

**|| PARTICULATE MATTER AND
HEAVY METAL CONTENT IN AIR
IN THE CITY OF NAIROBI. ||**

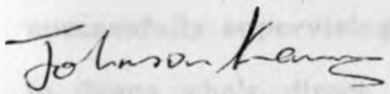
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A thesis submitted in part fulfillment for the degree of master
of science in the University of Nairobi.

This thesis is my original work and has not been submitted for a degree in any other University. It has been submitted for examination with the approval of the University Supervisors.



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ABSTRACT:

Nairobi City has a population of over 1.5 million and is growing at a rate of about 70 persons per day. Various activities in the City such as construction work, industrial processes, use of unroadworthy cars, and dust blown off unpaved roads do contribute enormously to suspended particulate matter in the air. In this work, the analysis by gravimetric and Energy Dispersive X-ray Fluorescence (EDXRF) of the suspended particulate matter in the air in the city centre, Industrial Area and one residential area was done. The values of lead obtained ($0.395-1.321 \mu\text{g}/\text{m}^3$) falls within the WHO recommendations, but compared to the values reported in some European countries, they are high. Most of the elements had low enrichment factors, EF, except for lead (EF 104-353), bromine (EF 429-1533) and zinc (EF 14-79). The bromine and lead were highly correlated to the number of light vehicles ($r=0.874$ and 0.942 respectively). In addition the ratio by weight of Br:Pb ranged $0.309-0.535$ while the correlation factor for Br to Pb was 0.951 leading to the conclusion that both elements came from the leaded gasoline.

CONTENTS:

Title	i
Declaration	ii
Acknowledgement	iii
Abstract	iv
Contents	v
List of figures and tables	vii
1. INTRODUCTION	1
1:1. Literature review	1
1:1:1. Air pollution awareness	3
1:1:2. Air pollution	5
1:1:2:1. Lead	8
1:1:2:2. Other toxic elements	14
1:2. Statement of the problem	17
1:3. Objectives	19
1:4. Theory of EDXRF Technique	20
1:4:1. X-ray radiation	20
1:4:2. X-ray interaction with matter	24
1:4:3. Instrumentation	29
1:4:4 EDXRF set up	32
2. EXPERIMENTAL	35
2:1. Quantitative analysis	35
2:2. Quality control	36
2:3. Sampling	37
2:3.1. Sampling stations	39
2:4. TSP determination	43

3. RESULTS AND DISCUSSION	45
3:1. TSP values	45
3:2. Correlation factors	52
3:3. Enrichment factors	55
3:4. Inter-city comparison	57
3:5. Conclusion and recommendations	58
4. REFERENCES	63

LIST OF FIGURES AND TABLES:

FIGURES:

Figure 1. Detector	23
Figure 2. Energy level diagram	27
Figure 3. Auger effect	28
Figure 4. EDXRF system	31
Figure 5. EDXRF set up	34
Figure 6. Sampling set up	41
Figure 7. Location of stations	42
Figure 8. TSP weighing balance	44

TABLES:

Table 1a. Mean elemental values at the sampling stations	46
Table 1b. Traffic flow data	47
Table 2. Atmospheric conditions	51
Table 3. Pearson correlation factors by weight	54
Table 4. Elemental enrichment factors	56
Table 5. Inter-city comparison of elemental levels	57

APPENDIX:

Appendix 1. Typical Xrfa spectra	62
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1. INTRODUCTION.

1:1. LITERATURE REVIEW.

Pollution is the presence of a foreign substance where it is not supposed to be. The foreign substances are introduced by human and natural activities. Environmental pollution is of great concern when self purification (natural) of the ecosystem fails. The magnitude of this problem depends on the pollutants concentration (emission rate), retention time, toxicity and self purification rate. Air pollution by particulate emission can be detected easily since particles in air scatter and absorb light affecting visibility. Inorganic ions are major constituents of atmospheric aerosol. These inorganic aerosol reduce visibility, contributes to dry acid deposition and presents a respiratory health hazard [1,2].

Unlike other kinds of pollution, air pollution does not know political boundaries. In fact the pollution in the northern hemisphere is finding its way to the southern hemisphere. This makes air pollution a global concern and there is great need to come out with a regulation that each individual country will respect and comply with. While we detest industries for polluting the environment, we also do need them for creating employment and manufacturing goods for both domestic and industrial consumption.

With the advent of industrialization, man has changed the "biogeochemical" cycling of a variety of trace metals. For many metals, man-made emissions, into the air and water, are now many orders of magnitude larger than the natural emissions. In some extreme instances, poisoning of soils, animals and even human beings has occurred because of metal pollution [3]. The following metals have been classified as potentially toxic to human and other organisms: Ag, As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, Te, Tl, V and Zn [4,5].

Heavy metals emitted by anthropogenic sources have been of environmental concern within the last few years. In some areas, their accumulation in soil has endangered soil fertility and vegetation. The residence times of these metals in the soil are of the order of several years [6].

The air we breathe at home, work-place, in towns and in the country side, contains various particulate matter at different levels. The primary sources of particulate matter can be divided into natural and anthropogenic. The natural sources include sea spray, volcano, wind, hurricane, pollen grains, forest fires, etc. The man-made particulate are generated in industrial processes, industrial emissions, power generation, tear and wear, etc. Niesser and Klockow [7] estimated global particulate matter and found that natural sources (2.3×10^{12} kg/year) are much more than anthropogenic one (0.3×10^{12}

kg/year). This holds true only for global consideration, while under local urban consideration the ambient pollutants may be totally dominated by particulate matter of human origin [8].

1:1:1. AIR POLLUTION AWARENESS.

The problem and concern of air pollution can be traced down to the thirteenth century. In medieval London, pollution from coal burning was regarded as a serious problem such that King Edward I in 1273 prohibited the use of sea coal for home heating in London during sessions of the Parliament. "Be it known to all within the sound of my voice, whoever shall be found guilty of burning coal shall suffer the loss of his head" [9]. Later he also set up what was probably the first environmental commission in 1285 [10]. But the "first" concern on air pollution research started in the 18th century when Marggraf reported nitric acid, chlorine and lime in rain water collected during the winter of 1749-1750 [11].

Pollution control is generally moving from the specific to the general, from local to the international, from reactive measures to foresight management, from emission based to technology forced, and from simple media managed to integrated management [10]. These are trends only, but there is a persistence in them. This suggests that air pollution legislation and regulation will be driven more by international protocol and

commitments than by national interests.

The enforcement of international protocol on air pollution will remain primarily a national responsibility because individual countries vary in their enthusiasm to meet externally imposed air pollution legislation. The weak link in the regulatory chain may well prove to be a hinderance in the implementation of legislative intent. The pattern of early period of air pollution legislation [10] has been as follows over the years:-

- (1) The phenomenon was originally for the most part urban and subsequently metropolitan, so early air pollution acts were generally place specific.
- (2) Particularly noxious fumes attracted early attention, notably the burning of sulphurous sea coal and subsequently emissions from chloro - alkali works, so the second phase was more process specific.
- (3) Tough and more comprehensive legislation awaited the emergence of the scientific method, notably careful observation and measurement and growing medical knowledge. This led to the introduction of a public health component to air pollution legislation that fell in line with sanitary reforms of the mid nineteenth century.

Since 1950, a new trend has appeared in the development of air pollution legislation and regulation. This has been prompted in part by the explosive growth in global air pollution monitoring

and measurement with instruments so sensitive that concentrations of trace gases and particles can be detected down to very minute levels.

The development of relatively inefficient car engines in an era of cheap fuel and expanding consumerism, has led to a series of exhaust-connected pollutants that cannot effectively be controlled by national actions given the international character of the modern manufacturing industry. But policies like imposing tax on "dirty car" sales may act as an incentive for "clean car" production. The growth of the chemical industry with its capacity of releasing volatile substances into the atmosphere in minute, but potentially toxic concentrations if channeled through biological routeways, has also required concerted action both from the chemical industry world wide and from national governments.

1:1:2. AIR POLLUTION.

During the past few years, large amounts of work has been carried out to assess the environmental pollution by heavy metals. Elevated levels of heavy metals have been observed in soils, vegetation and ambient air in urban areas due to burning fossil fuel, automobile exhaust and industrial emissions. It has been observed that population living in industrial areas have relatively higher concentration of metals like lead and cadmium

in their blood [12]. Due to their toxicity to man and the general ecosystem the heavy metals constitute a class of environmental pollutants which require particular attention in the management of the environment.

Environmental problems in air pollution and thermal stress are growing in many tropical countries partly on account of their rapid rate of industrialization/urbanization which outpaces the urban planning process. Nevertheless, the potential in air pollution generation in many of these countries has often been overlooked, being predicted solely on the basis of indicators of industrialization. Based on these indicators alone, an air pollution problem would hardly be expected to exist in Nigeria [13]. Yet air pollution has gradually become a fact to reckon with over the past 15 years, and total particulate matter released in the atmosphere is estimated as 2.75×10^8 kg per year [13]. The air over Lagos City has been credited with characteristic unpleasant odour and often the skyline in the city does not become visible until about midday due to a grayish haze [13].

The aerosol loading in the tropics are generally high compared to other latitudes. A five year averages of TSP for three metropolitan cities in India are in the range of 140–540 $\mu\text{g}/\text{m}^3$ with soil being the primary contributor to dust load [14]. Analysis of samples from Los Angeles Basin (Claremont)

California, and in Chicago, Illinois, has demonstrated that the coarse particle mass could be divided into two: crustal origin (Al, Ca, Fe, & Si) and material primarily of anthropogenic origin (Cd, Cu, Mn, Ni, Pb & Zn). The mass of the crustal material varied between 15 and 50% of total coarse particle mass [15].

The input of particulate matter to the atmosphere in the northern hemisphere is generally considered to be large enough to affect the atmospheric constitution even in remote areas. Reliable pollution baseline measurements should therefore be performed in the remote regions of southern hemisphere. Indeed 90% of the anthropogenic influx particles to the atmosphere originates in the northern hemisphere [16] and the interhemispheric transport of material is low as the ratio of the mass of air transfer in either hemisphere is only 0.007. Also layers of ice have been used to assess the record of pollution with time at the poles.

In case of the atmospheric aerosol, the gas matrix consists of N_2 , O_2 , CO_2 , water vapour, noble gasses and a wide variety of other gasses (NO_x , SO_x , H_2S , RSH , etc) present in trace levels. The unsuspended material (droplet and solid particle) are the particulate matter and exists in a size range between 0.001 to 100 micron [7]. The settling velocity (V) of particulate in the air depends on, density (P) and diameter (D) of the particle, viscosity (n) and density (P^1) of the air and gravitational

pull (g) [17-19].

$$V = \frac{gD^2(P-P^1)}{18n}$$

The behaviour of trace metals in the atmosphere depends on their chemical nature and also on their size distribution [20]. In recent years, there has been an increased interest in trace metals in atmospheric precipitation and their environmental effects. This is to a large extent because metals such as mercury, cadmium and lead accumulate in the biosphere and may be toxic to living systems. In some instances, atmospheric deposition is a major source of these and other metals to the ecosystems [6,21,22].

1:1:2:1. LEAD.

Lead is mined as $PbSO_4$ and $PbCO_3$, after smelting and refining, it is used to manufacture lead containing compounds and goods. Lead is added to petrol in the form of an organic tetra alkyl lead (TAL) anti-knock agent which raises the octane number of the fuel and reduces the wear of the engine. Knocking of the engine occurs when the gaseous combustion mixture is compressed too high. As a result the regular combustion of the fuel changes into a spontaneous ignition in that part of the mixture not yet consumed by the flame front.

This knocking effect is strongly dependent on the nature of the hydrocarbons used as a fuel. Aromatic and branched aliphatic hydrocarbons cause less earlier knock than straight chain hydrocarbons. One of the best antiknock additive is tetraethyl lead (TEL) discovered by Midgley in 1923 [23]. The commercial grade product, intended for knock prevention, contains also ethylene dibromide and dichloride roughly in a ratio of 3:1:1 to scavenge lead from the engine in form of volatile lead halide after combustion.

During combustion, alkyl lead reacts with ethylene dihalide (EDH) "scavenges", with consequent emission of the lead in an inorganic particle form predominantly $PbBrCl$ and the theoretical mass ratio of Br/Pb is 0.386 [24]. The concentration of bromide in atmospheric particles have been commonly used as an indication of vehicle emitted lead, since the two elements are associated in auto exhaust. The principle source of particulate lead in the atmosphere arises from combustion of leaded petrol in automobile engines, locally significant contribution may be made by industrial works such as lead smelting.

Khandekar and workers [12] reported a significant correlation between airborne Pb concentration and vehicular traffic density at the time of sampling in Bombay. Motor vehicle exhaust has been shown to be a major contributor to fine particle mass concentration using chemical mass balance (CMB)

[25,26]. The mass emission of lead is dependent on the lead content of the fuel. A 5.5 l V8 engine was observed at a simulated speed of 90 km/hr to emit 0.02 g/km of lead using petrol with 0.4 g/l lead content. Another study reported 0.01 g/km for similar engine at 50 km/hr using petrol containing 0.6 g/l of lead [27].

The alkyllead in the petrol also evaporates/escapes into the atmosphere. The values for alkyllead in the air in Oslo are reported to be from 0.010 to 0.100 $\mu\text{g}/\text{m}^3$ which is between 0.01 to 0.5% of the exhaust alkyllead [28]. In the same study, a parking basement was sampled and evaporation from parked car was estimated at 500 μg of alkyllead per day per car.

Among the heavy metals, lead has raised concern about its quantity in the environment as it has not been known to have any biological function in the body. But the level of lead in the body seems to rise with the environmental level [29,30]. This heavy metal gets into the body mainly through ingestion and inhalation. The average biological half-life of lead in human being is 1460 days (4 years) while in bones it can be as many as 10 years [29,31]. Hence with high air-lead concentration we would expect high accumulation of lead in the body.

The intake of lead into the body comes from food, water and air. Sources of lead in air are mainly emissions from lead

factories and from exhaust fumes of vehicles [32]. The lead from these exhaust gases has a diameter of less than 1 μm and penetrates down to the alveoli in the lungs [29,32].

When blood-lead level in children is above 36 $\mu\text{g}/\text{dl}$ it results in lead poisoning. Betts and workers [33] found anaemic children with the following blood-lead levels:

<u>Blood-lead level</u>	<u>Anaemic Children.</u>
37 - 60 $\mu\text{g}/\text{dl}$	36%
60 - 100 $\mu\text{g}/\text{dl}$	71%
Over 100 $\mu\text{g}/\text{dl}$	89%

Lead poisoning is known to result in abdominal cramp, colic and constipation, loss of appetite, anaemia, irritability, encephalopathy and central nervous system symptoms such as insomnia, fatigue, weakness and drowsiness [34]. In children, lead poisoning may result in subsequent kidney disease, mental retardation, recurrent seizures, cerebral palsy or optic nerve atrophy due to inhibition of growth of the central nervous system [35,36].

Investigations done on children in a lead smelting town [37] showed that 7% had over 30 $\mu\text{g}/\text{dl}$ of lead in their blood. These were children who had one or more of the following:

- (a) Having household members who worked with lead in their occupation.

- (b) Living in a house with flaking paint on the outside walls.
- (c) Children biting finger nails.
- (d) When in school, children having relatively dirty hands and dirty clothes.
- (e) Children who go back home to eat lunch during school days.
- (f) Children living in a house-hold block with large areas exposed to dirt.

Children within two districts next to a lead belt in Philadelphia were found to have elevated dentine lead. These were children from areas of deteriorated housing and toxicity was upto 20% [38]. Also children living within 1.6 km (1 mile) from a lead smelter were reported that 99% had over 40 $\mu\text{g}/\text{dl}$ and 22% were with over 80 $\mu\text{g}/\text{dl}$ of lead in their blood [39].

Effects of lead poisoning are more pronounced in developing tissues than those tissues with stable metabolism. Hence, subclinical form of poisoning is most dangerous to children because its effects emerge without associated symptoms that bring the victim to medical attention [40].

According to Lancrazan et al. [41] women working in lead factories tend to have high miscarriage rates, while workmen occupationally exposed to lead have shown a decrease in fertility, associated with an increased frequency of

fertility, associated with an increased frequency of asthenospermia, hypospermia, and teratospermia. The hypofertility induced by lead is due, perhaps, to its direct toxic effect on the gonads, as no interference with the hypothalamopituitary axis was evidenced [41]. The effect of low-level of lead in the air can be magnified by other factors: heavy drinkers have shown to have high blood lead concentration and low aminolevulinic acid dehydratase (ALAD) [42]. Lead poisoning is also common among the copper smelter workers [43]. The concentration of lead in the blood also depends on the residential area as reported in Aberyswyth [44]. These levels increased with year of residence up to twenty years. It was found that these elevated levels were not wholly dependent on air-lead concentration [45].

About 35% of the lead inhaled is deposited in the lungs, most of this is absorbed and adsorbed to the cell walls [46]. Food-stuff also contains 0-2.5 mg/kg of lead, while tap water has less than 62 µg/litre of lead [46]. Elimination of lead is mainly through urine and faecal lead [40,46]. A study done in South Africa showed that long distance road-runners have elevated blood-lead level [47]. While as much as 12,820 µg of lead per gram of street dirt have been determined [48]. Although in many cases of lead poisoning the sources remain undetermined, the lead in town (dirt and ambient) is mainly from automobile exhaust [32,48,49].

The number of road-licensed cars in Nairobi for the year 1987 was over 130,000 [50] while the area of the City and its environs (Nairobi Province) is approximately 680 square kilometers [51]. The number of cars that enter the city centre everyday is about 140,000 according to a 1991 survey by the Nairobi City Commission [52]. The regular and premium fuels have upto 0.85 grams of lead per litre of fuel and the typical amounts are 0.32 g/l for regular and 0.37 g/l for premium [53]. The refining of lead free fuel is expensive and this fuel has high engine wear resulting in higher expenditure [54]. Lead free petrol is not available in Kenya. This leaves leaded gasoline as the main source of lead pollution in our environment.

The areas with high vehicular flow are likely to have high levels of lead in the air. Studies that have been done on roadside soil samples have shown considerable high lead levels. Averages of 1251 $\mu\text{g/g}$ with a range of 332 to 3,760 $\mu\text{g/g}$ have been reported in Nairobi roadside soils [55-57].

1:1:2:2. OTHER TOXIC ELEMENTS.

The major source of other metals are industrial processes not to mention the tear and wear on the machineries. Buerki and workers [58] reported that the major source of pollution in Switzerland is emissions from:

- (1) Traffic.

- (2) Industrial plants burning heavy oils.
- (3) Residential heating.
- (4) Refuse incineration.
- (5) Resuspension of soil particles.

From the above sources, the toxic elements are as shown below:

<u>Element</u>	<u>Toxicity</u>	<u>Industrial sources</u>
As	Medium	Fungicides, pesticides.
Ba	Medium	Additives, filters, electronics.
Be	Very high	Optics, nuclear reactors, electronics.
Cd	High	Coatings, paints, pesticides.
Co	High	Alloys, glass.
Cr	Medium	Paints, wool, coatings, tanneries.
Cu	Low	Electricity, alloys, buildings.
Fe	Low	Metallurgy, buildings.
Hg	High	Instruments, paints, chemical lab.
Mn	Low	Metallurgy, fuel additives.
Ni	Medium	Alloys, fuel additives.
Pb	High	Buildings, chemical lab., electricity.
Sb	Medium	Metallurgy, alloys, rubber.
V	Medium	Metallurgy, chemical lab., refineries.
Zn	Controversial	Metallurgy, alloys, Buildings.

High levels of metal in human body result in several disorders, some of these are highlighted here [40]:

Iron:

High concentration results in hepatic failure, diabetes, testicular atrophy, arthritis, cardiomyopathy and hyperpigmentation.

Zinc:

Toxicity follows inhalation of zinc fumes, oral ingestion or intravenous administration. Inhalation of high concentration of zinc oxide fumes leads to an acute illness called "metal fume fever" or "brass chills" manifested by fever, chills, excessive salivation, headaches, cough and leukocytosis. Zinc toxicity also causes gastric ulcer, pancreatitis, lethargy, anemia, nausea, vomiting, respiratory distress and pulmonary fibrosis.

Manganese:

Miners who inhale large quantities of manganese dust over long periods of time develop asthenia, anoxia, apathy, headache, impotence, leg cramps and speech disturbances. Other toxic effects are encephalitis-like syndrome, parkinson-like syndrome, psychosis and pneumoconiosis.

1:2. STATEMENT OF THE PROBLEM.

Nairobi City has a population of over 1.5 million people [59] and is developing at such a rate that at any particular moment, there is some construction activity going on. Although all the roads in Nairobi City centre are tarmacked there are several areas and some sections of the road sides which are bare. The dust from these road sections, construction activities and exhaust emissions from factories and vehicles goes into increasing the particulate matter in the air around Nairobi City. Until recently, Nairobi was a garden city with a lot of open grounds where trees and other plants grew. Most of the open grounds have been cleared off the trees to make room for highrise buildings. The trees and other plants are very essential in self-purification of the air.

Although we are not yet on the scale of being called an industrial country, we definitely merit a place among the top ten of the "industrialized" countries in Africa. Recently workers and visitors in Nairobi's Industrial Area complained about air pollution where some factories are emitting toxic fumes leading to coughs, headaches and eye exhaustion among others [60]. Many workers and visitors even had to seek medical attention. A factory between Kariobangi South and Dandora estates along the Komorock bridge has been emitting fumes and substances which residents of the nearby estates complained affected their

health. They took the factory owner to court demanding its closure without much success [60].

There are laws that empowers the National Environmental Secretariat (NES) of the Ministry of Environment and Natural Resources to take to court the owners of the factories that have uncontrolled emissions into the air. These are the Factory and Water acts, but they are not adhered to as they need backing of scientific data as evidence in court.

Kenya is also one of the big importer of motor vehicles in Africa. This has made the NES very concerned about the high level of lead that is emitted by cars especially during peak hours when there are traffic jams. The NES is drafting the clean air bill and the chemical industries bill which are expected to empower the Secretariat to take offenders to court [61]. This act proposes that lead will no longer be added into petrol and Industries will be required to fit devices or gadgets that will destroy the dangerous fumes before they are allowed to be emitted into the atmosphere.

The work that was done by Ngugi [62] in 1982 showed that there was an average of $252.2 \mu\text{g}/\text{m}^3$ of Total Suspended Particulate matter (TSP) in Nairobi industrial area. This work did not look into the elemental composition of the TSP.

While the NES, Newspapers and other Environmentalists are concerned and raising their voices against air pollution, proper scientific data forms the best base for policy formulation. Hence the need for research on environment related problems.

1:3. OBJECTIVES.

(1) To determine the total suspended particulate matter in the air in Nairobi city. The city was divided into three areas that were expected to have different levels of air pollution. These areas were:

(a) The Town centre which is the central business area.

(b) The Industrial area, where most of the industries are situated. It should also be noted that this area is not very far from the city centre.

(c) A residential estate, where there is very little activity during the working hours.

2. To determine the concentration of lead in the collected TSP and then relate these to the amount in the air.

3. To determine the concentration of any other heavy metals in the TSP.

1:4. THEORY OF EDXRF TECHNIQUE.

EDXRF is a multielemental analytical method for elements between silicon and uranium. The technique is non-destructive and the detection range can go as low as parts per billion [24]. In EDXRF, X-rays from radioisotopes or an X-ray tube are used to excite atoms of various elements in a given sample. The atoms of these elements emit secondary characteristic X-rays which are detected by semi-conductor detector, Si(Li).

1:4:1. X-RAY RADIATION.

X-rays were discovered in 1895 by Roentgen and later on it became evident that X-ray energies are characteristic of the atomic structure of an element that discharges them [63]. The first positive evidence of X-ray emission spectra was obtained by Barkla in 1910, and that is when X-ray spectroscopy is considered to have started. In 1913, Mosely noted that copper lines were more intense than Zinc lines in a 70% Cu - 30% Zn brass and established the foundations of qualitative and quantitative X-ray spectrometry by postulating a relationship between the wave length of X-ray spectral lines and atomic number [63]. At the same time, Coolidge proposed the hot filament, high vacuum X-ray tube. In the mid-1920s, several workers pointed out that the use of X-ray source would eliminate most of the difficulties of electron source [64].

In those early times, the lower efficiency of photon excitation coupled with the fairly primitive detection instrumentation made the use of X-ray fluorescence analysis impractical. Coster and Schrieber [63] made use of the secondary excitation in 1928 and upto late 1940's, analysing substances by exciting and recording their X-ray emission remained an absolute activity of research scientists.

Technological advances (in the second half of the twentieth century) in ionisation detectors and X-ray spectrometry caused a renaissance of interest in X-ray spectrometry as an analytical method in chemical analysis and as a method for studying the solid state physics in general. In 1948 a prototype of the first modern commercial X-ray spectrometer, with a sealed X-ray tube, was developed by Friedmann and Birks [63]. The instrument was a modified form of North American Philips (Norelco) diffractometer which employed a diffracting crystal to separate X-ray into their corresponding wavelengths.

In the mid-1960s, the development of a semiconductor X-ray detector at the Lawrence Berkeley Laboratory heralded the advent of energy dispersive X-ray fluorescence spectrometry (EDXRFS) [63]. The present form of this detector, (figure 1) a single 3-mm or 7-mm thick silicon crystal is the complete X-ray detector of a typical EDXRF spectrometer system

[63]. Together with the appropriate electronic amplifiers and signal processors, the energy dispersive system collects emitted X-rays of various wavelengths (energies) and sorts them electronically. Simple electronic spectrometers which are now widely applied in X-ray fluorescence spectrometry and in analytical electron microscopes have been made possible due to the advent of semi-conductors. The first generations of these instruments allowed a fast analysis, but due to their inferior spectral resolving power compared with the wavelength dispersive spectrometers, the results were often not as good.

Improved techniques for deconvolution of the spectra steadily increased the usefulness of the energy dispersive systems. At present, EDXRF detectors can be used for quantitative determinations; methods of analysis based on the measurement of X-rays emitted from the core electron levels by either fluorescence of X-rays or excitation, by electrons or particles [64]. The detectors have a fairly uniform detection limit for a considerable number of elements and allow analysis of a wide variety of samples.

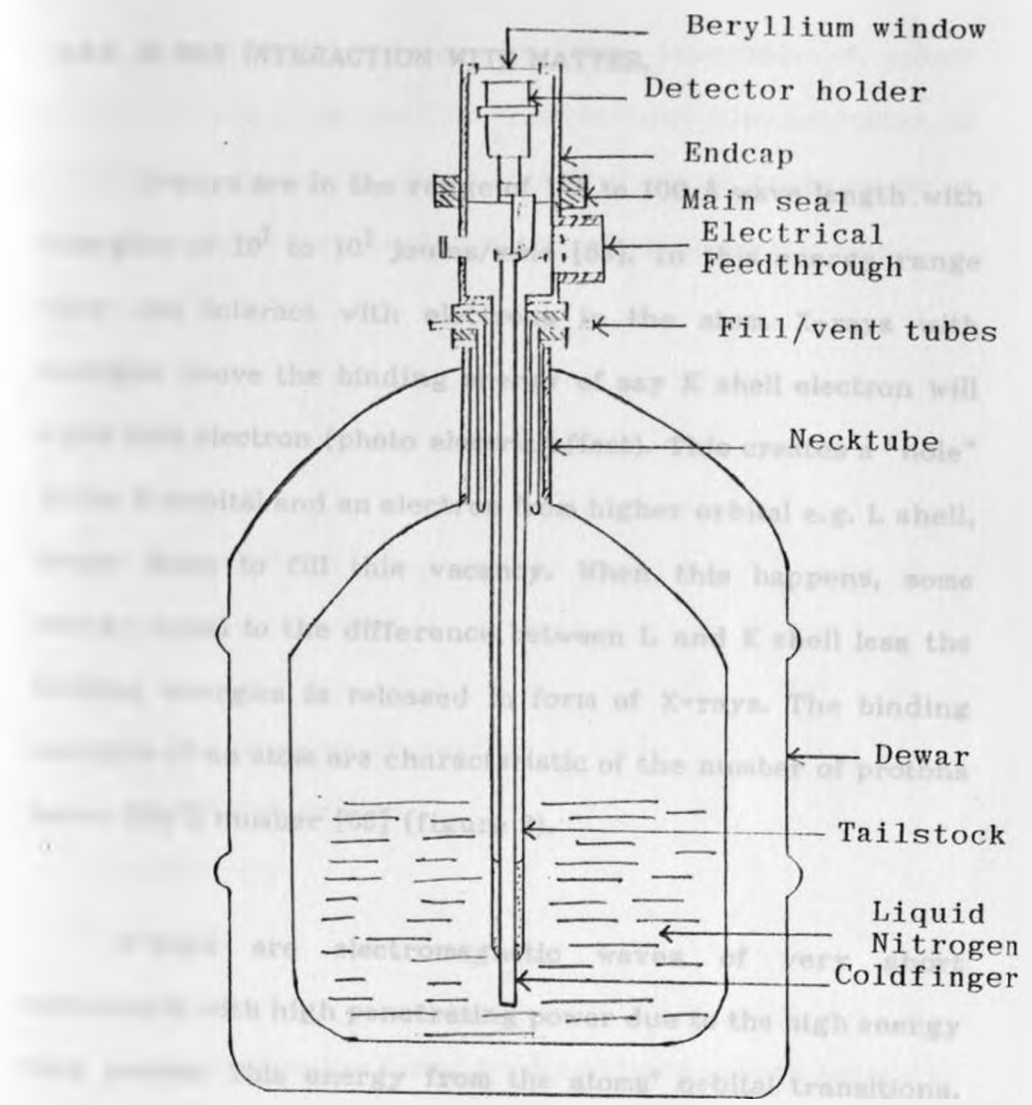


Figure 1. Detector

1:4:2. X-RAY INTERACTION WITH MATTER.

X-rays are in the range of 1 Å to 100 Å wave length with energies of 10^1 to 10^3 joules/mole [65]. In this energy range they can interact with electrons in the atom. X-rays with energies above the binding energy of say K shell electron will eject that electron (photo electric effect). This creates a "hole" in the K-orbital and an electron from higher orbital e.g. L shell, drops down to fill this vacancy. When this happens, some energy equal to the difference between L and K shell less the binding energies is released in form of X-rays. The binding energies of an atom are characteristic of the number of protons hence the Z number [66] (figure 2).

X-rays are electromagnetic waves of very short wavelength with high penetrating power due to the high energy they possess. This energy from the atoms' orbital transitions, that is the KLM... shells, may be expressed as:

$$hv = E_2 - E_1.$$

$$hv = \frac{hc}{\lambda}$$

Where:

E =energy.

h = planks constant.

c =speed of light.

λ =wavelength

X-rays are produced from the transition of atomic electrons from one shell to a lower one. The transition of electrons in the shells obeys certain quantum mechanic rules (selection rules) thus photo electric effect will occur when:

$$h\nu > E_i \text{ or } h\nu > E_j$$

and

$$\Delta n > 1$$

$$\Delta L = \pm 1$$

$$\Delta J = \pm 1 \text{ or } 0.$$

Where:

n =principle quantum number.

L =angular momentum.

S =spin = $\pm \frac{1}{2}$.

J = L + S.

In some cases the X-ray produced have enough energy to remove another electron from the L shell. This process is called Auger effect and result in auger electrons (figure 3). The process is predominant in light elements up to silicon. This makes the analysis of light elements by EDXRF method unreliable. Other process that occur in the interaction of X-rays with matter are the coherent and incoherent scattering processes.

The intensity of the emitted characteristic X-ray depends on the probability that, incident primary radiation will ionize a shell of a given atom and that vacancy in the shell will be filled by electron from outer shells. Hence the fluorescence yield, ω is defined as:

$$\omega = \frac{\text{number of X-rays photons.}}{\text{number of initial vacancies created.}}$$

The parameter is calculated from X-ray data tables and is utilized in quantitative analysis.

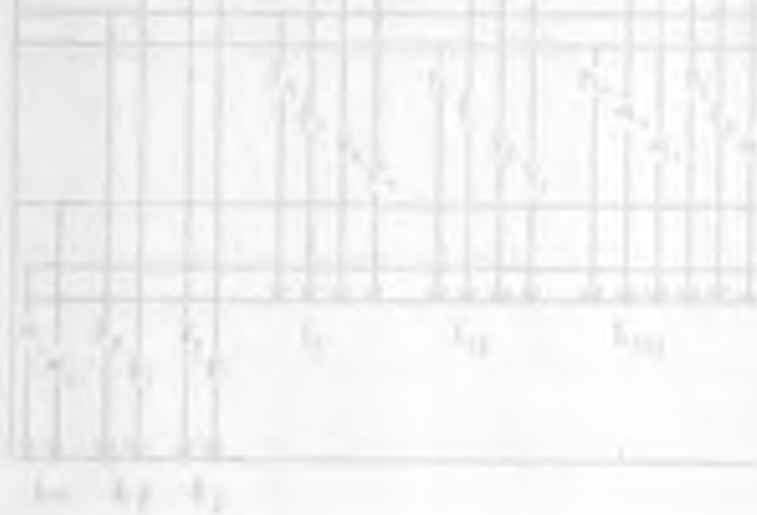


Figure 1. X-ray fluorescence spectrum.

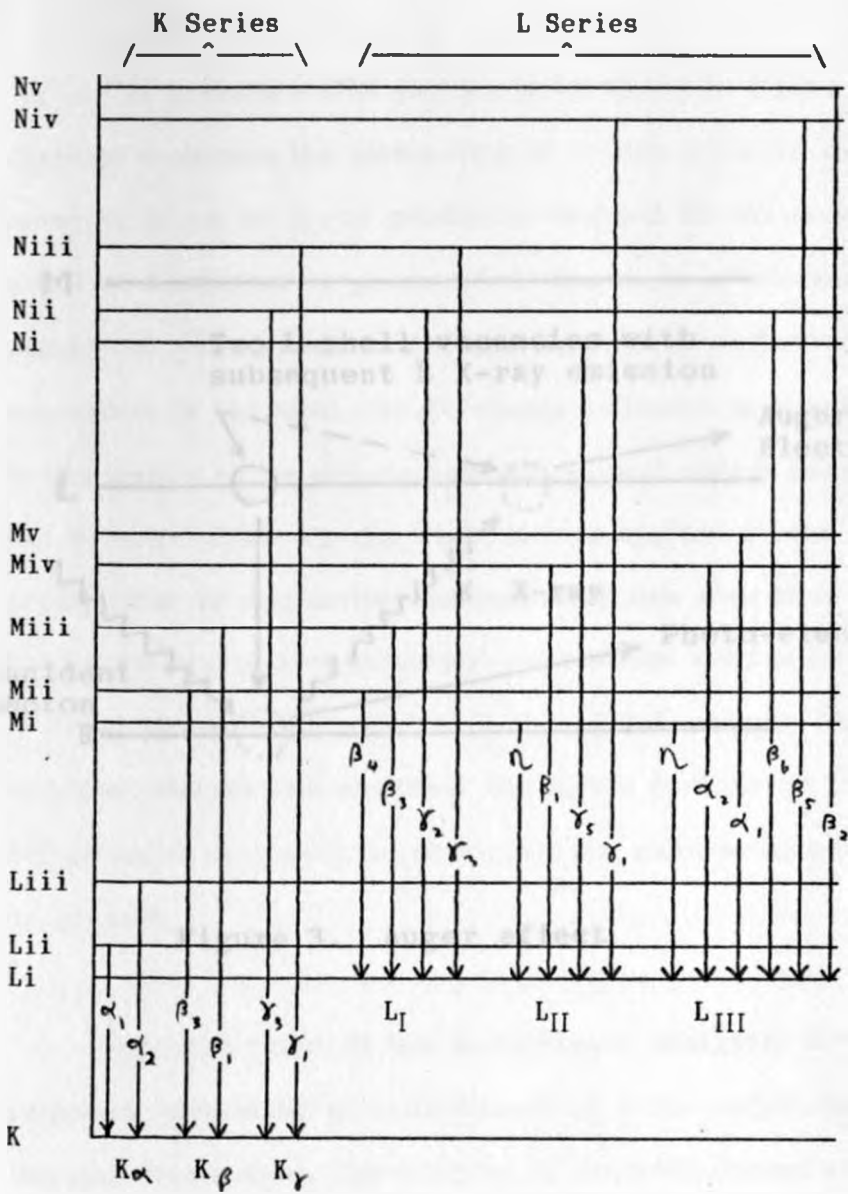


Figure 2. Energy level diagram

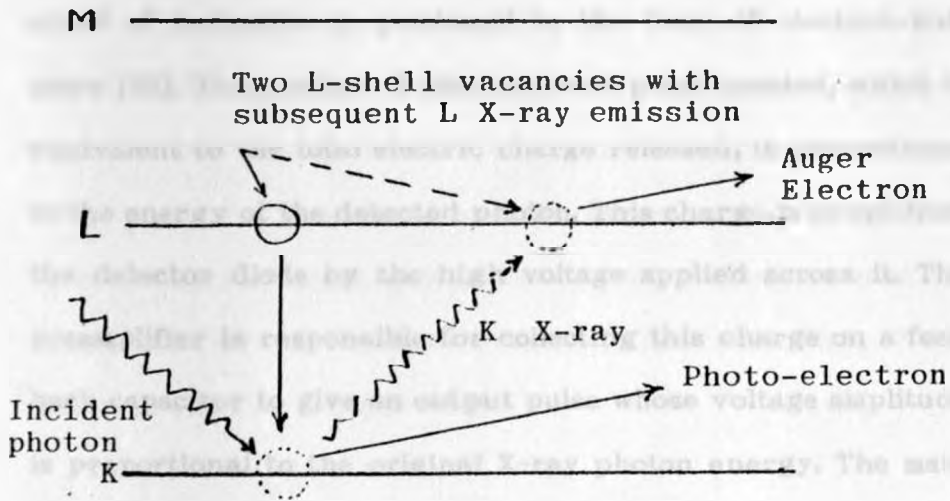


Figure 3. Auger effect

1:4:3. INSTRUMENTATION.

The general EDXRF system is as shown in figure 4. The detector registers the interaction of X-rays with the detector material. When an X-ray photon is stopped in the detector a cloud of ionization is produced in the form of electron-hole pairs [66]. The number of electron-hole pairs created, which is equivalent to the total electric charge released, is proportional to the energy of the detected photon. This charge is swept from the detector diode by the high voltage applied across it. The preamplifier is responsible for collecting this charge on a feedback capacitor to give an output pulse whose voltage amplitude is proportional to the original X-ray photon energy. The main amplifier shapes and amplifies the signal further so that the multichannel analyser can record it in the right memory location or channel.

Upto the input of the multichannel analyser, the signal is analog consisting of a continuum of pulse amplitudes from the amplifier output. The purpose of the multichannel analyser is to measure the pulse height of each pulse from the amplifier, record this as an integer number and store it in a particular memory channel in the MCA. This process is an analog-to-digital conversion process. The number of times a pulse of same height has been detected is accumulated in the analyser memory to form the spectrum of pulse heights. This information is then

displayed as a picture of the analysed energy spectrum. The display can then be presented with the X axis calibrated in terms of the mean energy of each interval while the Y axis display gives the number of X-ray photons counted in each energy interval during the entire data accumulation period.

In addition to the ability to display the spectrum on a cathode-ray tube or monitor, the analyser can usually drive an X-Y plotter to produce a permanent copy. Most quantitative fluorescence spectrometers include a small digital computer with approximately 16,000 words of memory plus some form of mass storage such as a floppy disk.

In such a system the computer software may control specimen presentation, the excitation conditions, and data accumulation in the multichannel analyser. At the end of data acquisition for each specimen, the computer software analyses the spectrum in the multichannel analyser, computes the raw element intensities, corrects for interelement effects, and computes the concentration of each element.



Figure 1. X-ray source.

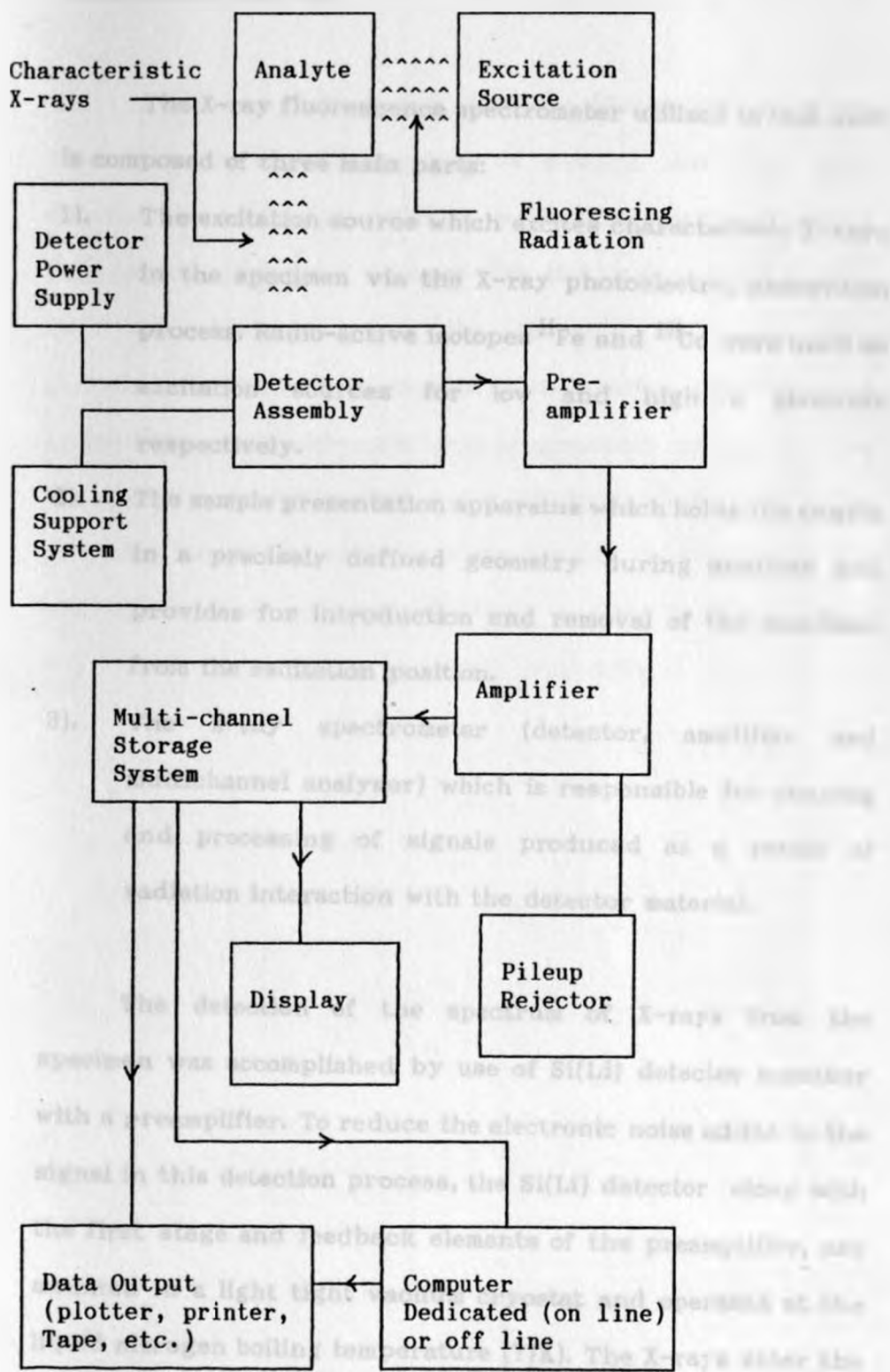


Figure 4. EDXRF system.

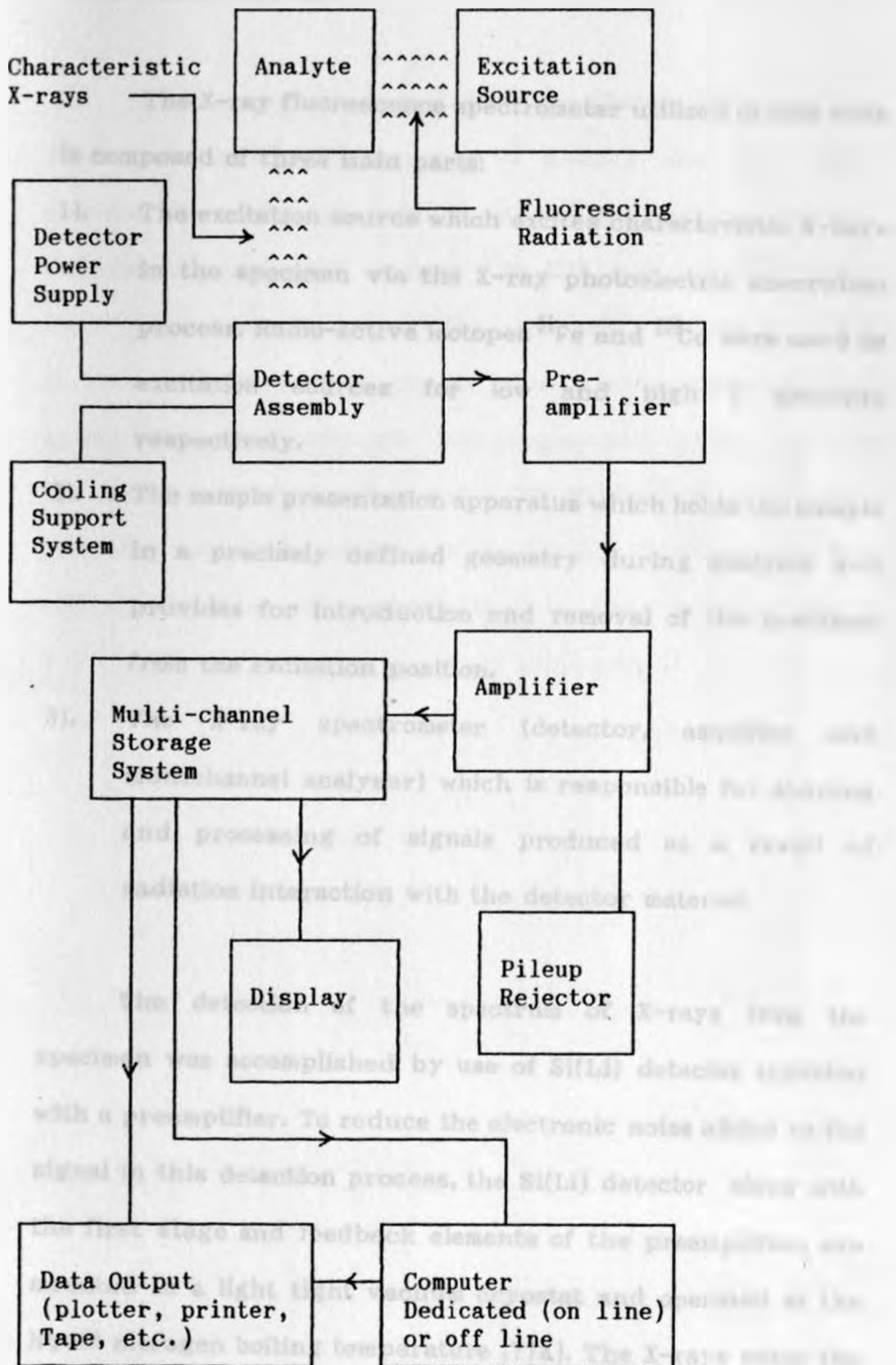


Figure 4. EDXRF system.

1:4:4. EDXRF SET UP.

The X-ray fluorescence spectrometer utilized in this work is composed of three main parts:

- 1). The excitation source which excites characteristic X-rays in the specimen via the X-ray photoelectric absorption process. Radio-active isotopes ^{55}Fe and ^{109}Cd were used as excitation sources for low and high Z elements respectively.
- 2). The sample presentation apparatus which holds the sample in a precisely defined geometry during analysis and provides for introduction and removal of the specimen from the excitation position.
- 3). The X-ray spectrometer (detector, amplifier and multichannel analyser) which is responsible for shaping and processing of signals produced as a result of radiation interaction with the detector material.

The detection of the spectrum of X-rays from the specimen was accomplished by use of Si(Li) detector together with a preamplifier. To reduce the electronic noise added to the signal in this detection process, the Si(Li) detector along with the first stage and feedback elements of the preamplifier, are mounted in a light tight vacuum cryostat and operated at the liquid nitrogen boiling temperature (77K). The X-rays enter the cryostat through a thin beryllium window to reach the Si(Li)

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crystal. The beryllium window was 23 μm thick (Figures 1 & 8).

A Canberra Multichannel Analyser (Series 40) which had 1024 channels in each quarter of memory was used. Each channel is associated with a particular energy interval. Calibration using point sources ^{55}Fe (5.9 keV) and ^{109}Cd (22.1 keV) was done to relate the channels to energy. The multichannel analyser is capable of calculating the total area under the peak through pre-programmed chips. It was interfaced to an X-Y plotter and a DEC Professional 350 micro-computer for off line analysis of the spectra. The computer had quantitative XRFA software [67] that was used to fit the peaks and calculate area under the peaks (appendix 1).



Figure 5. EDXRF set up.

2. EXPERIMENTAL.

2:1. QUANTITATIVE ANALYSIS.

The main equation for quantitative calculation in the X-ray fluorescence is as follows:

$$I_i = G_0 k_i (pd)_i \left(\frac{1 - \exp(-apd)}{apd} \right)$$

Where:

I_i = fluorescence intensity in counts per second.

G_0 = activity of the source in counts per second.

k_i = excitation detection efficiency for the detector in cm^2/g .

$(pd)_i$ = concentration of the element (i) in g/cm^2 .

a = total mass absorption of the primary and secondary fluorescence in the sample.

p = density of the sample (g/cm^3)

d = sample thickness in cm.

$\frac{1 - \exp(-apd)}{apd} = A_{\text{corr}}$ = Absorption correction factor.

$A_{\text{corr}} = 1$ For the thin samples ($apd \ll 1$)

hence:

$$(pd)_i = \frac{I_i}{G_0 k_i}$$

$$(m)_i = (pd)_i * \text{Area}$$

$$(m)_i = \frac{I_i * \text{Area}}{G_0 k_i}$$

Where:

$(m)_i$ = mass of the element (i) in the total exposed area of the filter.

This equation was used to calculate the concentration of each element determined in the samples. The EDXRF method detects elements from silicon to uranium in the periodic table and concentrations of upto parts per million (PPM). In this work only elements with Z higher than silicon were analysed and the organic part of TSP was not analysed.

2:2. QUALITY CONTROL.

The first part of the experimental work was the optimization of the experimental procedure starting from the sampling, analysis, and data handling. In this work, samples were collected at the University of Nairobi along Harry Thuku road and in the laboratory where loading rate, weighing, and analysis of these test samples was done. Also analysed was a reference standard material -Urban particulate, SRM 1648, whose results are given below (g/g):

Element	Amount	SRM value	Error %
Cr	0.000326	0.000403	19.07
Fe	0.040959	0.0391	4.60
Ni	0.000078	0.000082	4.59
Cu	0.000658	0.000609	8.17
Zn	0.004873	0.00476	2.39
Pb	0.006798	0.00655	3.80

In order to minimize the errors, weighing was done twice for each sample, the counting time for analysis was 1,000 seconds, and three samples were analysed. The error given is the mean deviation from certified value. The average error for the whole sample is $\pm 7.10\%$ which shall be taken as the error in my reported results.

2:2. SAMPLING.

Total suspended particulate (TSP) matter in the air was collected by filtration. Polyester filter membranes (Nuclepore), $0.4\ \mu\text{m}$ pore diameter, were used to trap these particles. These filter membranes have high trapping ability for all particulate matter. The small particles adhered to the sides of the pore while the big ones were trapped on top of the membrane. This method has been used by several workers to collect samples [14,28,49,68-74]. The big particles do not affect very much the air flow rate, but the small particles which adhere to the sides of the pore, reduce the pore diameter and hence the flow rate of the air.

The small particles have also low weight and hence more time was required to get substantial weight difference to reduce errors in weighing. This gave the loading time for each filter to be between two and three hours depending on the nature of the suspended particulate.

The sampling was mainly carried out during the working hours between 8.00 a.m. and 5.00 p.m., making the number of samples three per day. The school compounds have extra curricular activities during lunch break. The sampling was not done over the lunch hour hence obtaining only two samples per day. The project depended on one sampler hence sampling of all stations at the same time was not possible. A good average for each station was obtained by sampling for one week period, with at least morning and afternoon samples.

The set up (figure 6) was such that the filter membrane was held by a holder, which in turn was cocked (air tight) to a side armed conical flask. The one liter conical flask served as a pressure variation damper making the flow of air through the system steady. The side armed conical flask was then joined, using pressure tube, to the vacuum pump and a volume flow meter. The volume meter had been calibrated, using a Casella Flow Gauge, under the experimental conditions. An extension cable was needed to supply the vacuum pump with electric power at the sampling site, a 100 meter cable was available.

During sampling, the atmospheric weather conditions were recorded for each sample. The maximum wind speed attained during sampling was measured using a hand held anemometer. This wind speed was not however constant throughout any sampling duration. The temperature and relative humidity were

recorded using Zeal Whirling Psychrometer hygrometer. Average temperature and relative humidity during sampling were obtained from the values measured at the start and end of that sampling duration.

2:2:1. SAMPLING STATIONS.

The selection of the stations was such that it would reflect the extent of air pollution in the city (figure 7). The following factors were taken into consideration when choosing the stations:

- (1) They should cover the general area of interest,
- (2) There should not be any bias. They should not be near either a critical pollutant or some shielding that might prevent movement of the air.
- (3) While there was over 100 meters of extension cable, electrical power supply had to be within the vicinity.

In the city centre, three stations Moi Primary School, Government Press Bookshop and Saint Peter's Claver Church were chosen in such a manner that they formed a triangle enclosing the city. An additional two stations Catholic Parochial Primary School and Hilton Hotel were situated inside this triangle. This conveniently covered the city centre. In the residential estate three stations Kenyatta National Hospital, Kenya Medical Research Institute and Golf Course were also in

a triangular form. While in the industrial area, the industries are found along the roads with a linear arrangement. The stations Cooper Motor Corporation, Fire Station and Seventh Day Adventist Clinic had therefore the same linear arrangement as was for the Industries.

The stations were numbered as follows:

- 1) Moi Primary School on Moi Avenue.
- 2) Government Press Bookshop on Haille Selassie Avenue.
- 3) Catholic Parochial Primary School on Parliament road.
- 4) Hilton Hotel on City Hall road.
- 5) Saint Peter's Claver Church on Race Course road.
- 6) Cooper Motor Corporation on Lusaka road.
- 7) Fire Station on Enterprise road.
- 8) Seventh Day Adventist Clinic on Likoni road.
- 9) Kenyatta National Hospital off Ngong road.
- 10) Kenya Medical Research Institute off Mbagathi road.
- 11) Golf Course off Mbaruk road.

The sampling of at the stations was done in the order above and the duration was from August 1990 to April 1991.



Figure 6. Sampling set up.

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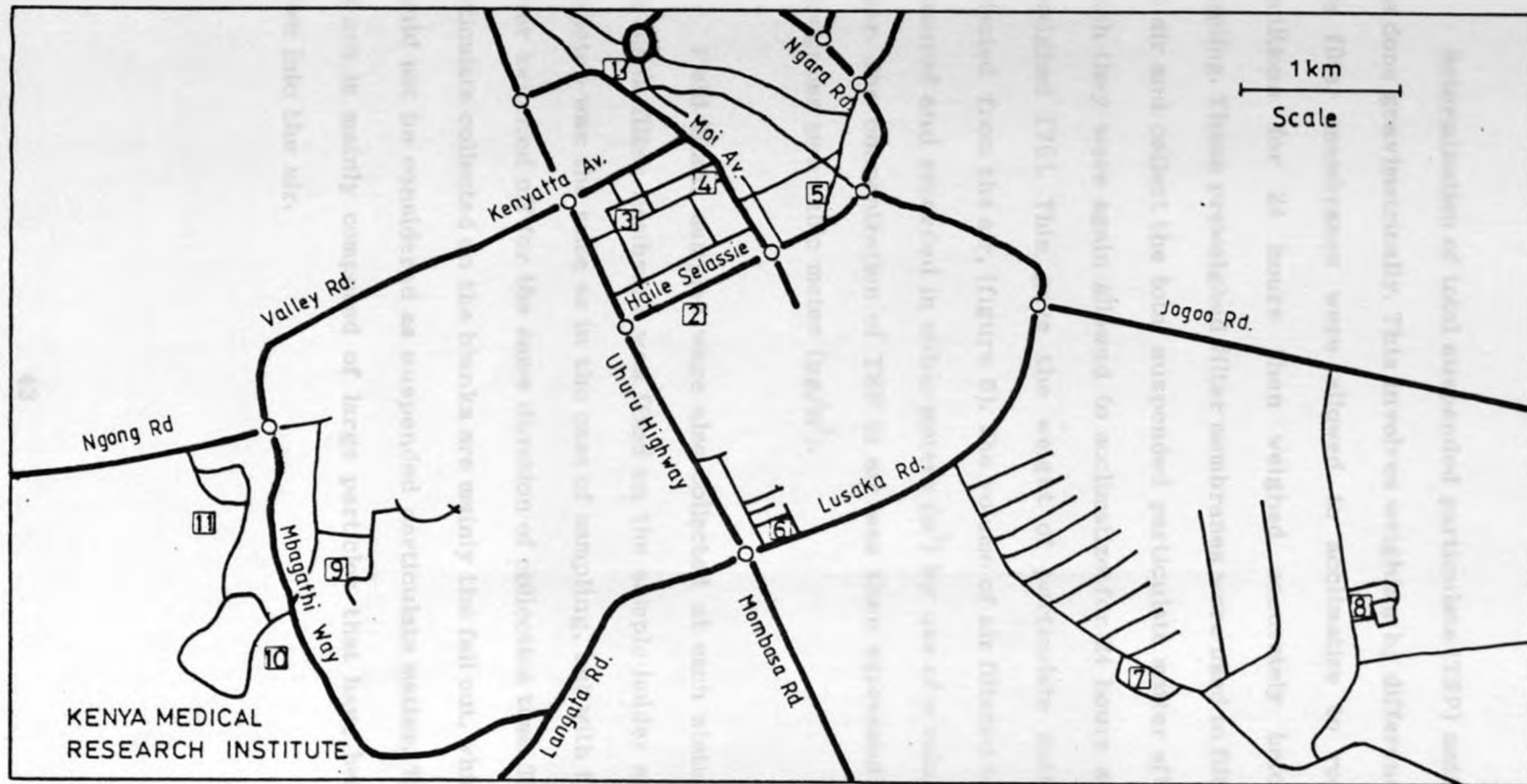


Figure 7. Location of stations.

2:3. TSP DETERMINATION.

Determination of total suspended particulate (TSP) matter was done gravimetrically. This involves weighing by difference. The filter membranes were allowed to acclimatize to room conditions for 24 hours then weighed accurately before sampling. These preweighed filter membranes were used to filter the air and collect the total suspended particulate matter after which they were again allowed to acclimatize for 24 hours and reweighed [75]. This gave the weight of particulate matter collected from the air, (figure 8). The volume of air filtered was measured and recorded in cubic meters (m^3) by use of a volume meter. The concentration of TSP in air was then expressed in micrograms per cubic meter ($\mu g/m^3$).

Field blank samples were also collected at each station. The blank filter membrane was fixed on the sample holder and the setup was the same as in the case of sampling, but with the power switched off for the same duration of collection time. The particulate collected on the blanks are mainly the fall out, which should not be considered as suspended particulate matter. The fall out is mainly composed of large particles that have been blown into the air.



Figure 8. TSP weighing balance.

3. RESULTS AND DISCUSSION.

3.1. TSP VALUES:

The mean value of the total suspended particulate matter (TSP) shown in Table 1 reflects the state of the stations in terms of ground cover and the activities found there. This is seen in the comparison of the primary schools involved. At Moi Primary School, the ground is bare and TSP mean value of $254.4 \mu\text{g}/\text{m}^3$ was collected, while the value at Catholic Parochial Primary School which has cobbled play ground was $165.0 \mu\text{g}/\text{m}^3$. The traffic volume at Moi Primary School is much higher than at Catholic Parochial Primary School.

The TSP collected at Government Press Bookshop was a mean value of $204.7 \mu\text{g}/\text{m}^3$ which reflects the very fast flow speed and volume of the traffic on Haille Selassie Avenue. At Hilton Hotel and St.Peter's Claver Church, a high mean TSP value of over $300 \mu\text{g}/\text{m}^3$ was obtained due to high traffic volume with low flow rate plus the presence of a nearby bus stop.

Table 2. Atmospheric conditions.

Station No.	1	1	1	1	4	4
Sample No.	16	17	32	33	55	56
Time: start	9.00	2.15	8.40	2.00	11.55	2.20
end	12.00	4.15	11.40	3.45	2.15	4.15
Temperature (°F)	70	77	66	78	82	81
R. Humidity (%)	48	34	62	35	32	34
Wind (m/s)	1	2	1	2	2	3
TSP ($\mu\text{g}/\text{m}^3$)	263.2	290.2	229.5	282.4	326.0	327.8

Station No.	4	4	5	5	5	5
Sample No.	61	62	75	76	78	79
Time: start	8.35	10.32	11.07	12.52	8.32	10.12
end	10.25	12.48	12.46	2.33	10.06	12.50
Temperature (°F)	69	75	76	78	65	69
R. Humidity (%)	66	50	52	48	82	65
Wind (m/s)	1	1	1	2	0	2
TSP ($\mu\text{g}/\text{m}^3$)	303.1	313.2	243.0	256.1	313.1	250.2

Table 1b. Traffic flow data [52].

Station.	Cars	Light good Vehicles	Heavy Good Vehicles	Buses	Total
1.Moi	11086	606	114	210	12016
2.Press	13063	1201	452	199	14915
3.Cathol.	10562	66	66	84	10778
4.Hilton	21020	1532	193	403	23148
5.Church	14949	2979	364	2019	20311
6.C.M.C.	16107	587	989	280	17953
7.Fire St.	13281	782	1176	320	15559
8.Clinic	15203	524	772	211	17710

Note:- Light Vehicles (LVeh) = Cars + Light Good Vehicles.

Heavy Vehicles (HVeh) = Heavy Good Vehicles + Buses.

Total Vehicles (TVeh) = LVeh + HVeh.

The highest mean TSP collected ($397.9 \mu\text{g}/\text{m}^3$) was from the industrial area at the Nairobi City Commission Fire Station site which is due to several combined factors:

high traffic volume with moderate speed;

several industries around the site;

a gentle wind breeze and;

uncovered road sides.

The mean TSP value at this station was $397.9 \mu\text{g}/\text{m}^3$ was higher than what was reported by Ngugi ($252.2 \mu\text{g}/\text{m}^3$) in 1982 [62].

The above factors also contribute to the TSP mean values at the other industrial area stations, C.M.C. $382.3 \mu\text{g}/\text{m}^3$ and S.D.A.

Clinic $387.9 \mu\text{g}/\text{m}^3$. The amounts of TSP collected in the residential stations are significantly low, mean values from 69.9

to $98.3 \mu\text{g}/\text{m}^3$. It should however be noted that the residential

stations were more than twenty meters away from the roads and

had very low traffic volume during the working hours. It has

been observed that the TSP values obtained depends mainly on

the nature and the kind of pollutants around the station [70].

Borm and workers [49] reported approximately 24% of the TSP collected as being elemental weights of some 22 elements.

Using same method as Borm, over 80% of the TSP collected was mainly organic matter as the metals detected were less than 20%

by mass. Fukuzaki and workers did similar work in Niigata,

Japan [70] they collected TSP at a distance of 6.5 meters from

the road and reported total mean TSP as $153 \mu\text{g}/\text{m}^3$. Other

workers in India [14, 73] have reported TSP mean range of 140 $\mu\text{g}/\text{m}^3$ to 540 $\mu\text{g}/\text{m}^3$ for Bombay, Bangalore, Jaipur and Nagpur cities. Romo-Kroger [72] reported mean TSP of 104 $\mu\text{g}/\text{m}^3$ to 308 $\mu\text{g}/\text{m}^3$ for three cities in Chile; and in Nigeria Ile-Ife town, Akeredulu [13] obtained 249 $\mu\text{g}/\text{m}^3$ of suspended matter.

The amount of TSP collected at any station on any particular time depends on:

- 1) the general state of the station and surrounding;
- 2) the wind speed and direction;
- 3) the weather (temperature, humidity and rain);
- 4) the activities at that particular time; and
- 5) the state of the previous day's weather.

The atmospheric conditions during sampling were recorded and it should be appreciated that the weather could not have been controlled and its change was natural. From the data of weather conditions recorded during sampling of three stations, (table 2) it is seen that the TSP collected increased with temperature and wind speed and decreased with relative humidity . This is seen by comparing sample No. 16 & 17, 32 & 33, and 75 & 76.

Samples collected when the wind speed was constant, samples No. 61 & 62, show that rise in temperature and consecutive lowering of humidity results in increased TSP

matter in the air. Sample No. 78 (TSP=313.1) was collected when there was very light drizzle and sample No. 79 (TSP=250.2) collected after the drizzle. The decrease in TSP collected did not follow the increase of the temperature, wind speed or the decrease of relative humidity. This suggests that these particulates are precipitated by drizzle. Samples No. 55 & 56 had nearly the same TSP value though the wind speed increased from 2 to 3 m/s and temperature dropped from 82 to 81°F as the humidity increased from 32 to 34%. This is the counter effects of wind versus temperature and humidity.

Parekh et al. [76] reported that samples collected during the day were 80% higher than night samples and these elevated levels were attributed to day time increase in wind velocity and anthropogenic activity.

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TSP ($\mu\text{g}/\text{m}^3$)	263.2	290.2	229.5	282.4	326.0	327.8

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Sample No.	61	62	75	76	78	79
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end	10.25	12.48	12.46	2.33	10.06	12.50
Temperature (°F)	69	75	76	78	65	69
R. Humidity (%)	66	50	52	48	82	65
Wind (m/s)	1	1	1	2	0	2
TSP ($\mu\text{g}/\text{m}^3$)	303.1	313.2	243.0	256.1	313.1	250.2

3:2. CORRELATION FACTORS.

The term correlation refers to the degree of correspondence or relationship between two (paired) variables. The most popular of the several available coefficients of correlations is the Pearson Correlation presented by r [77].

$$r = \frac{n\sum xy - (\sum x)(\sum y)}{\sqrt{[n(\sum x^2) - (\sum x)^2]} \sqrt{[n(\sum y^2) - (\sum y)^2]}}$$

When the r value is less than 0.300, this means low correlation and when between 0.300 and 0.700 is moderate correlation. Above 0.700 is high correlation. The negative sign indicates inverse proportion but when r is -0.750 or +0.750 the degree of relationship is the same.

The correlation Table 3 shows that most of the elements are correlated to the TSP with notable exceptions of manganese (0.375), iron (0.346), bromine (0.009) and lead (0.113). Manganese and iron are highly correlated and might have industrial based source. Bromine and lead are also correlated to each other (0.951) and the number of light vehicles (LVEH) (0.874 and 0.942 respectively). This strongly suggests that the major source is exhaust gases from light vehicles. The number of heavy vehicles (HVEH) have some correlation with TSP (0.583). This may be due

to resuspension of particulate matter in the air by these vehicles.

Potassium, calcium, titanium, zinc and zirconium are all correlated to the TSP indicating the major source to be crustal dust.

	Ca	Al	Si	Ti	Zn
PM10	0.001	0.002	0.003	0.001	0.001
PM2.5	0.001	0.002	0.003	0.001	0.001
PM10-2.5	0.001	0.002	0.003	0.001	0.001
PM2.5-10	0.001	0.002	0.003	0.001	0.001
PM10-2.5	0.001	0.002	0.003	0.001	0.001
PM2.5-10	0.001	0.002	0.003	0.001	0.001
PM10-2.5	0.001	0.002	0.003	0.001	0.001
PM2.5-10	0.001	0.002	0.003	0.001	0.001
PM10-2.5	0.001	0.002	0.003	0.001	0.001
PM2.5-10	0.001	0.002	0.003	0.001	0.001

	Ca	Al	Si	Ti	Zn
PM10	0.001	0.002	0.003	0.001	0.001
PM2.5	0.001	0.002	0.003	0.001	0.001
PM10-2.5	0.001	0.002	0.003	0.001	0.001
PM2.5-10	0.001	0.002	0.003	0.001	0.001
PM10-2.5	0.001	0.002	0.003	0.001	0.001
PM2.5-10	0.001	0.002	0.003	0.001	0.001
PM10-2.5	0.001	0.002	0.003	0.001	0.001
PM2.5-10	0.001	0.002	0.003	0.001	0.001
PM10-2.5	0.001	0.002	0.003	0.001	0.001
PM2.5-10	0.001	0.002	0.003	0.001	0.001

* Total, Light & Heavy Vehicle by Table ID (2015)

Table 3. Pearson Correlation Factors by weight (n=11).

	<u>TSP</u>	<u>K</u>	<u>Ca</u>	<u>Ti</u>	<u>Mn</u>
TSP	1.000				
K	0.925	1.000			
Ca	0.895	0.917	1.000		
Ti	0.617	0.786	0.747	1.000	
Mn	0.375	0.606	0.635	0.875	1.000
Fe	0.346	0.594	0.602	0.752	0.956
Zn	0.851	0.763	0.619	0.244	-0.036
Br	0.076	-0.084	0.081	0.292	0.228
Zr	0.893	0.935	0.989	0.786	0.698
Pb	0.280	0.163	0.306	0.519	0.365
TVeh [†]	0.573	0.476	0.487	0.674	0.424
LVeh [†]	0.478	0.339	0.386	0.555	0.340
HVeh [†]	0.583	0.769	0.625	0.906	0.668

	<u>Fe</u>	<u>Zn</u>	<u>Br</u>	<u>Zr</u>	<u>Pb</u>
Fe	1.000				
Zn	0.009	1.000			
Br	0.009	-0.322	1.000		
Zr	0.681	0.600	0.080	1.000	
Pb	0.113	-0.144	0.951	0.293	1.000
TVeh [†]	0.200	0.220	0.791	0.493	0.905
LVeh [†]	0.112	0.124	0.874	0.387	0.942
HVeh [†]	0.557	0.373	0.048	0.658	0.311

([†] Total, Light & Heavy Vehicles in Table 1b [52]).

3:3. ENRICHMENT FACTORS.

Enrichment factor is given as a ratio between elemental levels. Usually one element is taken as the standard and should be an element in abundance, such as iron, silicon, or aluminum [77]. In Table 4 iron (Fe) is the standard and the enrichment factor (E.F.) is given as [78]:

$$\text{E.F.} = i_a / Fe_a * Fe_c / i_c$$

Where:

i = element i.

a = concentration in air.

c = concentration in crust.

While most of the suspended matter may be thought to originate from the crustal material it can be concluded from Table 4 that bromine, zinc and lead have other sources. These three elements have enrichment factors greater than 10 [78]. The correlation shows low r values between TSP and manganese (0.375), iron (0.346) bromine (0.009) and lead (0.113), hence these elements have other sources apart from crustal dust. The lead and bromine is mainly from the automobile exhaust and the ratio of Br:Pb was 0.309-0.535. It is possible that the other three are from industrial processes. The amount of potassium and calcium collected was high but the enrichment factors were below 10, indicating that these metals are mainly from the crustal dust.

Table 4. Elemental enrichment factors.

<u>ELEMENT (*)</u>	<u>MOI</u>	<u>PRESS</u>	<u>CATHOL</u>	<u>HILTON</u>	<u>CHURCH</u>
K (25900)	0.38	0.47	0.46	0.57	0.52
Ca (36300)	0.41	0.52	0.76	0.66	0.44
Ti (4400)	0.42	0.57	0.49	0.79	0.81
Mn (1000)	3.06	2.91	3.02	3.78	3.73
Fe (50000)	1.00	1.00	1.00	1.00	1.00
Zn (132)	17.60	38.01	32.82	32.27	20.42
Br (1.6)	429.16	919.04	921.17	1533.01	587.53
Zr (220)	2.67	1.92	2.68	4.12	3.13
Pb (16)	103.80	215.13	250.21	352.54	167.81

<u>ELEMENT</u>	<u>CMC</u>	<u>FIRE</u>	<u>SDA</u>	<u>KNH</u>	<u>KEMRI</u>	<u>GOLF</u>
K	0.79	0.74	0.76	0.30	0.30	0.34
Ca	0.65	0.64	0.63	0.43	0.47	0.49
Ti	0.73	0.72	0.72	0.41	0.40	0.51
Mn	3.32	3.13	3.16	2.30	2.32	1.08
Fe	1.00	1.00	1.00	1.00	1.00	1.00
Zn	78.71	64.28	70.09	13.81	14.75	18.37
Br	661.05	559.88	601.14	725.95	645.16	495.26
Zr	4.27	4.68	4.38	1.66	1.67	0.67
Pb	192.80	167.84	175.52	210.97	193.11	197.35

(*) = Crustal amounts of the elements in g/ton[78].

3:4. INTER-CITY COMPARISON.

The elemental levels of Nairobi samples are as high as those reported in India and Japan (see table 5.)

Table 5. Inter-city comparison of elemental levels ($\mu\text{g}/\text{m}^3$).

	<u>ANTWERP</u> [†]	<u>GHENT</u> [†]	<u>NIIGATA</u> ^{**}	<u>BOMBAY</u> [†]	<u>NAIROBI</u> ^{**}
K	0.170	0.270	1.180	1.140	1.252-6.432
Ca	0.300	0.250	8.700	6.590	2.567-7.547
Ti	0.021	0.020	0.460	6.540	0.286-1.698
Mn	0.0096	0.015	0.100	0.188	0.158-1.683
Fe	0.330	0.200	1.950	5.430	6.014-23.722
Zn	0.041	0.090	0.177	0.700	0.159-0.678
Br	-	-	0.018	0.010	0.122-0.707
Zr	-	-	-	-	0.017-0.245
Pb	0.110	0.170	0.056	0.630	0.395-1.321

[†] Sampling on top of a 15 meters building 5 km from the city centre with the wind direction towards the city (Belgium) [49 79].

^{**} Samples taken in front of a seven store building at a distance of 6.5 meters from the road (Japan) [70].

[†] Sample taken at 15 meters above the ground and 15 km from town centre (India) [74].

^{**} The Nairobi samples were collected 1.5 meters above the ground and 20 meters from the road.

In similar work done by Tripathi [12] in two Indian cities, the lead levels were 0.21-1.14 $\mu\text{g}/\text{m}^3$ in Bombay while in Moradabad city it was 0.30-6.51 $\mu\text{g}/\text{m}^3$. The zinc levels were 0.36-1.78 $\mu\text{g}/\text{m}^3$ and 2.46-56.02 $\mu\text{g}/\text{m}^3$ respectively.

3:5. CONCLUSION AND RECOMMENDATIONS.

The values of lead concentration measured in the air falls within the WHO guidelines range, (0.5-1.0 $\mu\text{g}/\text{m}^3$) [80] except for Hilton and Church stations. In general these values are about five times higher than the values reported in the European countries. Some of the European countries have lead free petrol while others have only 0.15 g of lead per litre added to petrol [10]. In Kenya we have above 0.3 g of lead per litre added to the petrol [53]. The major source of lead in our environment is vehicle exhaust, despite the country being "unindustrialised" and with low vehicle population. The amount of lead added to the petrol should be reduced heading for the lead-free petrol.

The TSP reported in this work shows a considerable increase since 1982 [62] at the rate of 14.6 $\mu\text{g}/\text{m}^3$ per year. This can be attributed to higher level of activities that generate and/or resuspend particulate matter in the air. The lead level is quite high at the sampling stations and correlates with the

number of light vehicles ($r=0.942$). Inter-cities comparison of this work shows that Nairobi air is quite polluted, further work should be done to ascertain the level of pollution in the City including the use of different analytical techniques. The use of other techniques will make it possible to detect other elements (with low Z) in the atmosphere, which could not be analysed by EDXRF method for example Chlorine (also added in petrol as ethylene dichloride). Similar levels are reported from Indian cities. The amounts of bromine determined correlates very well with the lead values ($r=0.951$) while the Br:Pb ratio by weight was 0.309-0.535. These results show that the two elements are from the vehicles' exhaust gasses as they are added in petrol during refining, lead as anti-knock and bromine as a "scavenger" for the lead. Lead and bromine have also high enrichment factor.

The rest of the elements assessed, except zinc, have enrichment factors below 10. This has the implication that these elements are mainly from the crustal dust. The amounts of dust in the air is quite high as shown by the TSP collected in most of the stations.

Developing countries like Kenya are caught up between health concern and industrial development. The TSP levels in Nairobi is growing bigger due to construction and industrial activities, felling of trees and increase of vehicles. The urban

centres are also poorly planned. This urban growth is resulting in:

more traffic jams;

residential areas next to industrial premises; and

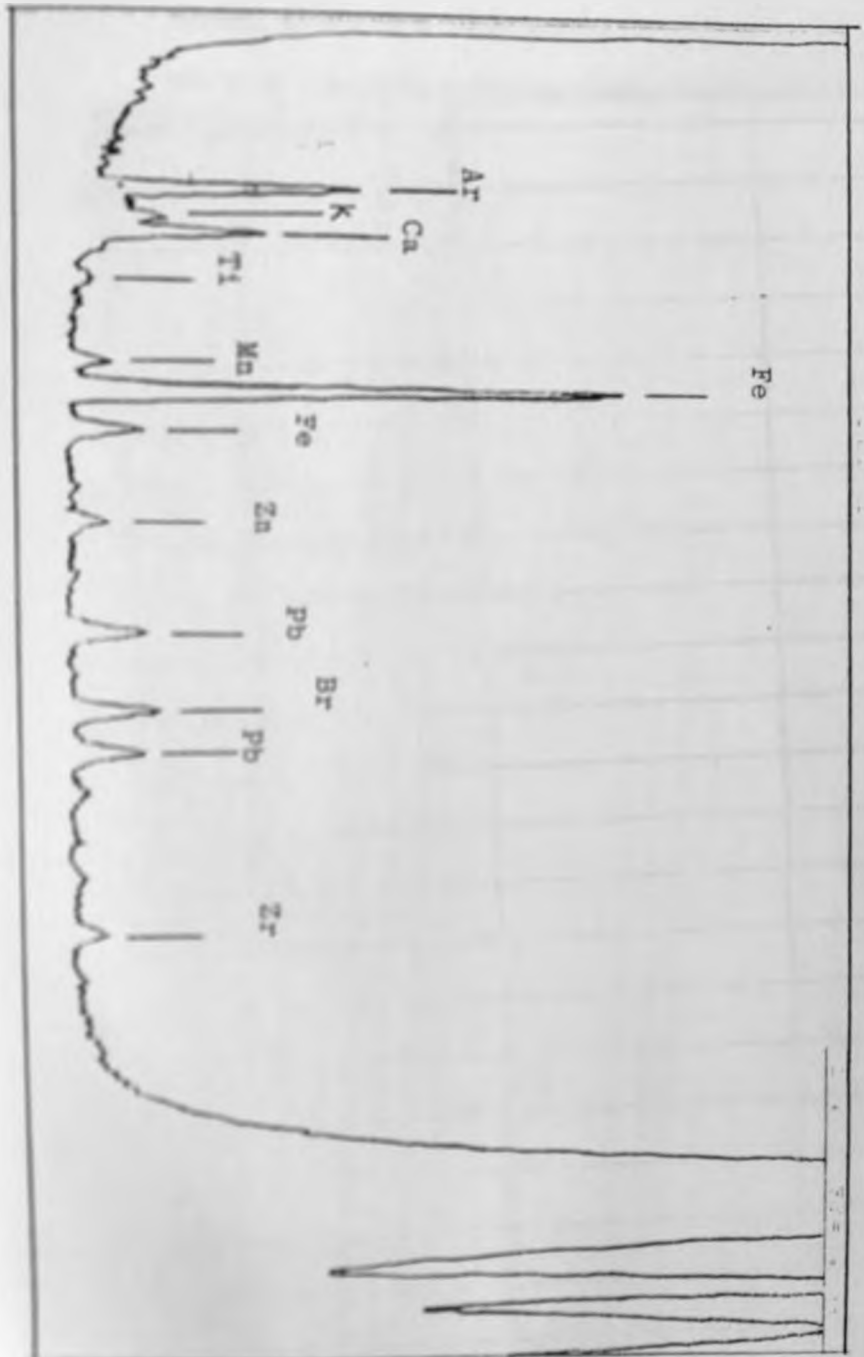
the crowding in both residential and central business area.

The planning of the City should take into consideration air pollution just like the other necessary factors in urban planning. Roads should be constructed so as to ease traffic congestion and should be tarmacked including the pedestrian path. This will reduce the rate of soil dust resuspension which is the major composition in the TSP. The sweeping of the roads and pavements should be done daily. Laws on vehicles exhaust emission must be enacted and enforced to make sure that vehicles are roadworthy. Guidelines on vehicle exhaust composition should be properly formulated and enforced.

The mean TSP values collected from industrial area in this work was higher than what Ngugi reported in 1982 [62]. The air quality has deteriorated. Further research in this area of air pollution should be done. The research activities should meet two important objectives: to identify pollution sources and to determine their relative contribution. Chemical mass (or elemental) balance and multivariate analysis are two approaches in receptor modeling often employed to meet these objectives

[76]. Specific sources should be analysed for emission composition and indoor sampling with an emphasis on factory based analysis.

Out door sampling should be done continuously and changes in the level of pollutants over a number of years would give the trend of air pollution in Nairobi. This kind of sampling should be done at two or three stations so that in case of extra activities at one station (eg. construction nearby) then the other station(s) would continue giving the true data.



Appendix 1. Typical Infra spectra

Ar - Argon, K-Potassium, Ca-calcium, Ba-Barium, Fe-Iron, Zn-Zinc, Pb-lead

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