Sudan University of Science &Technology

College of Graduate Studies

Evaluation of some Mineral Concentrations of Cheese by using Inductively Coupled Plasma-Atomic Emission Spectrometer

تقييم تراكيزبعض المعادن في الجبنة بإستخدام جهاز مطيافية الإنبعاث الذري لبلازما الحث المزدوج

Thesis Submitted for Partial Fulfillment of Requirement for the degree of M.Sc.in physics

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الآية

قال تعالى:

{ وَإِنَّ لَكُمْ فِي الْأَنْعَامِ لَعِبْرَةً ۖ نُسْقِيكُمْ مِمَّا فِي بُطُونِهِ مِنْ بَيْنِ فَرْثٍ وَدَمٍ لَبَنًا خَالِصًا سَائِغًا لِلشَّارِبِينَ }

(سورة النحل-الاية 66)

I

Dedication

To

My fathers

My mothers

My families

My Friends

Acknowledgements

Abstract

In this research concentrations of 10 different mineralswere evaluated in commercial whitecheese, pigtail cheese and triangles cheese. Ten minerals were analyzed by an Inductively Coupled plasma-Atomic Emission Spectrometer(ICP-AES). Respective mean mineral concentration (ppm) of white cheese, pigtail cheese and cheese triangles were:Al 94.125,73.75,64.0;Cr 0, 0, 0 ; Mn 1.40,1.2875,0.6875;Fe 13.075,16.45,6.675;Ni 8.6125, 8.8, 6.925; Cu 0, 0, 0 ; Zn 22.4125,22.9125,14.7875;Cd1.2, 0.6625, 0.4375; Ba 0, 0, 0 ;Pb 16.375,4.9,4.6125.

These results show that there is some minerals (Cr, Cu and Ba) were not exist and other found with high concentration in comparison with the standard specification.

مستخلص

في هذا البحث تم تقييم تراكيز عشرة معادن مختلفة في كل من الجبنة البيضاء والمضفرة وجبنة المثلثات، المعادن العشرة تم تحليلها بواسطة جهاز مطيافية الإنبعاث الذري-لبلازما الحث المزدوج,وجد أن متوسط تراكيز هذه المعادن (ppm)في الجبنة البيضاء والمضفرة وجبنة المثلثات على التوالي هو كالتالي الألمونيوم 94.125، 73.75، 64.0 الكروم 0، 0، 0المنجنيز 1.40، 1.2875، 0.6875 الحديد 13.075، 16.45، 6.675 النيكل 8.6125، 8.8، 6.925 النحاس 0، 0، 0 الزنك 22.4125، 22.9125، 14.7875 الكادميوم 1.2، 0.6625، 0.4375 الباريوم 0، 0، 0 الرصاص 16.375، 4.9، 4.6125 . أظهرت النتائج أن هناك بعض المعادن (كروم، نحاس وباريوم) غير موجودة ومعادن أخرى توفرت بتراكيز عالية مقارنة بالمواصفة القياسية.

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Chapter One

Introduction and Literature Review

1-1 Introduction

Cheese is a food derived from milk that is produced in a wide range of flavors, textures, and forms by coagulation of the milk protein casein. It comprises proteins and fat from milk, usually the milk of cows, buffalo, goats, or sheep. During production, the milk is usually acidified, and adding the enzyme rennet causes coagulation. The solids are separated and pressed into final form (Fankhauser,2016), Some cheeses have molds on the rind or throughout. Most cheeses melt at cooking temperature.

Hundreds of types of cheese from various countries are produced. Their styles, textures and flavors depend on the origin of the milk (including the animal's diet), whether they have been pasteurized, the butterfat content, the bacteria and mold, the processing, and aging. Herbs, spices, or wood smoke may be used as flavoring agents. The yellow to red color of many cheeses, such as Red Leicester, is produced by adding annatto. Other ingredients may be added to some cheeses, such as black pepper, garlic, chives or cranberries.

For a few cheeses, the milk is curdled by adding acids such as vinegar or lemon juice. Most cheeses are acidified to a lesser degree by bacteria, which turn milk sugars into lactic acid, then the addition of rennet completes the curdling. Vegetarian alternatives to rennet are available; most are produced by fermentation of the fungus Mucor miehei, but others have been extracted from various species of

the Cynara thistle family. Cheese makers near a dairy region may benefit from fresher, lower-priced milk, and lower shipping costs.

Cheese is valued for its portability, long life, and high content of fat, protein, calcium, and phosphorus. Cheese is more compact and has a longer shelf life than milk, although how long a cheese will keep depends on the type of cheese; labels on packets of cheese often claim that a cheese should be consumed within three to five days of opening. Generally speaking, hard cheeses, such as parmesan last longer than soft cheeses, such as Brie or goat's milk cheese. The long storage life of some cheeses, especially when encased in a protective rind, allows selling when markets are favorable.

There is some debate as to the best way to store cheese, but some experts say that wrapping it in cheese paper provides optimal results. Cheese paper is coated in a porous plastic on the inside, and the outside has a layer of wax. This specific combination of plastic on the inside and wax on the outside protects the cheese by allowing condensation on the cheese to be wicked away while preventing moisture from within the cheese escaping.

A specialist seller of cheese is sometimes known as a cheese monger. Becoming an expert in this field requires some formal education and years of tasting and hands-on experience, much like becoming an expert in wine or cuisine. The cheese monger is responsible for all aspects of the cheese inventory: selecting the cheese menu, purchasing, receiving, storage, and ripening, (G.Stephen Jones, 2013).

1-2 Research Problem

This study is focus on determination of Mineral contents in different types of cheeses using ICP-AES analysis. ICP-AES analysis is powerful tool for determination of concentration of elements in sample. Strictly speeding, it is used rarely in food analysis, to make sure that it is free from contamination.

Although a few studies may have been reported, very limited research data have been available on mineral profiles, (Karen Hernandez1, Young W. Park2, 2014).

1-3 Literature Review

Hernandez, K. and Park, Y.W. (2014) Evaluated 20 Macro and Trace Mineral Concentrations in Commercial Goat Milk Yogurt and Its Cow Milk Counterpart in reference to goat milk yogurt manufactured from Fort Valley State University (FVGY), Fort Valley, GA, USA. Three different lots of CGY and CCY each were purchased from local retail stores at Warner Robins, GA, and 3 batches of FVGY were made using goat milk from the University milking herd. All 3 types of experimental yogurts were stored at 4°C refrigerator for 4 weeks. Twenty major and trace minerals were analyzed by an Inductively Coupled Plasma Optical Emissions Spectrometer (Thermo Jarrel Ash Enviro 36, Worchester, MA), using argon as the carrier gas and the EPA method 6010. Total solids (TS) content (%) of FVGY, CGY and CCY products were 11.03, 13.1 and 11.3, respectively, indicating CGY had higher TS than the CCY and FVGY yogurt. Respective mean mineral concentrations (ppm, wet basis) of FVGY, CGY and CCY were: Ca 1057, 1162, 1160; P 838, 974, 929; K 1327, 1717, 1208; Mg 102, 133, 113; Na 545, 449, 475; Fe 4.28, 3.33, 2.11; Mn 0.24, 0.19, 0.13; Cu 10.5, 9.85, 7.22; Zn 17.5, 11.7, 11.8.

Levels of all macro minerals except potassium were higher in commercial goat and cow yogurts than FVGY, which may be due to the higher TS contents. FVGY had higher Fe, Mn, Cu and Zn than both commercial products. The heavy metal (Pb, Cd and Ni) contents (ppm) appeared to be normal range, while Al contents of FVGY, CGY and CCY were 11.9, 8.66 and 7.65, respectively, which were higher than those of Pb, Cd and Ni. Both commercial products contained higher major mineral contents than the university yogurt, which might be attributable to the differences in diet, breed, and stage of lactation of milking animals, as well as the tapioca additive used in the commercial products, (Karen Hernandez1, Young W. Park2, 2014).

González-Martín, et al (2009) studied the effect of different factors on the mineral composition and the correlation between minerals (Ca, Fe, Mg, K, Na, and Zn) and the type of milk used. The One-Way ANOVA procedure revealed that the effect of cow's milk was statistically significant on Fe, K, P, and Zn; goat's milk was statistically significant for Fe and Mg, and ewe's milk was statistically significant for K. The effect of the ripening time was statistically significant in all cases, except for Zn; the effect of the season was statistically significant for K, Mg and P and the effect of the year was statistically significant in the case of K, Na, P, and Zn. The percentage of cow's cheese was positively correlated with K and P; the percentage of ewe's cheese was negatively correlated with K, Mg, Na, and P and the percentage of goat's cheese was negatively correlated with Na, and P, (Gonzalez Martin et al, 2009).

Mustafa WA, Suleiman AME, Abdelgadir WS, Al-Khalifa EA (2013) determined chemical composition of Jibna-beida produced at small scale-level in Dueim city, the largest market of Jibna-beida in Sudan. Their results showed that the protein content of cheese ranged from 14.17 ± 0.058% to 15.73 ± 0.150%, with an average value of 14.57%.

Statistically, no significant differences (P ≥ 0.05) in protein of collected cheese samples were found. However, the fat content of cheese samples ranged between 18.92 ± 0.012% and 22.27 ± 0.087%, with an average value of 20.84%. And the ash content of cheese samples ranged from 3.77 ± 0.012% to 5.60 ± 0.087%, with an average of 4.45%. The macro-elements sodium, potassium, calcium, lead and phosphorus where found in relatively high concentrations, whereas concentration of micro-elements was very low. The fatty acids content varied, and the most abundant were palmitic (C16: 0), stearic (C18: 0) and myristic (C14: 0) acids), which ranged between 14.56 to 39.41, 0.04 to 19.31, and 0.59 to 1.30 g/100 g, respectively. Most of the amino acids were found in cheese samples. The study concluded that collected Jibna-beida has high nutritional value; it contains appreciable amounts of protein, fat and minerals, (Mustafa et al., 2013).

1-4 Aim of the work

The aim of this work is to determine the concentration of metals and some vital elements in different types of cheeses.

The aims of this study were to: quantify the levels of 10 different mineral element in commercially marketed white cheese, pigtail cheese and cheese triangles; and ascertain any differences in those minerals among three different types of the cheese, (Karen Hernandez1, Young W. Park2, 2014).

1-5 Layout of the research

This thesis is contents of four chapters; the first chapter explains introduction, research problem, literature review and aim of the work. In chapter two the Basic Concepts.. In chapter three Experimental Part. In chapter four the Results and Discussion.

Chapter Two

Basic Concepts

2.1Spectroscopy

Spectroscopy is the study of the interaction between matter and electromagnetic radiation (Crouch, Stanley; Skoog, Douglas A, 2007). Historically, spectroscopy originated through the study of visible light dispersed according to its wavelength, by a prism. Later the concept was expanded greatly to include any interaction with radiative energy as a function of its wavelength or frequency. Spectroscopic data is often represented by a spectrum ,a plot of the response of interest as a function of wavelength or frequency.

2.1.1 Introduction

Spectroscopy and spectrography are terms used to refer to the measurement of radiation intensity as a function of wavelength and are often used to describe experimental spectroscopic methods. Spectral measurement devices are referred to as spectrometers, spectrophotometers, spectrographs or spectral analyzers.

Daily observations of color can be related to spectroscopy. Neon lighting is a direct application of atomic spectroscopy. Neon and other noble gases have characteristic emission frequencies (colors). Neon lamps use collision of electrons with the gas to excite these emissions. Inks, dyes and paints include chemical compounds selected for their spectral characteristics in order to generate specific colors and hues. A commonly encountered molecular spectrum is that of nitrogen dioxide. Gaseous

nitrogen dioxide has a characteristic red absorption feature, and this gives air polluted with nitrogen dioxide a reddish brown color. Rayleigh scattering is a spectroscopic scattering phenomenon that accounts for the color of the sky.

Spectroscopic studies were central to the development of quantum mechanics and included Max Planck's explanation of blackbody radiation, Albert Einstein's explanation of the photoelectric effect and Niels Bohr's explanation of atomic structure and spectra. Spectroscopy is used in physical and analytical chemistry because atoms and molecules have unique spectra. As a result, these spectra can be used to detect, identify and quantify information about the atoms and molecules. Spectroscopy is also used in astronomy and remote sensing on earth. Most research telescopes have spectrographs. The measured spectra are used to determine the chemical composition and physical properties of astronomical objects (such as their temperature and velocity).

2.1.2 Theory

One of the central concepts in spectroscopy is a resonance and its corresponding resonant frequency. Resonances were first characterized in mechanical systems such as pendulums. Mechanical systems that vibrate or oscillate will experience large amplitude oscillations when they are driven at their resonant frequency. A plot of amplitude vs. excitation frequency will have a peak centered at the resonance frequency. This plot is one type of spectrum, with the peak often referred to as a spectral line, and most spectral lines have a similar appearance.

In quantum mechanical systems, the analogous resonance is a coupling of two quantum mechanical stationary states of one system, such as an atom,

via an oscillatory source of energy such as a photon. The coupling of the two states is strongest when the energy of the source matches the energy difference between the two states. The energy (E) of a photon is related to its frequency (ν) by $E = h\nu$ where h is Planck's constant, and so a spectrum of the system response vs. photon frequency will peak at the resonant frequency or energy. Particles such as electrons and neutrons have a comparable relationship, the de Broglie relations, between their kinetic energy and their wavelength and frequency and therefore can also excite resonant interactions.

Spectra of atoms and molecules often consist of a series of spectral lines, each one representing a resonance between two different quantum states. The explanation of these series, and the spectral patterns associated with them, were one of the experimental enigmas that drove the development and acceptance of quantum mechanics. The hydrogen spectral series in particular was first successfully explained by the Rutherford-Bohr quantum model of the hydrogen atom. In some cases spectral lines are well separated and distinguishable, but spectral lines can also overlap and appear to be a single transition if the density of energy states is high enough. Named series of lines include the principal, sharp, diffuse and fundamental series.

2-1-3 Classification of methods

A huge diffraction grating at the heart of the ultra-precise ESPRESSO spectrograph.

Spectroscopy is a sufficiently broad field that many sub-disciplines exist, each with numerous implementations of specific spectroscopic techniques. The various implementations and techniques can be classified in several ways.

2-1-4 Type of radiative energy

Types of spectroscopy are distinguished by the type of radiative energy involved in the interaction. In many applications, the spectrum is determined by measuring changes in the intensity or frequency of this energy. The types of radiative energy studied include:

Electromagnetic radiation was the first source of energy used for spectroscopic studies. Techniques that employ electromagnetic radiation are typically classified by the wavelength region of the spectrum and include microwave, terahertz, infrared, near infrared, visible and ultraviolet, x-ray and spectroscopy. Particles, due to their de Broglie wavelength, can also be a source of radiative energy and both electrons and neutrons are commonly used. For a particle, its kinetic energy determines its wavelength, Acoustic involves radiated pressure waves, Mechanical methods can be employed to impart radiating energy, similar to acoustic waves, to solid materials, Nature of the interaction.

Types of spectroscopy can also be distinguished by the nature of the interaction between the energy and the material. These interactions include:

Absorption occurs when energy from the radiative source is absorbed by the material. Absorption is often determined by measuring the fraction of energy transmitted through the material; absorption will decrease the transmitted portion.

Emission indicates that radiative energy is released by the material. A material's blackbody spectrum is a spontaneous emission spectrum determined by its temperature; this feature can be measured in the infrared by instruments such as the Atmospheric Emitted Radiance

Interferometer (AERI). Emission can also be induced by other sources of energy such as flames or sparks or electromagnetic radiation in the case of fluorescence.

Elastic scattering and reflection spectroscopy determine how incident radiation is reflected or scattered by a material. Crystallography employs the scattering of high energy radiation, such as x-rays and electrons, to examine the arrangement of atoms in proteins and solid crystals.

Impedance spectroscopy studies the ability of a medium to impede or slow the transmittance of energy. For optical applications, this is characterized by the index of refraction.

Inelastic scattering phenomena involve an exchange of energy between the radiation and the matter that shifts the wavelength of the scattered radiation. These include Raman and Compton scattering.

Coherent or resonance spectroscopy are techniques where the radiative energy couples two quantum states of the material in a coherent interaction that is sustained by the radiating field. The coherence can be disrupted by other interactions, such as particle collisions and energy transfer, and so often require high intensity radiation to be sustained. Nuclear magnetic resonance (NMR) spectroscopy is a widely used resonance method and ultrafast laser methods are also now possible in the infrared and visible spectral regions.

2.1. 5 Type of material

Spectroscopic studies are designed so that the radiant energy interacts with specific types of matter.

Atoms

Atomic spectroscopy was the first application of spectroscopy developed. Atomic absorption spectroscopy (AAS) and atomic emission spectroscopy (AES) involve visible and ultraviolet light. These absorptions and emissions, often referred to as atomic spectral lines, are due to electronic transitions of outer shell electrons as they rise and fall from one electron orbit to another. Atoms also have distinct x-ray spectra that are attributable to the excitation of inner shell electrons to excited states.

Atoms of different elements have distinct spectra and therefore atomic spectroscopy allows for the identification and quantitation of a sample's elemental composition. Robert Bunsen and Gustav Kirchhoff discovered new elements by observing their emission spectra. Atomic absorption lines are observed in the solar spectrum and referred to as Fraunhofer lines after their discoverer. A comprehensive explanation of the hydrogen spectrum was an early success of quantum mechanics and explained the Lamb shift observed in the hydrogen spectrum led to the development of quantum electrodynamics.

Modern implementations of atomic spectroscopy for studying visible and ultraviolet transitions include flame emission spectroscopy, inductively coupled plasma atomic emission spectroscopy, glow discharge spectroscopy, microwave induced plasma spectroscopy, and spark or arc emission spectroscopy. Techniques for studying x-ray spectra include X-ray spectroscopy and X-ray fluorescence (XRF).

Molecules

The combination of atoms into molecules leads to the creation of unique types of energetic states and therefore unique spectra of the transitions between these states. Molecular spectra can be obtained due to electron spin states (electron paramagnetic resonance), molecular rotations, molecular vibration and electronic states. Rotations are collective motions of the atomic nuclei and typically lead to spectra in the microwave and millimeter-wave spectral regions; rotational spectroscopy and microwave spectroscopy are synonymous. Vibrations are relative motions of the atomic nuclei and are studied by both infrared and Raman spectroscopy. Electronic excitations are studied using visible and ultraviolet spectroscopy as well as fluorescence spectroscopy.

Studies in molecular spectroscopy led to the development of the first maser and contributed to the subsequent development of the laser.

Crystals and extended materials

The combination of atoms or molecules into crystals or other extended forms leads to the creation of additional energetic states. These states are numerous and therefore have a high density of states. This high density often makes the spectra weaker and less distinct, i.e., broader. For instance, blackbody radiation is due to the thermal motions of atoms and molecules within a material. Acoustic and mechanical responses are due to collective motions as well. Pure crystals, though, can have distinct spectral transitions, and the crystal arrangement also has an effect on the observed molecular spectra. The regular lattice structure of crystals also scatters x-rays, electrons or neutrons allowing for crystallographic studies.

Nuclei

Nuclei also have distinct energy states that are widely separated and lead to gamma ray spectra. Distinct nuclear spin states can have their energy separated by a magnetic field, and this allows for NMR spectroscopy.

Other types

Other types of spectroscopy are distinguished by specific applications or implementations:

Acoustic resonance spectroscopy is based on sound waves primarily in the audible and ultrasonic regions, Auger is a method used to study surfaces of materials on a micro-scale. It is often used in connection with electron microscopy, Cavity ring down spectroscopy,Circular Dichroism spectroscopy,Coherent anti-Stokes Raman spectroscopy (CARS) is a recent technique that has high sensitivity and powerful applications for *in vivo* spectroscopy and imaging (Evans, C.L.Xie.X.S., 2008), Cold vapor atomic fluorescence spectroscopy, Correlation spectroscopy encompasses several types of two-dimensional NMR spectroscopy, Deep-level transient spectroscopy measures concentration and analyzes parameters of electrically active defects in semiconducting materials, Dual polarization interferometer measures the real and imaginary components of the complex refractive index, Electron measures physicochemical properties and characteristics of electronic structure of multicomponent and complex molecular systems, EPR spectroscopy, Force spectroscopy, Fourier transform spectroscopy is an efficient method for processing spectra data obtained using interferometers. Fourier transform infrared spectroscopy (FTIR) is a common implementation of infrared

spectroscopy. NMR also employs Fourier transforms,Hadron spectroscopy studies the energy/mass spectrum of hadrons according to spin, parity, and other particle properties. Baryon spectroscopy and meson spectroscopy are both types of hadron spectroscopy, Hyper spectral imaging is a method to create a complete picture of the environment or various objects, each pixel containing a full visible, VNIR, NIR, or infrared spectrum, Inelastic electron tunneling spectroscopy (IETS) uses the changes in current due to inelastic electron-vibration interaction at specific energies that can also measure optically forbidden transitions, Inelastic neutron scattering is similar to Raman spectroscopy, but uses neutrons instead of photons, Laser-Induced Breakdown Spectroscopy (LIBS), also called Laser-induced plasma spectrometry (LIPS)Laser spectroscopy uses tunable lasers and other types of coherent emission sources, such as optical parametric oscillators, for selective excitation of atomic or molecular species, Mass spectroscopy is an historical term used to refer to mass spectrometry. Current recommendations, (Murray, Kermit K; Boyd, Robert K, et al, 2013), are to use the latter term. Use of the term mass spectroscopy originated in the use of phosphor screens to detect ions, Mossbauer spectroscopy probes the properties of specific isotopic nuclei in different atomic environments by analyzing the resonant absorption of gamma-rays. See also Mossbauer effect, Neutron spin echo spectroscopy measures internal dynamics in proteins and other soft matter systems Photo acoustic spectroscopy measures the sound waves produced upon the absorption of radiation, Photoemission spectroscopy, Photo thermal spectroscopy measures heat evolved upon absorption of radiation, Pump-probe spectroscopy can use ultrafast laser pulses to measure reaction intermediates in the femtosecond timescale, Raman optical activity spectroscopy exploits Raman

scattering and optical activity effects to reveal detailed information on chiral centers in molecules, Raman spectroscopy, Saturated spectroscopy, Scanning tunneling spectroscopy, Spectrophotometer, Time-resolved spectroscopy measures the decay rate(s) of excited states using various spectroscopic methods, Time-Stretch Spectroscopy (Solli , D. R.; Chou, J.; Jalali, B, 2008). Thermal infrared spectroscopy measures thermal radiation emitted from materials and surfaces and is used to determine the type of bonds present in a sample as well as their lattice environment. The techniques are widely used by organic chemists, mineralogists, and planetary scientists, Ultraviolet photoelectron spectroscopy (UPS), Video spectroscopy, Vibrational circular dichroism spectroscopy, X-ray photoelectron spectroscopy (XPS)

2-2 Inductively Coupled Plasma-Atomic Emission Spectrometer:

2-2-1 Theory

ICP-AES, or Inductively Coupled Plasma-Atomic Emission Spectroscopy (also known as ICP-OES, Optical Emission Spectroscopy), is a type of emission spectroscopy that is often used to detect the presence of trace metals in a sample. Through the use of the eponymous Inductively Couple Plasma, an ICP-AES produces excited ions and atoms (By ionization in an intense electromagnetic eld) that emit detectable amounts of light at characteristic wavelengths, with intensities proportional to the concentration of the ion. As indicated by the name, the spectra is measured and analyzed by an atomic emission spectrometer (AES) using concentration-intensity correlations that are similar to how the Beer-Lambert Law applies to AAS.ICP-AES is invaluable for its

ability to record the spectra of multiple trace elements simultaneously, assuming they do not

Signicantly overlap in characteristic wavelength, as well as the minimization of matrix eects due to the extreme nature of the plasma. If good wavelengths are chosen for the metals used, the amount of interference between spectra will be minimal; however, it is Possible for interference eects to cause two spectra to overlap, wildly skewing readings. Nowadays, the presence of commercial ICP-AES software makes calculation of optimal Wavelengths to minimize and account for overlap, through the use of proprietary software and inter element correction factors . Like AAS, AES is widely used to measure the Concentration or presence of trace elements in samples, and sees much modern use in environmental testing and protein analysis (Jonathan Melville, 2014).
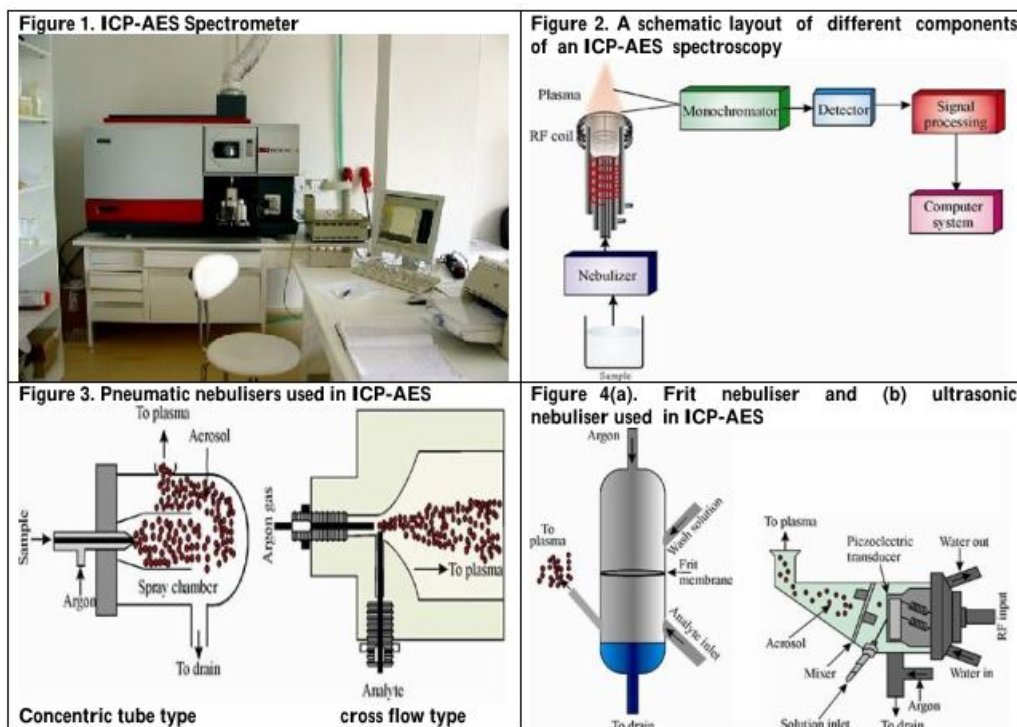
Figure(2-1) Inductively Coupled Plasma-Atomic Emission Spectrometer

2-2-2 Principle of ICP-AES:

In the ICP-AES a plasma source is used to make specific elements emit light, after which a spectrometer separates .This light in the characteristic wavelengths Spectrometer "ICP".

2-2-3 Specifications:

Simultaneous with solid state detector.

Detector: CID detector (C-PAD) with 0.007nm optical and 0.005 pixel-t-pixel resolution at 200nm, and include purged and stabilized optical system.

Bench top model, Water re-circular and that re-circular have the ability to be situated at a distance from the instrument, or water chiller. Viewing of the plasma is computer controlled. Spectrum range from 167 to 847 nm or more.

Nitrogen or Argon may be used as purge gases. Plasma ignition and shut-down is computer controlled and totally automated. The Prism ICP offers excellent resolution (0.007 nm & s200 nm), so spectral interferences are minimized.

Bias corrections.

Relative percent difference of duplicates. Data can be stored in "folders" which can be user assigned by sample type. With a data station: Dell Pentium IV, # GHz, 512 MB RAM, 1 GB cache, HD 250GB, 52x/32x CD-R/W, 17" SVGA flat color monitor, 3.5" 1.44 Floppy, Windows XP loaded, Microsoft Windows XP Professional Full CD, SP2. Mouse, 104 Key Windows Keyboard wireless, 4 USB ports, integrated Audio speakers and HP laser Printer. Unit include: Argon Cylinder and Regulator, Exhaust system with blower and ventilation tubes.

Axial View: Permits axial viewing of torch for maximum sensitivity through horizontal positioning of RF load coil and the torch.

To be used for the determination of all cations and inions. 1000 ppm Standard solutions (Extremely pure) "Merck" of B, Mo, P, Fe, Cu, Zn, Mn, Cd, Pb, Ni, Ca, Mg, Na, K, S, Al, Si.

Provided with suitable split air condition for the ICP room. Fixing the cooling unit.

2-2-4 Components of an Inductively Coupled Plasma—Atomic Emission Spectrometry System (ICP-AES)

Overviews:

An ICP-AES system can be divided up into two basic parts; the inductively coupled plasma source and the atomic emission spectrometry detector.

1 shows the common components of an ICP-AES system from the late 1980s to the 1990s. The inductively coupled plasma source has mostly been unchanged since its invention with the exception of innovation in monochromatic type, which enables greater suppression of interference phenomena. Modifications of this common system will be explained in the following sections. Sample solutions include digested soil or other solid material or natural water. Typically the sample solution is acidified up to 2-3% in HNO3to prevent adsorption of metals onto polypropylene sample bottle or onto instrument tubing or glassware prior to introduction into the plasma. In Figure 2-2, the sample is introduced to the nebulizer chamber via a peristaltic pump and tygon tubing attached to an automatic sampler. A peristaltic pump operates by sequentially compressing flexible tubing with evenly spaced and rotating rollers that pull/push the liquid through the system. The rate of sample introduction into the plasma changes as the rotation rate of the peristaltic rollers increases or decreases. Flow of sample and Ar gas through the small aperture of the nebulizer creates very small droplets that form a mist of μm-sized

particles in the nebulizer chamber. Larger sample droplets collect on the chamber walls and are removed through a drain, while smaller particles travel with the Ar flow and enter the torch.

Evaporation, atomization, and excitations/ionizations occur in the plasma at temperatures reaching 10 000 K. Ar not related to the sample is also excited and ionized because this gas both carries the sample aerosol and confines the location of the plasma to prevent damage to the rest of the instrument. As the excited/ionized atoms leave the hot portion of the plasma, excited valence electrons relax and emit a photon characteristic of the electron transition. This photon is specific to the element but does not yield any information about the isotopic state of the element, unlike in mass spectrometry. Visible and UV radiation emitted from the sample constituents enters the monochromatic through a small slit where the wavelengths are separated by grating(s) and/or prism(s) before being captured and measured by a wide variety of detectors. Because spectral interferences may still occur, the choice and configuration of the monochromators in the instrument is important and has been the target of innovation. In Figure 2-2, the most common form of a monochromatic (a Rowland circle) and detector (photomultiplier; PMT) is shown: The Rowland system utilizes a concave Echellette-style grating monochromatic to separate the various emission lines and simultaneously focus individual wavelengths on to a series of slits, with each slit aligned to allow a specific wavelength of radiation to pass to a detector. The standard detector, a photomultiplier tube (PMT). Some systems use multiple PMTs at fixed locations to monitor each wavelength simultaneously (Figure 2-2) whereas other systems use a single PMT and move it to different locations to detect each wavelength. Data from these detectors are processed by a computer because multiple wavelengths are measured in an ICP-AES system at the same time.
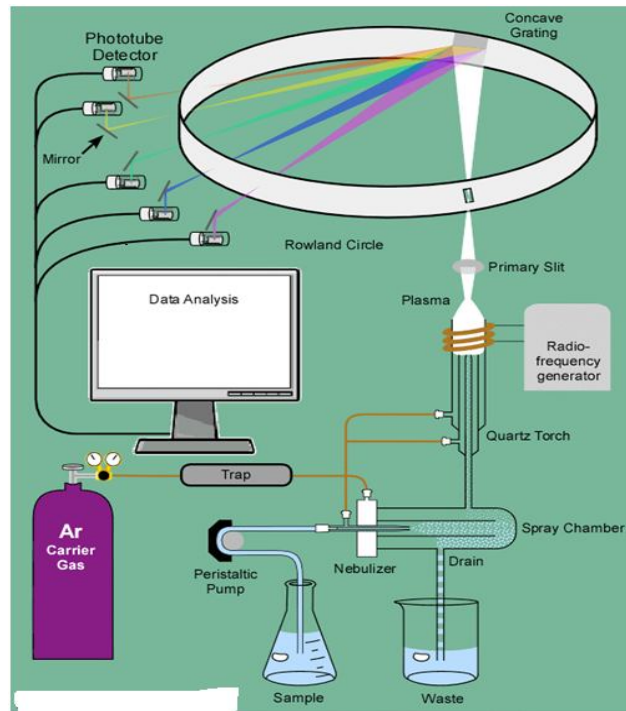
Figure (2-2) Overview of a Basic Inductively Coupled Plasma—Atomic Emission Spectrometry (ICP-AES) from the 1990s.

Sample Introduction and Optimization

The predominate form of sample matrix in ICP-AES today is a liquid sample:

acidified water or solids digested into aqueous forms. Given the automated nature of the ICP analysis, all modern systems are purchased with automatic samplers where a computer-controlled robotic sampling arm takes liquids from each sample via a peristaltic pump from plastic tubes located in specific locations in a sampling tray. Liquid samples are pumped into the nebulizer and sample chamber via a peristaltic pump as shown below. Then the samples pass through a nebulizer that

Creates a fine mist of liquid particles. Larger water droplets condense on the sides of the spray chamber and are removed via the drain (pumped out of the chamber also by the same peristaltic pump) while finer water droplets move with the argon flow and enter the plasma. Nebulizers help

ensure that the sample enters into the plasma at a uniform flow rate and specific droplet size. Droplets that are great than 5 μm in diameter are likely to interfere with plasma stability.
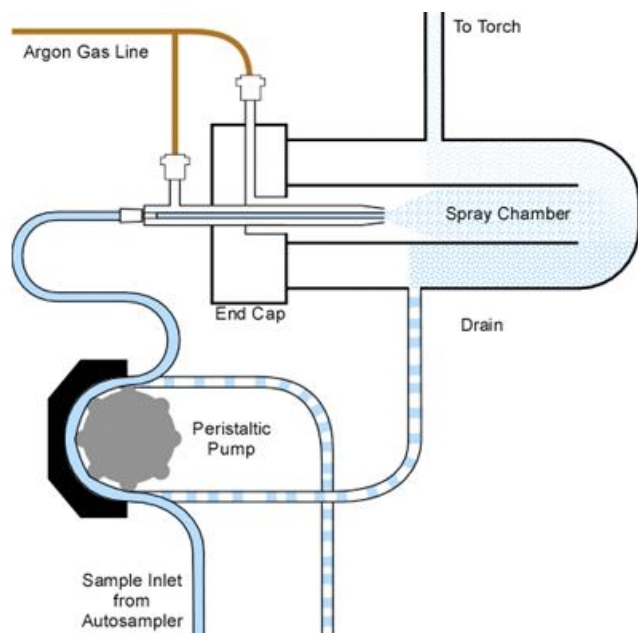
Figure (2-3) An Overview of Sample Introduction and the Nebulizer Chamber.

(The nebulizer shown here is a pneumatic style, described below.)While there are numerous types of nebulizers for a variety of specific applications, the three most commonly types are the pneumatic, ultrasonic, and grid. Because argon is used in generating the plasma(discussed below) it is most often used as the gas in these various nebulizers, but other gases can be used. The most common pneumatic nebulizer for samples containing low concentrations of total dissolved solids is the concentric nebulizer shown in Figure (2-4), but higher suspended solids and dissolved solids samples are commonly introduced to the plasma via the Babington nebulizer.

Figure (2-4) Diagram of a Pneumatic Concentric Nebulizer.

Figure (2-5) Diagram of a Pneumatic Babington Nebulizer.

Figure (2-6) Diagram of a Pneumatic Cross-Flow Nebulizer

Ultrasonic nebulizers are used to provide more sample delivery to the plasma and thus improve detection limits. An ultra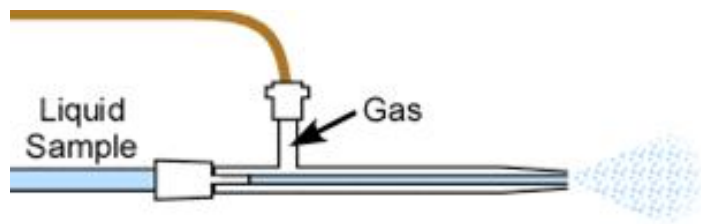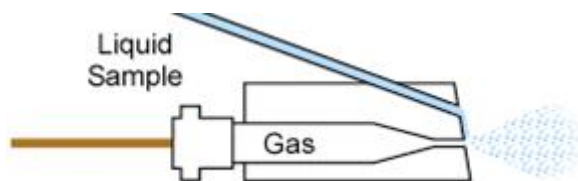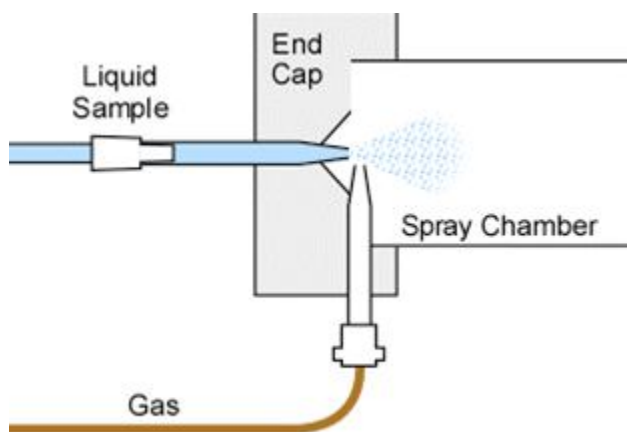sonic generator surface, usually a piezoelectric crystal that rapidly vibrates to generate sonic energy, is used to create extremely fine droplets that, at low flow rates, are completely transferred to the plasma (unlike considerably lower efficiencies from pneumatic nebulizers). Grid nebulizers create a fine mist by placing a grid in front of the argon flow. The liquid sample is allowed to flow down the grid and as argon passes through the grid it creates fine droplets. Again, the most common commercially available nebulizers use the pneumatic design ICP systems have a few sample requirements or limitations.

Micrometer sized particles must be removed by filtration or centrifuge or dissolved prior to introduction to a sample vial because the particles can easily clog the tip of the nebulizer. A clogged tip will not be automatically detected by the instrument, but will be detected by a trained operator by the absence of any sample, internal standard, or standard analyte concentrations in the final.

Another limitation of the nebulizer is the presence of high total dissolved solids (TDS) that will eventually cause the accumulation of solids in the tip of the nebulizer, as well as in the sample chamber and on the sampler cones located just after the plasma (in ICP-MS instruments only). Most ICP instruments limit the sample TDS level to approximately 0.1 to 0.2 percent salts by weight. Higher salt contents can enhance atomization and ionization of some elements and suppress or interfere with others (Walsh, 1997). Likewise, the acid concentration of liquids entering the plasma should be limited to approximately two to three percent for nitric and hydrochloric acid. Rarely hydrofluoric acid may be used if a particularly refractory element is of interest, but then the acid concentrations are less than 0.5% because it will degrade the quartz torch

with time. Some samples, such as food-based beverages or plant extracts, can contain high concentrations of organic matter. It is best to oxidize this organic matter in an acid or peroxide digestion prior to analysis since carbon will rapidly accumulate on the components of the instrument if high organic matter containing samples are directly injected into the plasma. This carbon can reduce sample flow and capture elements and ions as the carbon builds up, specifically at the cone apertures that facilitate the transition from ambient pressure in the plasma region to the high vacuum detector region (in ICP-MS systems). When a portion of a carbon plaque drops back into the analytical stream, an anomalously high, and false, measurement can occur.

Other forms of sample introduction are used but are not as common as liquid injection. These include direct insertion of 10-30 mg of sample on a graphite probe into the plasma via the normal nebulizer entry port, the injection of the effluent from chromatographic separation systems, especially from high performance liquid chromatography (HPLC), supercritical chromatography, and ion chromatography (IC) units where compounds containing elemental analyses of interest are first separated by chromatography and then introduced into the plasma for elemental analysis, where the cold vapor techniques described in Section 2.4 for mercury analysis is connected to the plasma inlet via the nebulizer port, and where the hydride generation system from Section 2.4 for selected metals can also be connected to the nebulizer port.

The Inductively Coupled Plasma Torch

The torch unit of an ICP is used to create and sustain plasma. A plasma is an electrically conducting gaseous mixture containing enough cations and electrons (though the plasma has a neutral charge overall) to maintain the conductance. One common example of a simple plasma is a regular flame which will conduct an electrical current across it; cations

and electrons are created upon ignition of the fuel and travel upward in the flame until they are cooled above the flame. Another common plasma is used in scanning electron microscopy (SEM) where a sample is coated with graphite or a metal in a vacuum chamber in order to make the surface conductive (a standard requirement for obtaining high quality images). DC arc and microwave plasmas can also be used to generate plasmas, but for purposes of metal analysis, the inductively coupled plasma system described below is most important. The purpose of the torch is to evaporate the solvent (usually water) from the analyses salts, atomize the atoms in the salt (break the ionic bonds and form gaseous state atoms), and excite or ionize the atoms. In the case of ICPAES, only excitation is needed as in FAES but given the extreme temperatures (up to 10 000 K) of the argon plasma used in modern ICP systems, the excitation of atoms is virtually complete for most elements. A modern torch system is illustrated in Figure 2-7 and 2-8. The torch described here is composed of three concentric quartz tubes. The samples and the argon gas used to aspirate it pass through the center tube. The plasma generating gas (argon) passes through the middle tube, and the argon passing through the outer tube is used to cool the quartz torch.

The plasma is sustained by a radio-frequency generator that creates an oscillating magnetic field around the torch that results in ohmic (inductive) heating of the charged gases at the end of the torch. Ohmic heating occurs when an electrical current is passed through a conductor that in turn, creates more heat. Three types of radio frequency generators have been used. Older types are based on piezoelectric crystal oscillators and "free-running" generators in which the oscillation is set according to the combinations of the components of the circuit; examples include the Armstrong, Hartley, Colpitts, and tuned-anode tuned gate oscillator electronic circuits. Most modern analytical ICP systems use solid-state

semiconductor generators where the circuit consists of a capacitor used to store a high electrical charge (thus requiring the 220-240 V electrical power requirements) and an inductor coil to deliver the oscillating current to the torch and generate the magnetic field around the torch. The capacitor is

hidden from view in ICP systems and buried in the electronics of the instrument. The inductor coil is visible and is the approximately 3-mm hollow copper coil wrapped three times around the end of the torch. The capacitor responsible for generating the plasma from argon gas, oscillates an electrical field at a rate between approximately 27 and 41MHz (a frequency regulated by the FCC) and through induction creates a magnetic field in the plasma.

 The intensity of the frequency, measured in Watts, is sufficient to promote the valance electrons in some of the Ar atoms but not ionize them sufficiently to initiate or sustain a plasma. The creation of plasma occurs when a spark (from a Tesla coil; basically an automatic gas grill lighter) introduces free electrons at the end of the torch when the electrical field is being oscillated at a specific frequency by a RF generator. The seed electrons from the Tesla coil oscillate in an angular path and periodically collide with argon gas atoms and ionize them, releasing more electrons. Due to their kinetic energy and collisions with other atoms a large amount of heat is generated, enough to generate and sustain a plasma at temperatures up to 10 000 K. In terms of an electrical analogy, the term "inductively coupled" in ICP is a result of the coupling of the induction coil and the electrons. The copper induction coil serves as the "primary winding" of the radiofrequency transformer and the "secondary winding" is the oscillating electrons and cations in the plasma; the two "windings" are thus coupled together because the second winding depends on the presence of the first. The RF generator also

contains a feedback loop where the interaction of the electronic/magnetic field in the capacitor/induction coil is monitored. If the flow rate of argon gas is too low or if small amounts of O2 or high amounts of water vapor are present in the torch during the initiation of the plasma, the RF generator will sense their presence by a change in the feedback between the oscillation and the RF generator. When this happens, the RF generator shuts down to protect the electronics in the system from overheating. Thus,

Atmospheric O2 cannot be present in the Ar and the flow rate of nebulizer sample

(Water) must also be controlled to successfully light the torch. The process of lighting the plasma is visualized in Animation 3-1. In this animation the argon is turned on and the pressures are allowed to equilibrate without the introduction of any sample or blank solutions to the nebulizer. The radiofrequency generator then ramps the wattage through a series of cycles. A typical ramp cycle begins by turning the RF generator to 200 Watts. Subsequently the electronics go through a preliminary check that adjusts the electronics and minimizes the resistance between the RF generator and the induction coil. Next the RF wattage is ramped to 900 W where excitation of valence electrons in some Ar atoms occurs and the Tesla coil initiates the excitation and ionization of Ar atoms and the plasma is lit. The circulation of electrons and Ar cations in close Association results in ohmic heating that generates more electrons, collisions between Ar atoms, and an increase in temperature. The wattage is then increased to 1200 and the resistance is minimized again via electronic adjustments. Finally the wattage is adjusted to the suggested energy level for the elements of interest; this is usually between 1250 and 1550 W.
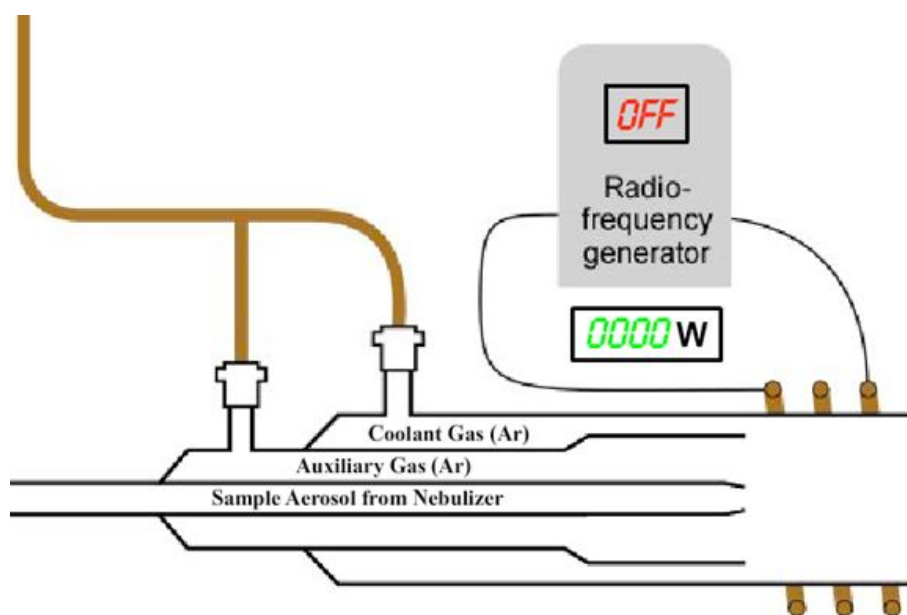
Figure (2-7) Animation of the Gas Flow, RF Wattage Adjustment, and Lighting of the Plasma Torch Commonly used in ICP Systems.

If the region of ohmic heating is not controlled, the plasma would continue to heat until it melted the quartz torch (and the other components of the ICP spectrometer). The torch is cooled in two ways, the first is by the tangential introduction of relatively large volumes of argon gas through the outer tube of the torch. This argon flow spirals around the middle tube resulting in uniform cooling.

Furthermore cooled water flows through the copper induction coil of the RF generator that is wrapped around the end of the torch. These combined cooling systems promote an equilibrium maximum temperature of approximately 10 000 K in the hottest portion of the plasma. The portion of the plasma that ICP-AES measurements are concerned with is about 5000-6000 K and is located in coneshaped region outside the quartz torch. After successful ignition of the torch, samples are introduced into the system through the nebulizer (Figure 2.8). Upon entry into the

plasma, the solvent evaporate and salts form. Then, these compounds decompose as they move farther into the hotter portions of the plasma. Next, the valence electrons on the analyte atoms are excited (for ICP-AES measurements) or completely removed (ionized for ICP-MS measurements). The intense heat that sample molecules encounter in the plasma is sufficient to decompose most refractory compounds, thus only atoms or atomic ions are present in the plasma. This heat also causes complete excitation of atoms and leads to higher detection limits, compared to FAES where the extent of excitation is element and flame temperature-dependent. In ICP-AES, as the atoms exit the plasma and cool to approximately 6000 K, they relax and emit a characteristic photon that enters one of the monochromatic/detector systems described in the next section. In the plasma enters a vacuum chamber where the cations are separated by a mass filter (mass analyzer) and detected by a specialized photomultiplier tube. An illustration of the drying, atomization, and excitation and ionization is shown in Figure 2-8
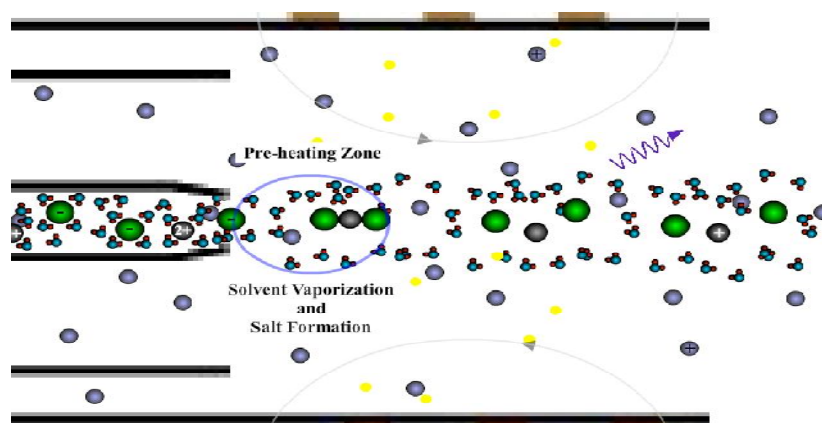

Figure **2.8 Animation of Sample Introduction and the Subsequent Reactions in the Torch of an ICP System.**

Note that this animation is a simplistic illustration of a complex process. Charge transfer to the cations actually occurs due to Rayleigh explosion.

The consumption rate of Ar gas is an important issue and accounts for most of the operational costs of an ICP. Older systems can use up to 20 L/minute, while modern systems have reduced the flow to below 10 L/minute. Systems are being designed that are portable and use far smaller flow rates of Ar gas. Many laboratories use cryogenic sources of Ar to reduce operational costs. Current prices for *liquid* Ar (equivalent to approximately 5000 cubic feet at STP) are approximately $325, whereas the cost of three T-size cylinders of *gaseous* Ar (equivalent to approximately 334 cubic feet at STP) is approximately $420. Thus, use of a cryogenic tank is far more economical than individual gas cylinders. Gases generated from a cryogenic tank are often more pure thanthose obtained from a standard T-sized gas cylinder.

Separation and Detection

After the atoms are excited or ionized in the plasma, they exit the high temperature region and electronically relax. This results in the emission of at least one element-specific photon available for detection. The first choice to be made by the analyst is the position of the monochromatic entrance relative to the plasma source. Two choices are available, axial and radial alignment. A radial design allows photons to move from the side of the plasma (at the end of the torch) to the entrance slit while an axial design gives higher intensities (and better detection limits) since the photons come from the center and end of the plasma. Thus, depending on the concentration of analyses in a given sample, the analyst may choose to monitor the emissions from the radial angle for higher concentrations; this avoids burning out the detector, which is costly to replace. Or the analyst may choose to use the axial

monochromatic alignment for lower concentration samples. Changing the angle of observation can potentially avoid Additional sample preparation such as dilutions. Many brands of instruments allow a selection between radial and axial monitoring.

Three broad categories of detection are available for analyzing the emitted photons: sequential, simultaneous multi-channel, and Fourier transform systems.

In the first two, all wavelengths enter a monochromatic where they are dispersed by prisms and/or grating monochromators and are then transmitted to the detector Fourier transform systems produce spectral separations by capitalizing on constructive interference techniques as first developed for Michelson's interferometer in 1881. In Fourier transform systems, no slits or monochromators are required, and this creates better detector limits because more intense radiation reaches the detector. Fourier transform systems also have higher spectral resolution (and thus have fewer spectral interferences) and can simultaneous monitor all wavelengths for longer times. This text will only cover sequential and simultaneous multi-channel systems that use

monochromators because Fourier transform systems extend past the basic ICP instrumentation goal of this Textbook and are considered "higher end" systems. The first ICP-AES systems used a sequential monochromatic to separate the analyze-emitted photons by wavelength before detecting them with a single detector. This approach is analogous to the FAES system where only one element could be analyzed at a time. In a sequential system, if a sample needed to be analyzed for multiple elements, the grating system was rotated to direct the appropriate wavelength to the exit slit of the monochromatic and into a PMT (described in Section 2.2.9). While ICP-AES provided superior detection

limits compared to FAES instruments, it was just as slow and labor intensive as FAES.

Simultaneous multi-channel systems rapidly became economical as component production costs decreased and as labor costs have increased with time. In these systems, multiple elements can be detected at the same time using one of two designs. One way is to use a standard grating monochromatic that separates the photons based on wavelength and directs the photons of interest to specific exit slits. Then, a single detector was rapidly moved from one slit to the other to analyze photons of various wavelengths. This type of system is shown Figure 3-6. Another way to accomplish multiple element detection is by placing an individual detector, again usually a PMT, at each exit slit. Such a system, the Rowland circle, was shown in Figure 2.8 and is shown again here as Figure 2-9. The Rowland design increases the upfront cost of an instrument and the running cost as PMT are replaced but this design significantly decreases the analysis time.
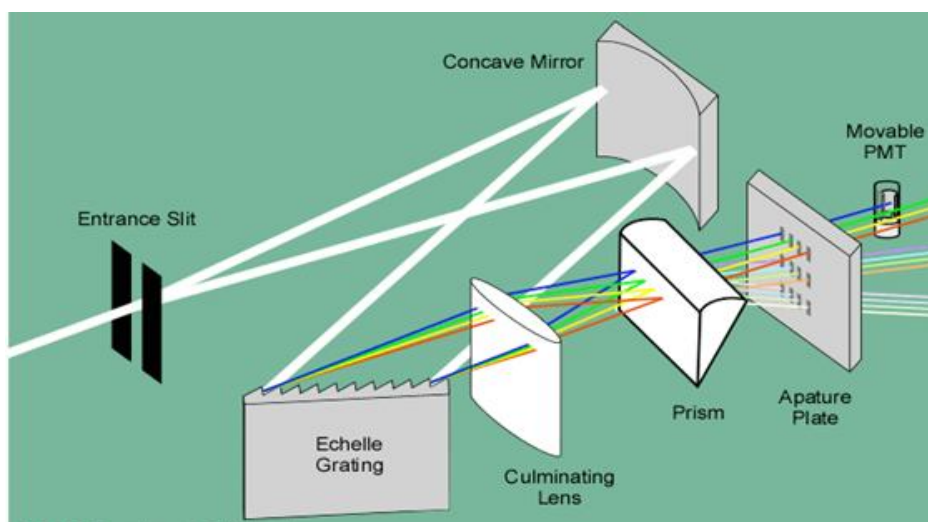

Figure (2-9) Single Detector (sequential type monochromatic) ICP-AES System.
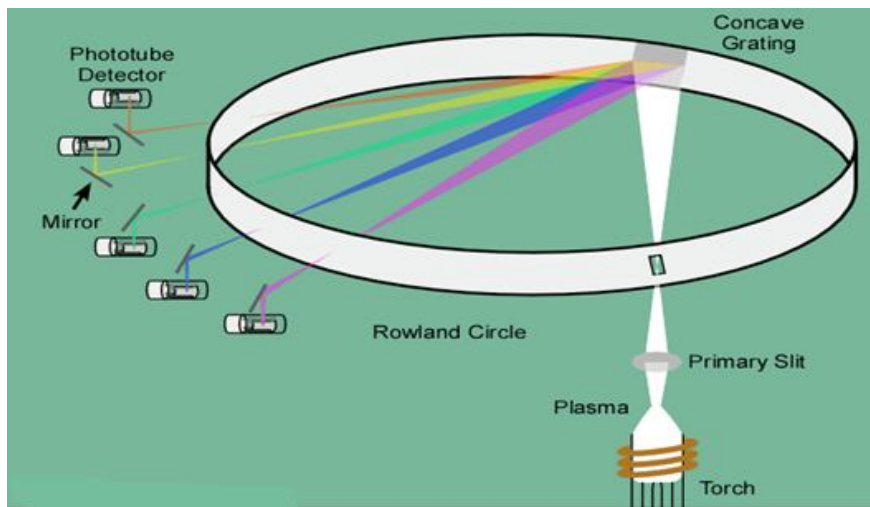
Figure (2-10) Rowland Circle ICP-AES System.

More recent advances, use a combination of two monochromators (one prism and one Echelle grating, or one conventional grating monochromator and one Echelle grating), remove the exit slit, and place a multiple element detection system, such as a charge coupled device in the path of the separated wavelengths .
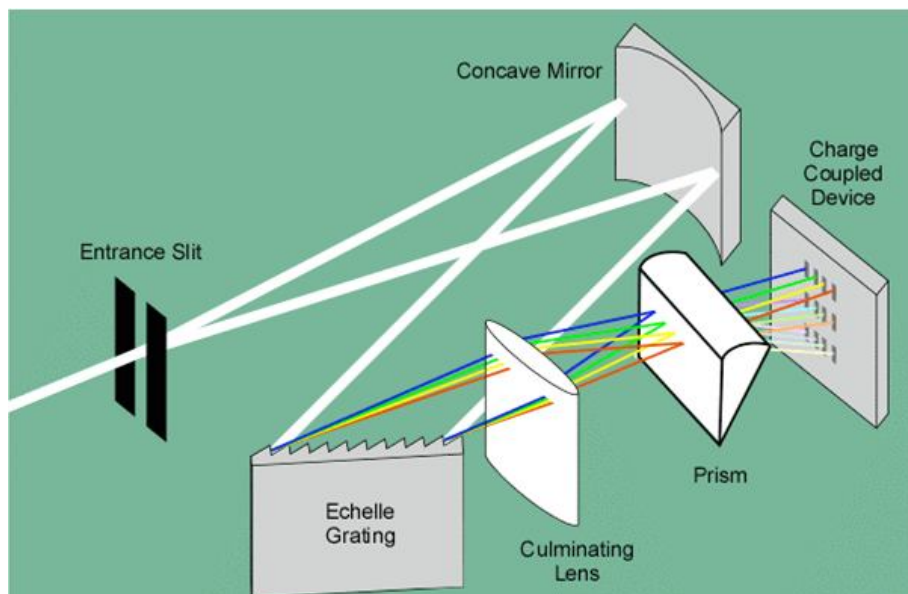

Figure (2-11) Multiple Monochromatic ICP-AES Instrument.

Some instruments use one detector for UV wavelengths and another for visible wavelengths. There are a variety of designs for these latter systems illustrated below. These more advanced instruments have an increased cost but are more economical recently due to decrease in the production costs of CCDs and CIDs versus PMTs. They also significantly reduce the lab bench space requirements. Instruments such as the one in illustrated offer superior resolution compared to a Rowland circle due to the advance monochromator systems, offer the immediate option to monitor secondary or greater diffraction that can be used in high concentration samples, (3) reduce the size of the instrument due to the reduced size of the detector(s), and (4) offer more inexpensive instruments as the cost of CCDs and CIDs become more economical.
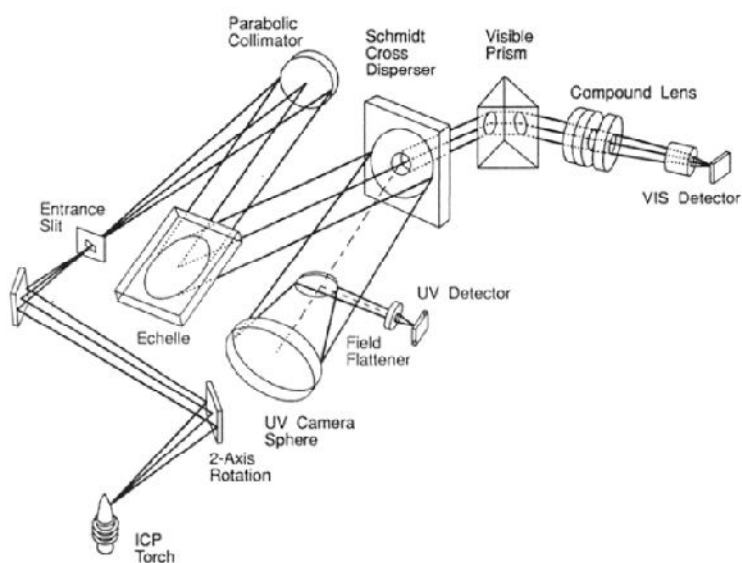

Figure (2-12) A Dual Echelle Grating – Prism Monochromator ICP with Dual CCD
Detectors. From Barnard et al., *Anal. Chem.*, 1993, 65, 1231. Reprinted with
permission from ACS.

2-3 Data Collection

When single element detection was the goal of instrumentation, a simple chart recorder or digital display was sufficient for data collection. However, with the advances in ICP-AES technology today, computers are a necessity, not only to control the automatic sampler and the instrument control but also for data collection. Data collection systems are divided into a "method file" to run the instrument and "sequence file" to tell the instrument where a sample is in the sample tray, when to run it, and where to store the collected data file.

2-4 Advantages of ICP:

It can be used for determination of concentration of almost all elements in the periodic table accurately and with the least interference. Limit of detection OD about 0.05 ppb for some elements. Doesn't require specific element's lamp enabling multi element detection, i.e. reducing time and sample volume needed for analysis. Presence of hydraaa instrument that analyze mercury using Cold Vapor Atomic Absorption Spectroscopy (CVAAS) technique. Sample measurement in solid, liquid and gaseous state.

2-5 APPLICATIONS:

Mining and petroleum industry:

Determination of ore quality in mining or manufacturing processes.

Determination of impurities in crude oils and residual fuels.

Environmental:

Determination of water pollution by heavy metals in industrial sewages.

Determination of mercury in water.

Determination of lead in fuels.

Medical:

Determination of mercury, lead and arsenic in food salt.

Determination of iron, calcium, sodium, potassium and/or phosphorus in blood.

Determination of elements content in pharmaceutical raw materials and some drug capsules in medical industries.

Other applications:

Determination of impurities in chemicals

Chapter Three

Experimental Part

3-1 Introduction

In this work samples of cheese were analyses by using icp-aes technique to see degree of their contamination with heavy to sic elements.

3.2 Materials and Equipments

3.2.1 Inductively coupled plasma-Atomic emission spectrometer

The equipment used in this experiment is the ICP-AES spectrometers known ICPE 9000,the ICP-AES provides a method for chemical analysis or sample identification (sorting) directly from samples in various forms. Figure 3.1 shows the Inductively Coupled plasma-Atomic emission spectrometer apparatus.

Figure3.1 Inductively coupled plasma-Atomic emission spectrometer

3.2.2 Cheese samples:

The samples of cheese were taken randomly, the white cheese sample was a commercial sample with 150 grams weight, see figure 3.2 below.

Figure3.2 White Cheese

The Pigtail cheese sample was a commercial sample with 150 grams weight, see figure 3.3 below.

Figure3.3 Pigtail Cheese

The Cheese triangles sample was a commercial sample with 150 grams weight, see figure 3.4 below

Figure3.4 Cheese triangles

3.3 Method

Accurately weighed three samples of 0.2gm from the homogenous mixture , each; were drawn from white cheese, pigtail cheese and triangles cheese, Sample were put in bowls and transfered to an oven adjusted at550c for eight hours, to get rid of organic compounds and to estimate the mineral content in ash, then adding 5ml of concentrated nitric acid (HNO_3) to the bowls to transfer the elements in the ash to dissolving nitrate salt .

Alitle mount of deionized water (ultra pure water) was added for dilution, then to be filtered with a funnels (with filter paper) in 25ml standard flasks, then the flask was filled up to25ml with deionized water (ultra pure water) ,then the solution was injected in inductively coupled plasma-atomic emission spectrometer (icp-aes).

Wavelengths used for determination of the tested 10 minerals were: Al, 308.2;

Ba, 493.4; Cd, 228.8; Cr, 267.7; Cu, 324.7; Fe,269.9; Mn, 257.6; Ni,231.6;

 Pb, 220.3; Zn, 213.9 nm, respectively.
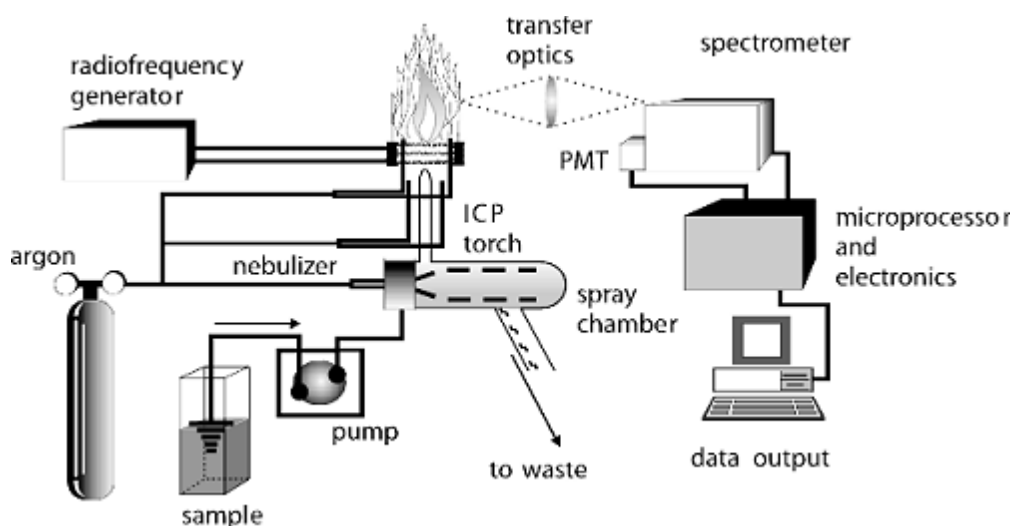

Figure 3.4 Schematic diagram of Inductively Coupled Plasma Atomic Emissions Spectrometer

Chapter Four

Results and Discussion

In this chapter we will show the results obtained and discuses it.

4.1 Results:

Table (4-1) below shows the information of the white cheese result obtained from ICP-AES.

Table 4.1 Element concentration of white cheese

No	Element	Atomic number	Concentrations/ppm	Standard specification
1	Al	13	94.125	10
2	Cr	24	0.0	0.05
3	Mn	25	1.40	0.3
4	Fe	26	13.075	0.3
5	Ni	28	8.6125	1
6	Cu	29	0.0	1
7	Zn	30	22.4125	5
8	Cd	48	1.2	0.1
9	Ba	56	0.0	1
10	Pb	82	16.375	0.5

Table(4-2) below shows the information of the Pigtail Cheese result obtained from ICP-AES.
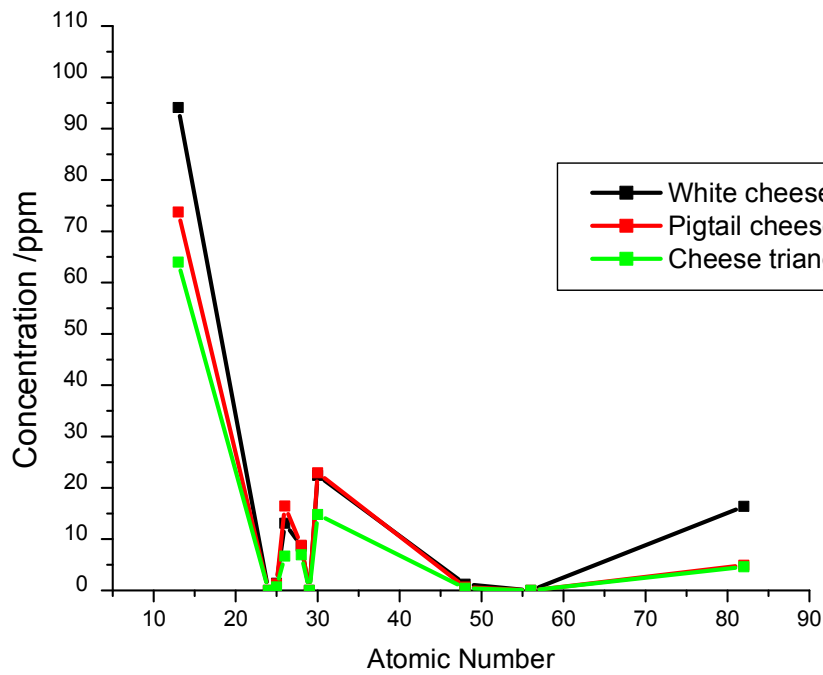
Table 4.2 Element concentration of Pigtail Cheese

No	Element	Atomic number	Concentrations/ppm	Standard specification
1	Al	13	73.75	10
2	Cr	24	0.0	0.05
3	Mn	25	1.2875	0.3
4	Fe	26	16.45	0.3
5	Ni	28	8.8	1
6	Cu	29	0.0	1
7	Zn	30	22.9125	5
8	Cd	48	0.6625	0.1
9	Ba	56	0.0	1
10	Pb	82	4.9	0.5

Table(4-3) below shows the information of the Cheese triangles result obtained from ICP-AES.

Table 4.3 Element concentration of Cheese triangles

No	Element	Atomic number	Concentrations/ppm	Standard specification
1	Al	13	64.0	10
2	Cr	24	0.0	0.05
3	Mn	25	0.6875	0.3
4	Fe	26	6.675	0.3
5	Ni	28	6.925	1
6	Cu	29	0.0	1
7	Zn	30	14.7875	5
8	Cd	48	0.4375	0.1
9	Ba	56	0.0	1
10	Pb	82	4.6125	0.5

Figure(4-1) Element concentration/ppm in the three cheeses sample
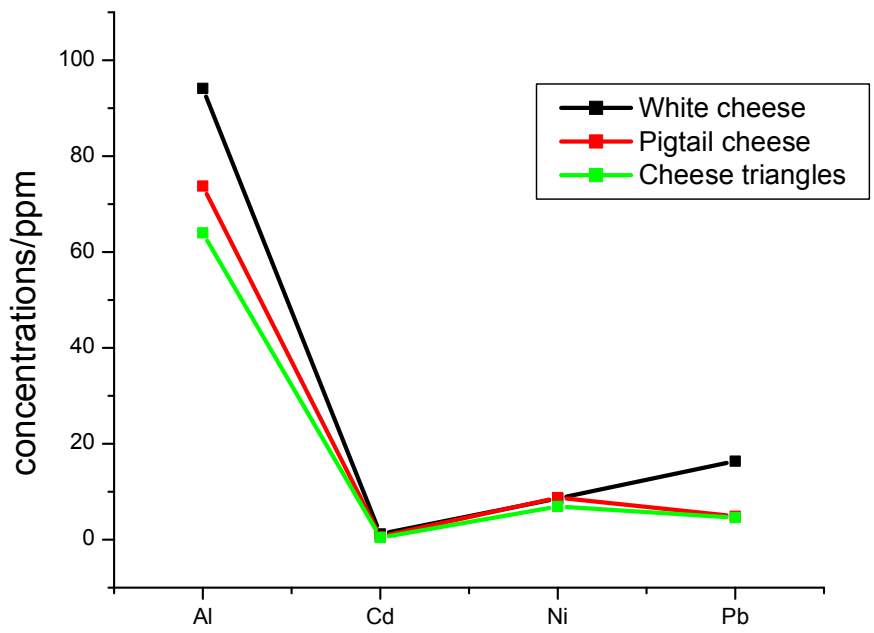
Figure (4-2) Comparison of concentrations (ppm) of heavy metals among three types of white and pigtail cheese, and cheese triangles
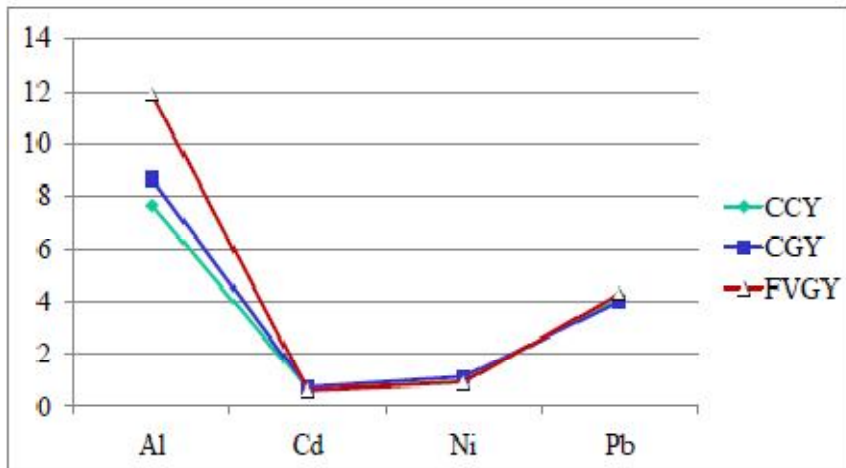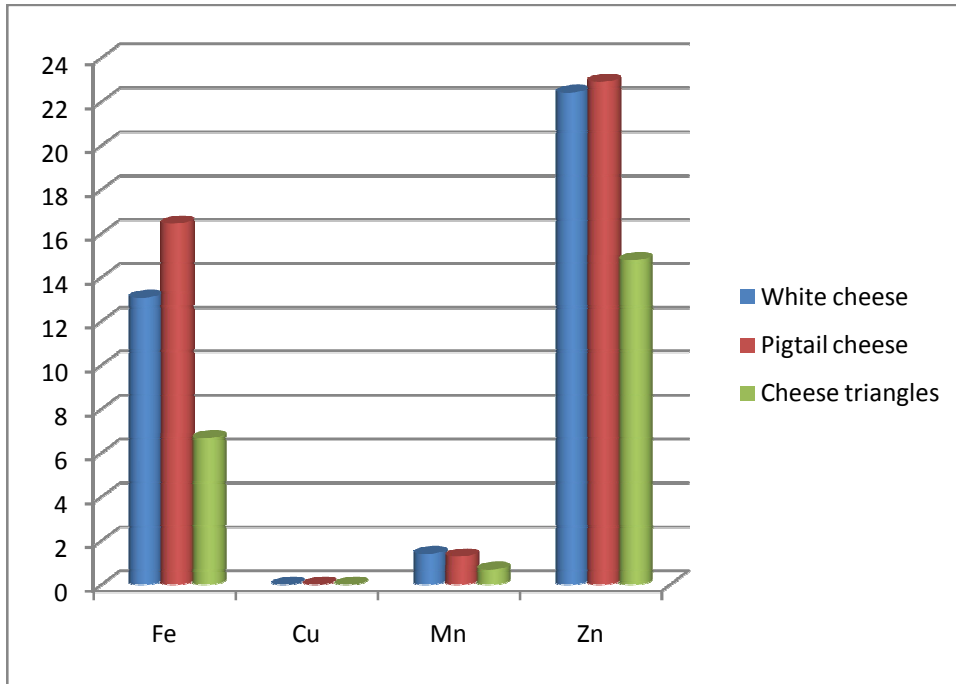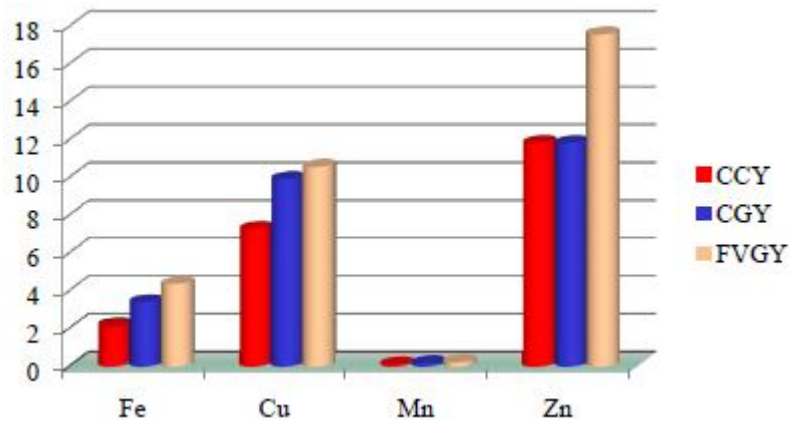

Figure (4-3) Comparison of concentrations (ppm) of heavy metals among three types of cow and goat milk yogurts (Karen Hernandez1, Young W. Park2, 2014)

Figure(4-4) Profiles of Zn,Fe,Cu and Mn concentration (ppm) in commercial whitecheese, pigtail cheese and cheese triangles.

Figure(4-5) Profiles of Zn,Fe,Cu and Mn concentration (ppm) in commercial cow and goat milk yogurts and fort valley goat yogurt (Karen Hernandez1, Young W. Park2, 2014)

45

4-2 Discussion:

In light of mineral concentrations, all minerals were lower in commercial products of cheese triangles than both white cheese and pigtail cheese. Average mineral concentrations/ (ppm) of Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Ba, Pb for white cheese and pigtail   cheese   and cheese triangles were: 94.1, 0, 1, 13, 9, 0, 22.4, 1, 0, 16.4; 74, 0, 1, 16, 9, 0, 23, 0.7, 0, 5 ; 64, 0, 0.7 ,7 ,7 , 0 , 15, 0.4, 0, ,5 , respectively. These data indicate that white cheese contained higher values of all minerals except Fe, Ni and Zn which is lower than pigtail cheese. Figure **(4-**1) clearly displays that white cheese had approxmatly higher levels of the minerals than the pigtail cheese and cheese triangle. Among the ten trace elements, Al is the highest mineral among all for all products. The differences in Al contents among the three products were greater than the other heavy metals, whereas the differences in Mn, Cd and Ni contents between the products were negligible . The respective Al contents of white cheese, pigtail cheese and cheese triangle were 94.125, 73.75 and 64.0, suggesting that there was some differences in Al levels in all tested cheese product.

The results also show that all samples there is no (Cr, Cu, and Ba) in white cheese, pigtail cheese and cheese triangles.

These results are agreement with the observations on Al contents in the previous studies (Park, y. w,   1991)(Park, Y. w, 1994)(Karen Hernandez1, Young W. Park2,2014) .

Figures (4-2 and 4-4) show that there a great agreement with previous study figures (4-3 and 4-5) (Karen,2014).

The comparison also shows that Cu in yogurt is exist with quit amount, while there is no Cu in cheese.

Mn and Zn exist with approximately equal amount, Fe is exist in cheese four times greater than in yogurt

4.3 Conclusions:

Among all tested 10 minerals of the three types of experimental white cheese and pigtail cheese samples, concentration of aluminum was the highest one from all minerals in commercial products in all cheese samples.

White cheese contain higher Al, Mn, Cd and Pb contents than both pigtail cheese and cheese triangles products, while pigtail cheese contained higher (Fe, Ni, and Zn) than white cheese.

While Al contents were higher than the levels of Pb, Cd and Ni in all three products.

4-4 Recommendations:

Future study could be by using the same device to samples from dairy sources to determining the elements , its concentrations, study fat, proteins and to compare these results to find out the difference and improvement of it.

It also recommended studying the same samples to determine the elements and focus by another device analyze and compare the results of the ICP-AES and compared with the results of each of the two devices and use the best hardware.

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