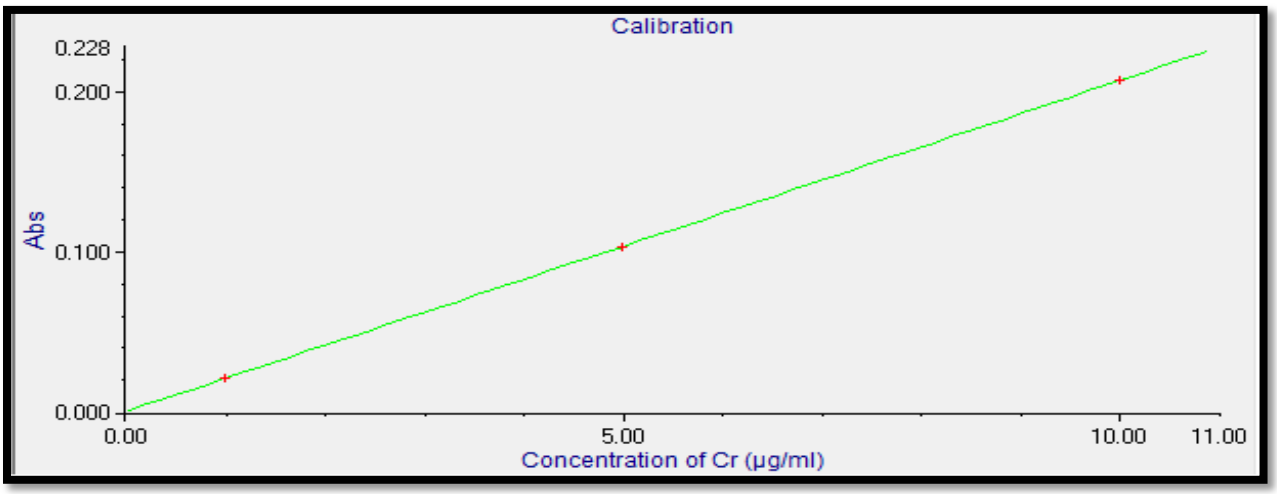
I gm of copper element dissolved in dissolved in ales amount of nitric acid and then diluted to a liter of water.

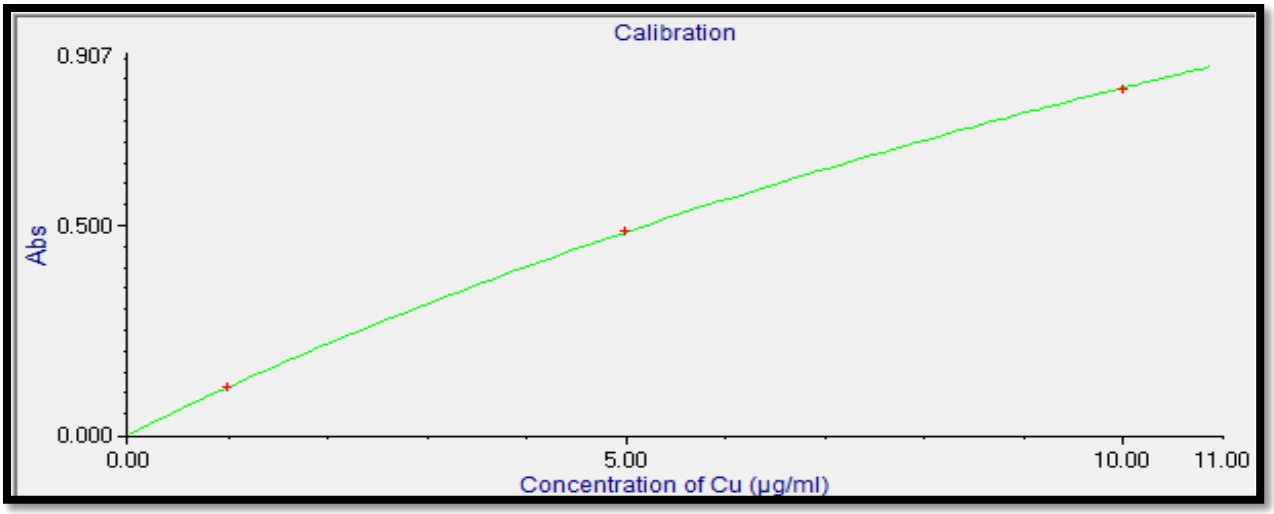
2.2.2Preparation of calibration curves:

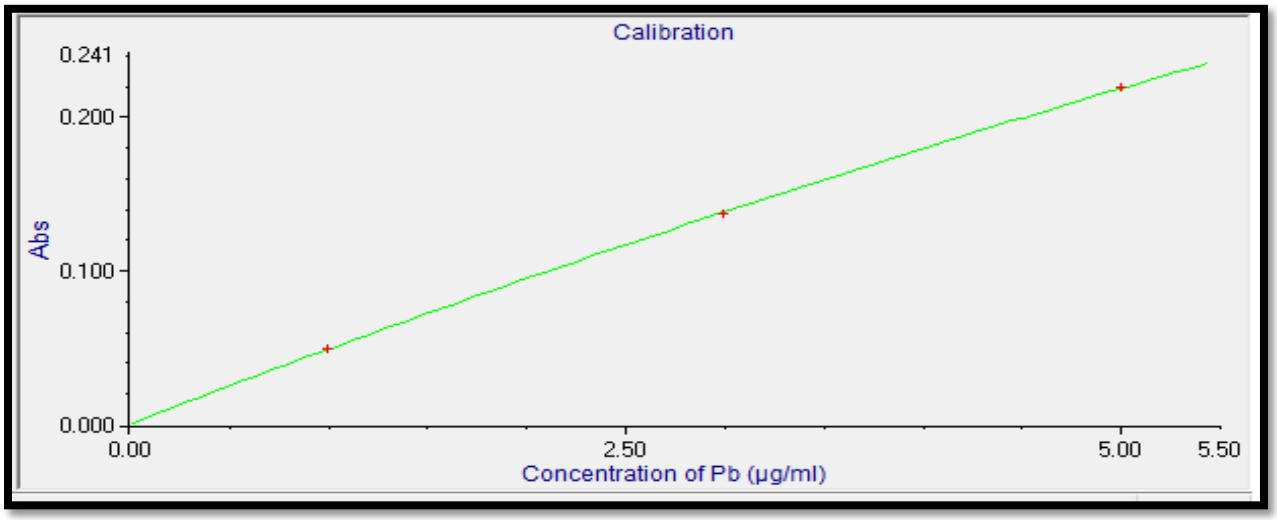
10 ml of 1000 ppm stock (standard solution) into 100 ml volumetric flask and then several standards were prepared from this solution for all elements depend on the concentrations wanted 1ppm, 3ppm and 5ppm.

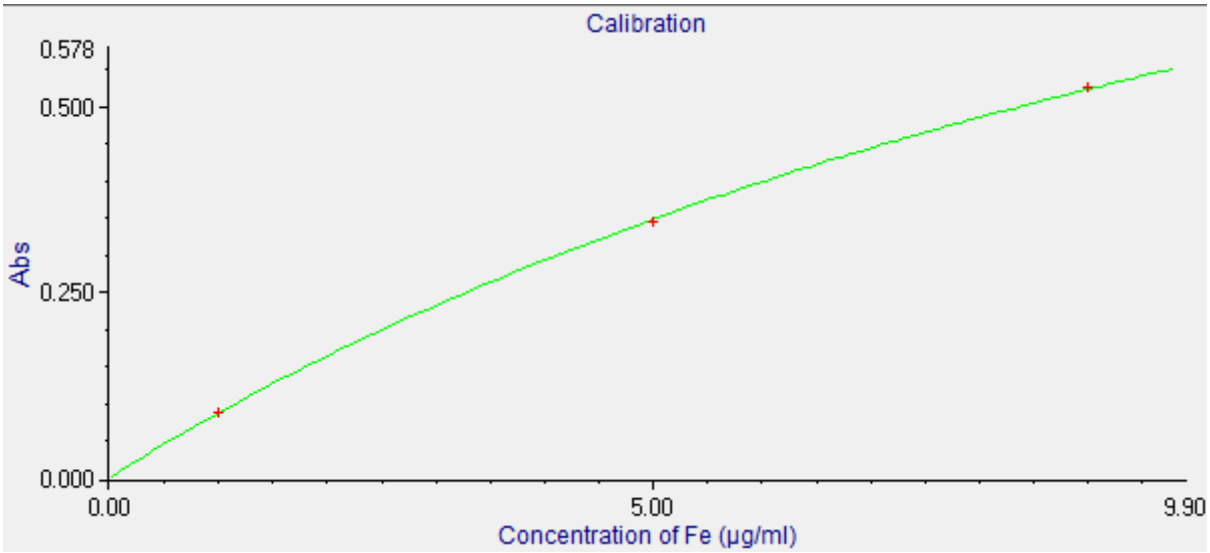



Calibration
0.413
0.200
0.000
Abs
0.00
2.50
5.00
5.50
Concentration of Co (µg/ml)


Calibration
0.228
0.200
0.100
0.000
Abs
0.00
5.00
10.00
11.00
Concentration of Cr (µg/ml)


Calibration
0.907
0.500
0.000
Abs
0.00
5.00
10.00
11.00
Concentration of Cu (µg/ml)


Calibration
0.241
0.200
0.100
0.000
Abs
0.00
2.50
5.00
5.50
Concentration of Pb (µg/ml)


Calibration
0.578
0.500
0.250
0.000
Abs
0.00
5.00
9.90
Concentration of Fe (µg/ml)

First A.A.S:

1. Weight about 0.1 gm of sample in a beaker.

2. Add 10 ml conc. HF + 5 ml conc. HNO_3 + 2.5 conc. $HClO_4$.

3. Heat on a hot sand bath to dryness.

4. Dissolve the residue with 10 ml HCL 50%.

5. Heat on hot plate for 10 mints.

6. Transfer the solution to 50ml volumetric flask complete the volume with distilled water. Let the contents for a day.

After trying many acids and finely HF hydrofluoric acid (48%) was chosen. For analysis of trace metal, acid digestion is much recommended

Second: IR SPECTROSCOPY

Liquid sample cells can be sandwiched using liquid sample cell of highly purified alkali halides normally NaCl other salts such as KBr and CaF_2 can also be used.

Aqueous solvents cannot be used because they can dissolve alkali halides. Organic solvents like chloroform can be used.

The sample thickness should be selected so that the transmittance lies between 15-20 % the sample cell thickness is 0.01-0.05 mm. the washing reagents must be anhydrous so we use the detergent solution which used by workers and they calling it (wash**)** (pharma analysis).

Chapter Three

Results and Discussion

3.1 Results:

Table 1 Equipment: A.A.S

A cid digestion

Sample no.		ppm	ppm	ppm	ppm	ppm	ppm
No	sample	Fe	Pb	Cd	Co	Cr	Cu
1	Black ink	3.149	N.D	N.D	1420	1735	418
2	Red ink	3.026	N.D	N.D	7050	1604	205
3	Blue ink	2.817	N.D	N.D	1153	1911	416
4	Yellow ink	3.561	N.D	N.D	N.D	1282	663

Read on AAS:

Calculation: for trace element

Concentration = reading of AAS * volume of flask/Wt*1000

Concentration ppm = reading of AAS *50/0.1

Concentration ppm

= volume of flask * reading of AAS * dil factor /Wt. Of the sample *1000

Table 2 IR spectroscopy:

No.	Sample name	Sample nature
1	Sample 1	Sheet – fed presses
2	Sample 2	Black ink
3	Sample 3	Red ink
4	Sample 4	Blue ink
5	Sample 9	Yellow ink
6	Sample 12	solvent
7	Sample 5	Cleaner (wash)

Functional groups observed are:

- Carbonyls (aldehydes) (1700-1740 cm^{-1}).
- Alcohols (3300-3600 cm^{-1}).
- Amine (3300-3500 cm^{-1}).

3.2 Discussion:

This work was directed towards the investigation and analysis of printing inks

The samples of printing inks were taken from FAB printing press in Khartoum industrial area.

The inks were treated by acid digestion for atomic absorption spectroscopic analysis and show heavy metals such as Iron $_{(2)}$ in the black ink (3.149 ppm) and in red ink (3.026 ppm), in blue ink (2.817ppm) ,and in yellow ink (3.561 ppm)

lead was not found in any ink, and also cadmium.

Cobalt in black ink(1420 ppm), in the red ink (7050 ppm)and in the blue ink(1153 ppm) .Chromium in black ink (1735 ppm) red ink(1604 ppm),in the blue ink(1911 ppm) and in the yellow ink(1282 ppm)

copper in black ink (418 ppm)red ink(205 ppm) ,in the blue ink (416 ppm)and in the yellow ink(663 ppm) .

And FT- IR spectroscopy spectra show carbonyls aldehydes (1700-1740 cm^{-1}) ,amines(3300-3500 cm^{-1}) and alcohols(3300-3600 cm^{-1}) functional groups.

From analysis and results:

Workers or dealer may suffer health effects when dangerous chemicals enter the body. The main routes of exposure are:

a) Inhalation: breathing of chemicals.
b) Absorption: through skin contact or splash in the eye.
c) Ingestion: via contaminated food or hands.

So we must adopt the following:

- Inks should handled and used carefully.
- Safety measures must be applied.
- Store ink and ink cartridges safely.
- Wear gloves when refilling inkjet cartridges to avoid getting ink on skin.
- Dispose of empty ink cartridges or recycle them at local office supply store
- Avoid contaminating food with the chemicals from regular ink residue.

- Find alternatives such as electronic press .
- The workers must take care during dealing with it and we must find safety alternative materials that can replace them and friendly to humans and environment.

3.3 Conclusion:

Based upon the results obtained in this study using instrument such as AAS and FT-IR ; dealing with printing inks which are containing heavy metals are classified hazardous and likely carcinogenic in a long term exposure.

The results prove that the printing inks contain both inorganic materials such as Fe, Co, Cu and Cr salts as well as organic materials such as alcohols, aldehydes and amines.

1.4 References:

1. J.H Duffus, 2003, The Edinburgh center for toxicology, Pure appl. Chemistry. Vol.75 No 9, pp 793 – 807.
2. Kipphan, Helmut 2001, HandBook of print media: technologies and production mehpds.
3. Colin Braid and Michael Cann, 1995, Environmental chemistry: 5th addition. WF Freeman, London.
4. Erik J. Tokar, Wei Qu, and Michael P. Waalkes. Toxicology sciences oxford university press.
5. Charles Finely, 1997, Ph.D., Printing paper and ink. DELMAR PUBLISHERS.
6. Kirk-Othmer, 1981, Encyclopedia of Chemical Technology (3rd Edition), Wiley & Sons, New York, V.13 (374-397) & V. 19 (110-175).
7. J. B. TUTTLE, W. H. SMITH, 1914, Analysis Of Printing Inks ,Govt. Print off , USA.
8. Stallman, J.M (1998) encyclopedia of occupational health and safety. International labor org.
9. Blumenthal, Ivan (1 june2001) carbon monoxide poisoning .JR Soc MED. The royal society of medicine.
10. Brooks PJ (1997). DNA damage. DNA repair and alcohol toxicity – a review.
11. Eller, Karsten; Henkes (2000) amines aliphatic Ullmanns Encyclopedia of industrial chemistry.
12. (Infra red spectroscopy: fundamentals and applications, Bar Bara Stuart "2004" John Wiley and Sonus).
13. Lewis ,J.A1996, Thin –layer chromatography of writing inks – quality control consideration, journal of Forensic Sciences ,Vol.41, No. 5 pp.874-877.
14. Zettlemoyar A.C,.lower G.W,1955,The rheology of printing inks, Journal of Colloid Science Vol. 10 pp29-45.
15. Farag F A , 2008 ,The risks of dealing with printing inks.
16. Pharma analysis, IR spectroscopy.
17. https://WWW.lenntech.nl.

18.http://Wikipedia.org.
19.http://google.com .sa

Appendix

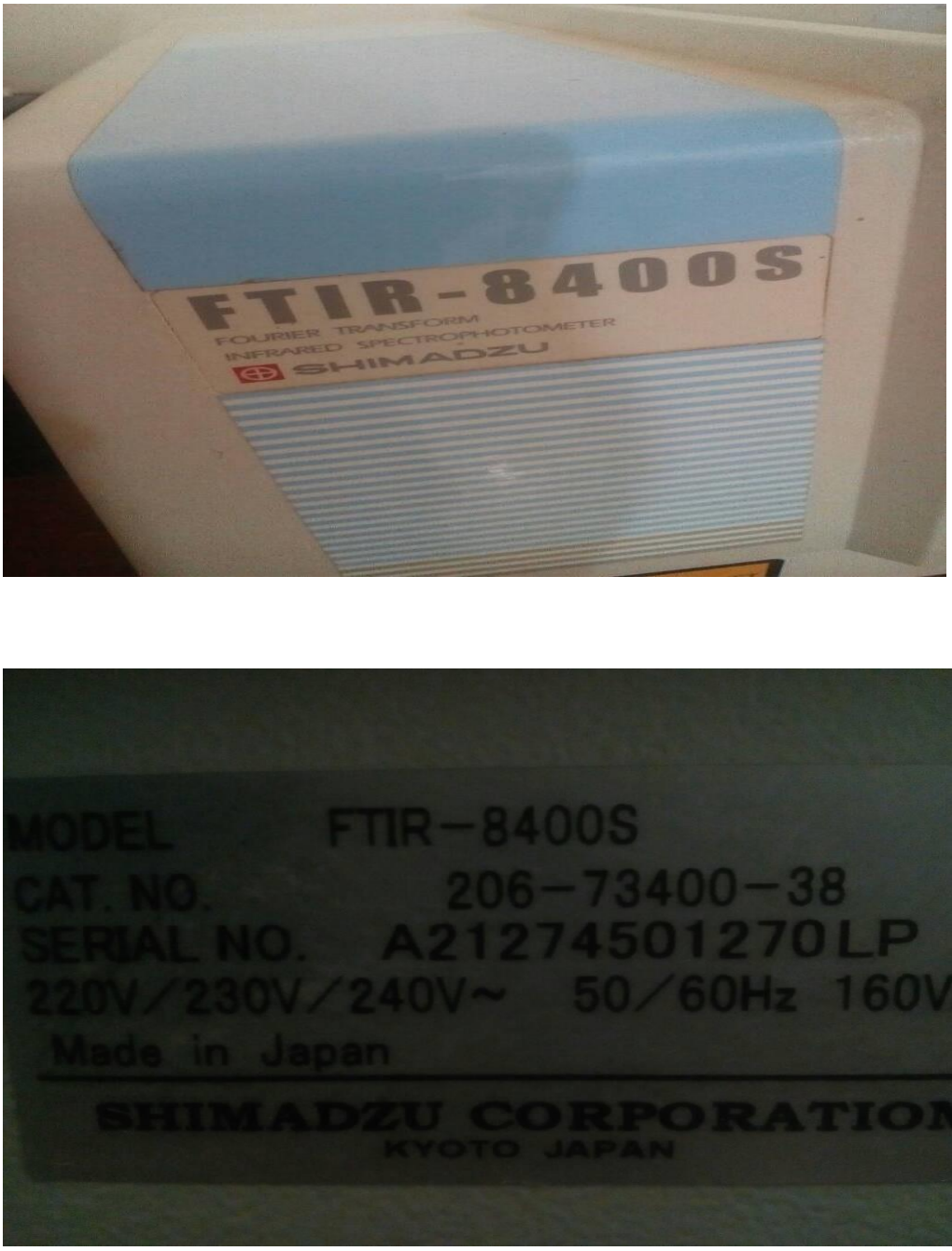


Figure 1: FT-IR spectroscopy equipment.

Figure 2: atomic absorption spectroscopy equipment.