Nutrition Labelling and Proximate Analysis

Food Constituents:

- MACRONUTRIENTS

(Total calories, CHO, fat, protein contents:Daily Reference Values:DRV)

- MICRONUTRIENTS

(Vitamins,minerals:% of Reference Daily Intakes-RDI)

Are nutritionally important for their effects on chronic and deficiency diseases

Examples:RDI and DRV

- RDI
- VitaminA.....5000 IU
- VitaminC....60mg
- VitaminD.....400IU
- VitaminE.....30IU
- Iron 18mg
- Zinc.....15mg

- DRV*
- Fat.....65g
- Saturated FA...20g
- Cholesterol....300mg
- TotalCHO.....300g
- Fiber.....25g
- Protein.....50g
- *Calorie.....2000

Nutritional Claims

- Free
- Low
- Reduced/less/lean/light
- Good Source/contains/provides
- More/added/extra/plus/
- High/rich/excellent source
- Modified
- (See: Tables3.5-3.9 in textbook)

Health Claims

- Calcium and osteoporosis
- Sodium and hypertension
- Dietary fat and cancer, CHD
- Fiber and cancer, CHD
- Sugar alcohols nad dental caries
- Folate and neural defects

PROXIMATE ANALYSIS

I. Moisture

II. Carbohydrates and Crude Fiber

II. Lipids

IV. Proteins

V. Ash

Purpose of Proximate Analysis:

Estimation and determination of how much of the major food components, which are Moisture, CHO, Lipids, Proteins, Ash, Crude Fiber, exist in a given food. The proximate analyses therefore are:

1. Moisture Analyses
2. Crude Fat Analyses
3. Crude Protein - (Non-protein nitrogen also included) most proteins contain 16% nitrogen. Therefore the general "protein factor" is 100/16=6.25. If we multiply the percent nitrogen by 6.25 ,we obtain crude protein.

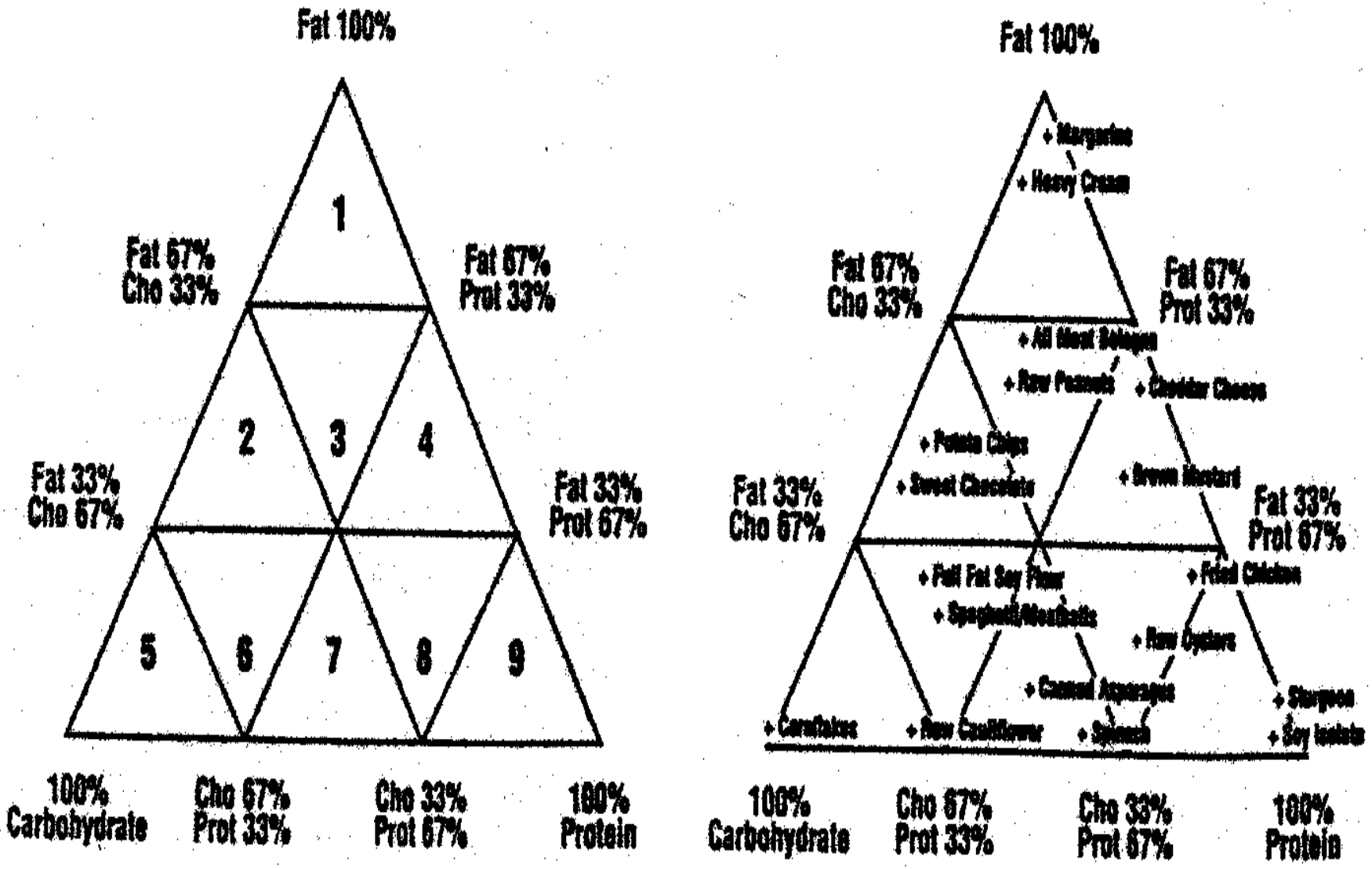
4. Ash - residue after burning all organic material. Some minerals become volatile at high temperatures of burning and therefore can be lost. Also some minerals occur in the form of salts of organic acids like citrates which contain carbon and are lost.

5. CHO and Crude Fiber

Total carbohydrate = 100 - [moisture + crude fat + crude protein + ash].

Crude fiber: residue left after alkaline and acid digestion of organic matter

If we subtract the total of 1-5 from 100, we get the nitrogen free extract by difference. Doing this normally underestimates nitrogen-free extract.



1-1 figure Schematic layout of food matrixes based on protein, fat, and carbohydrate content, excluding moisture and ash. Reprinted with permission from (12), *Inside Laboratory Management*, September 1997, p. 33. Copyright 1997, by AOAC International.

MOISTURE and Total solids ANALYSIS Ch.8

I. Importance of Water

II. Properties of Water

III. Classification of H_2O Determinations

-Direct Methods:Drying and Distillation

- Methods Measuring Physical Properties

-Methods Based on Colligative Properties

- Methods Measuring Chemical Properties

I. Importance of Water

WATER has great importance in foods, because :
1. Of its economic importance to the processor and the consumer, permitting material balances, yield and loss calculations, also for realizing legal standardsto protect consumers , since food companies want to sell as much water as law permits.

2. Of its effects on stability, therefore quality issues, since high moisture levels accelerate all types of food deterioration(chemical, enzymatic, microbial).

3. It permits uniform expression of analytical results, for food labelling and for regulations concerning food.

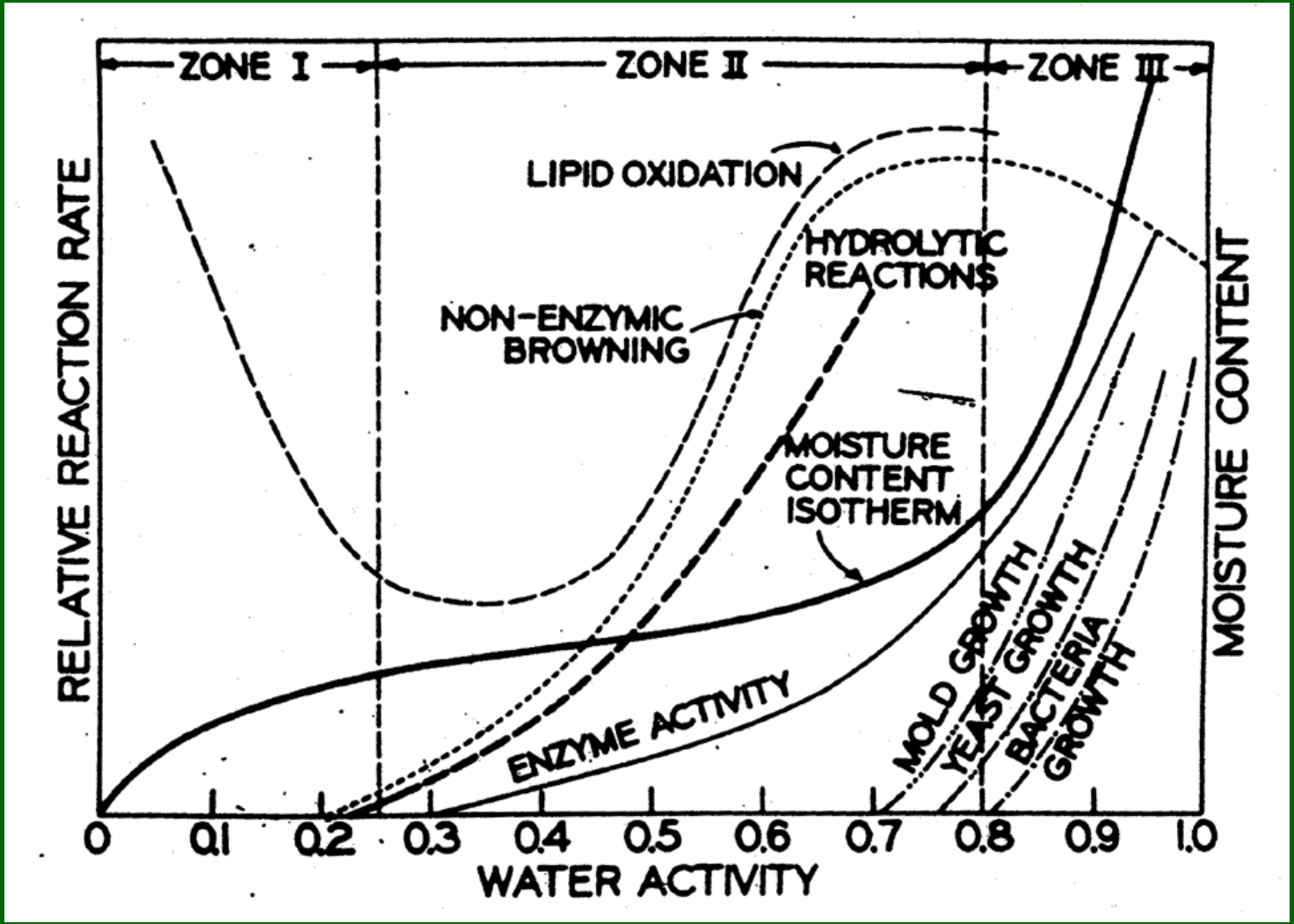
WATER

Water Functions

Important properties of water:

1. Universal solvent (salt, vitamins, sugar, gases, pigment)
2. Capable of ionizing ($H3O^{+}$, OH^{-})
3. Affects the texture
4. Enters chemical reactions (hydrolysis of protein = n amino acids)
5. Stabilizes the colloids by hydration
6. Necessary for micro-organisms growth

REACTION RATES IN FOOD AS A FUNCTION OF WATER ACTIVITY



MOISTURE ANALYSIS

WHY DO WE NEED MOISTURE ANALYSIS?

1. Material balance
2. Meeting the standards of product
3. Product stability (prevent deterioration, mold, bacteria, insect damage)
4. Express the composition on Dry Weight Basis
5. Economic importance (H_2O is cheap)

WATER DETERMINATION METHODS

1. Drying methods
2. Distillation method
3. Chemical methods
4. Physical methods

As a general rule in all analyses, choose the fastest simple convenient method which will give results within the desired range of accuracy - savings on time, labor costs, will quickly cover capital expenditure.

CONSIDERATIONS IN SELECTING THE METHODS OF WATER ANALYSIS

1. Form of water present (free vs. bound water)

   Example: % water in milk vs. non-fat dried milk.

2. Nature of product:

   Volatile compounds

   Heat stable - loss of some food compounds

   Unsaturated fat - oxidation - weight.

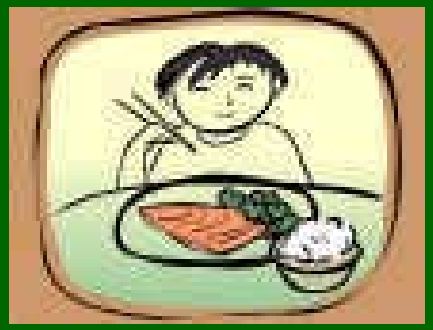
3. How fast you can analyze sample.

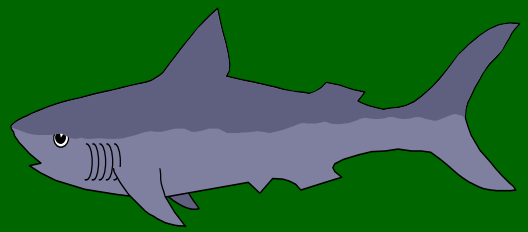
4. Accuracy and reproducibility.

5. Availability and cost of equipment.

The moisture content of foods varies greatly between food products - e.g.

Product	Moisture content %
Milk	87-91
Melons	92-94
Milk powder	4
Cucumbers	96
Butter and margarine	~15
Meat and fish	50-70





• There are many alternative methods, thus many different principles of operation. Choice of method depends on following criteria:

Speed - resources available – desired levels of accuracy / precision –operating costs

• If you work at a routine laboratory, you prefer quick methods. However, for reference laboratory accuracy is most important. Following are steps to be followed for determining the overall composition of a food sample or content of a specified component:

KINDS OF WATER - DEGREE OF WATER BINDNESS

Monolayer Water is bound in food - restricted in its movement due to charges, hydrogen bond, physical entrapment. Hard to remove from food. Never be able to remove water completely.

Multilayer Water - additional layer of water around food particle. Not as hard to remove as the monolayer.

Mobile or Free Water - consisted with ideal solution.

Forms of Water in foods and their Properties

Water may occur in several forms in foods:

1. Free H_2O (within the pores of material in the inter granular spaces) :
As solvent for molecular dispersion of solutes, colloids, etc. When it exists as a solvent, it can be thought of as free water, not bound to any thing and therefore available for chemical reactions, microbial growth, and physical changes.
It can be obtained by evaporation; it retains its usual properties as solvent, it is available to microorganisms.

2. Adsorbed water can exist in mono or polymolecular layers on the internal or external surfaces of molecules in the food. It is held tightly in cell walls or on particularly proteins and starches which have strong tendencies for forming such interactions with water.

Because fat is hydrophobic, it does not usually interact with the water phase in food, however, there are phospholipids and lipoproteins that associate at lipid-water interfaces.

These can act as emulsifiers. Van der walls forces are effective for physically adsorbed H_2O (is found in a mono layer on the surface of macromolecules).

3. Water of Hydration: Sometimes, water can be chemically bound to certain compounds like lactose (forming a stable monohydrate), salts (tartarate), proteins (hydrogen bonded) and polysaccharides (hydrogen bonding). This bound water may vary from 0.5 to 30% of the total water present. This water is particularly difficult to remove for analytical purposes. Chemically bound water is in the form of water of hydration or crystalization, It is unavailable as solvent.

Ex: $MgSO_4.3H_2O$: Here, H_2O is completely different from the other forms.

~6% of H_2O in animal tissues,
~10% of H_2O in fruits is in this form.

III. Classification of H_2O Determinations

Principles of methods used for moisture determination:

I. DIRECT METHODS:

These are based on separation of water from food solids and measuring the loss in weight or the volume of water removed.

A. Oven Drying Methods: Vary greatly in conditions for drying (over dessicants or in atmospheric or vacuum ovens)

B. Distillation Techniques: Co-distilling water with a high boiling point solvent that is immiscible with water.

II. Methods based on chemical reactions of water.

III.Methods measuring some physical(a) or colligative(b)property that is correlated to moisture content

IA. Drying Methods

These are essentially thermal methods. Moisture los is a function of time and temperature. In most cases, drying methods rely on gravimetric difference before and after drying, using heat transfer by conduction on convection.

Drying methods have advantages of being:
-Simple
-Fast(infraredmethod),
-Handling large number of samples
- Inexpensive (equipment)

Principles governing moisture loss:

*Heat transfer rate (seldom a limiting factor)
*Temperature *
*Surface area of product, particle size
*Diffusion of water through product
*Vapor pressure differences (RH at surface vs. product), number of samples in oven, air exchange rate in oven, vacuum applied or not, air movement in dryer, etc.

*1 mole of solute dissolved in 1liter water raises its boiling point by ~0.5°C.Thus boiling point elevation continues during moisture removal process.

DRYING METHODS –

DRY THE FOODS UNDER THE SPECIFIC CONDITIONS

Types of Oven, Temperature, Time.

Advantages: Simple, Relatively rapid, Analysis of large number of samples at a time.

Disadvantages: Loss of other organic compounds or gases formed by thermal decomposition of organic compounds.

Oxidation of oil.

Error Source: Crust formation from sugar.

DRYING METHODS

1. Air-oven Method --- put the sample (10g) in flat, tarred dish - specified time and temperature (150C for 1 hr) - measure the loss of water.

2. Vacuum oven Method --- use it if you do not want to expose to high temperature. Use 50 mm Hg and around 100C. Food rich in fructose must be dried at 70C or below.

3. Hot plate Method ---rapid, quality control, use some time, put in vacuum at 100C, cool in desiccators, "Mojonnier".

4. Moisture-balance --- balance in oven with IR light and heat. Measure the moisture loss.

•Disadvantages:

•Precautive measures have to be taken to avoid decomposition of solute components:

Example: Fructose containing foods may decompose with uncontrolled heating since fructose is destroyed above the 100°C,

•Solution: Apply vacuum, reduced temperature and longer drying time.e.g. Also may place in vacuum desiccator over concentrated sulfuric acid, phosphorus pentoxide, or magnesium perchlorate).

•Oven methods are not good for products that have a lot of bound water.

•Dried fruits contain a lot of bound water and will lose only 75% of their moisture by drying methods. Dehydrated finely ground carrots require 6-9 months in a vacuum over Mg perchlorate to attain constant weight.

DRYING methods have many other disadvantages:

It is not specific for all types of water, therefore may lead to mistaken calculations
Optimal drying temperature may notbe attained
Drying can be destructive to other components (nondestructive vs. destructive methods)

Heat Sources used are air-ovens, vacuum-ovens, microwave ovens, infrared ovens and lamps. In ideal drying procedure for the determination of water, weight losses should result from quantitative and rapid volatilization of water only. This depends largely upon:

- *Air movement in the drying chamber
- *Vacuum in the chamber.

Factors influencing results (the rate of evaporation of water in ovens).

a-Diameter or surface area of containers.
b-Depth of containers
c-Material of containers (Al; porcelain etc.Drying rate is highest in Al dishes)
d-Position and number of containers in the oven.
*Dessicants like P_2O_5; calcium carbide, silica gel will speed drying..
e-Drying is a function of time, temperature and water vapor pressure. Therefore in order to be able to decrease the temperature, we have to either increase the time or apply vacuum. In vacuum ovens, water vapor pressure of air in oven can be effectively used at much lower temperatures thus avoiding decompositions or destructions.

Vacuum is generally applied in 2 steps,i.e.First go down to ~310 mm Hg for 30 minutes,and then attain <15 mm Hg. Typical vacuum levels for specific commodity types are:100 mmHg for fruits, oils, nuts;50 mmHg for sugars and sugar products; 25 mmHg for cereals and eggs.

*Drying time is inversely related to drying temp. Especially in drying cereals , normal ovens require 14 hours whereas microwave ovens require 3-10 minutes for 10 gr samples when power input ~100 watts.
*In infrared ovens drying is even faster. However there is a risk of surface carbonization since the filament of the IR lamp(~500W) develops ~2000° K, thereby might lead to surface carbonization

Drying Conditions

Ovens in which there is hot air circulation or an inert atmosphere with vacuum (70-130°C)is applied for a specified time until successive weighings differ by <3 mg.

Goal: Reach highest temperature without decomposition or chemical reaction (Temperature-time optimisation)

Types of Equipment:

Hot Air Ovens

- Either working on convection or forced air, it should be accurate and uniform in temperature. So first rule in drying is:use a GOOD oven.
- May have balances built into oven, so permitting semi-automatic assays
- Some have humidity sensors to determine when drying is complete.

Vacuum ovens

- Vacuum helps to get rid of the 1%+ moisture that is bound in most foods. We can use lower temps, reduced RH (vapor pressure in oven).

It MUST HAVE LEAKS to reduce VP ,For this aim, air is passed through a dryer such as conc. H_2SO_4 or drierrite..

*Optimal Time-Temp combination: i.e. 16 hrs at 100°C is most common.

*Cold trap is essential for collecting the water from sample to protect the vacuum pump and reduce RH.

Other ovens:

Microwave: Very rapid heat transfer/drying:i.e. 6-8 min for 10g sample of meat. Built-in balances. Air exchange systems. But requires centrally located and evenly distributed samples.

Infrared: (Filament T:2000-2500K) more rapid heat transfer,thus shortens time,but may be too fast and burn sample. Use IR lamp ca. 10 cm from sample. Thin bed of food 10-15 mm. Drying times should be 10-20 min max.

Accuracy Problems

1. Sampling errors.
2. Retention of water by adsorption, occlusion or chemical combination makes loss by vaporization difficult. Reaching a constant weight does not always guarantee that all water has been removed.
3. There might be barriers to water diffusion in food role of diffusion in drying.

4. Chemical decomposition reactions possible especially for sugars like fructose and sucrose

5. Other volatiles

6. Effects of Oxidation

7. Absorption of water from air:

A. Adsorption of moisture from air in drying oven

B. Adsorption of water from the air during weighing.

Procedural Considerations

1. Preparation of Sample: Different for Liquid products - Bread vs.Fruits

2. Drying Conditions: regulation of temperature to ± 1°C may yield a 0.1% difference in moisture content.The vacuum required for different products is different:100 mm Hg is ideal for fruits, nuts, oils, and fats; 50 mm Hg for sugar and sugar products, 25 mm Hg for cereal foods, eggs, and egg products.

3. Preparation of the drying dish: The drying dish should be pre-dried and held in a desiccator until use.

I.B. DistillationProcedures:

Reflux Distillation with immiscible solvents (Entrainment)

This type of method is used for samples which contain other volatile components.

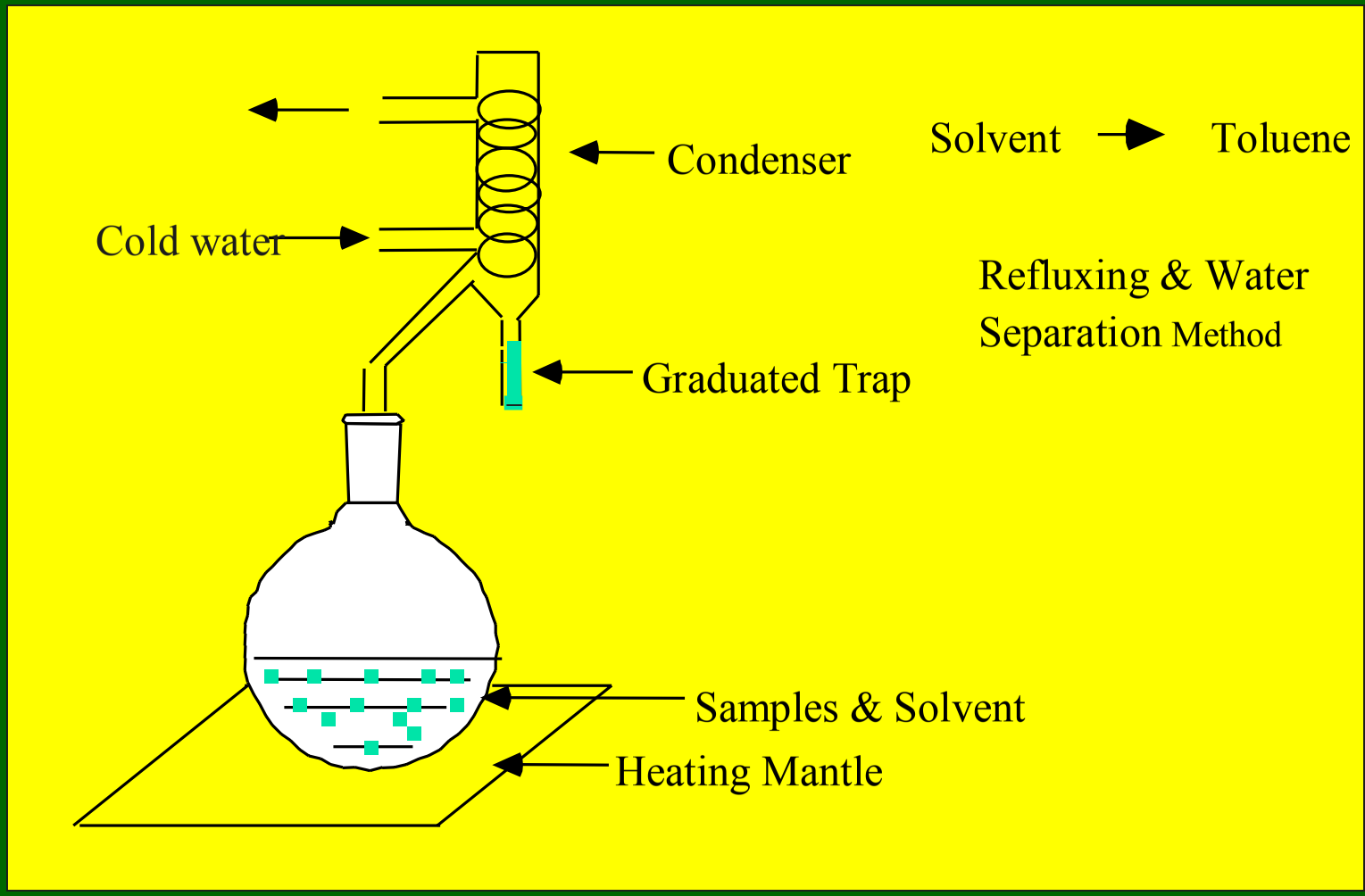
Ex:Spices

Principle: A solvent immiscible with water is added to sample and the mixture (H_2O + solvent) is boiled off as an azeotropic mixture. Upon cooling, the 2 phases will separate (volumetric determination).

Depending on your purpose, your solvent's density has to be either higher or lower than that of water. Apparatus types: p. 92-95.

Distillation was originally developed as a rapid method for food quality control, however, for foods that might decompose on heating, you can only get approximate results from distillation methods. Distillation is preferred for cereals, nuts, oils, waxes, and powdered products.

DISTILLATION METHOD



There are three general types of distillation:

1. Direct distillation from immiscible liquids with very high boilng point – e.g. mineral oil.

2. Direct distillation with immiscible liquids that have boiling points near that of water e.g. toluene or xylene.

3. Reflux distillation with an immiscible liquid – toluene(B.P.110°C), xylene(B.P.137 °C) or tetrachloroethylene

Problems that can be encountered when using entrainment distillation include:

1. Incomplete recovery of water as a result of emulsions between water and solvent.
2. Drops of water clinging to the condenser or side of the receiving trap.
3. Decomposition of sample - more problems with high boiling point solvents.
4. Toluene may condense too soon in the trap and thus does not carry much water over into the trap.

II. Chemical Methods

1. Karl Fischer Method: Very popular method, but Karl-Fischer Titration is seldom used in high moisture foods. For low moisture foods like candies, chocalate, dried fruits and vegetable, bakery doughs, baked products reasted coffee, fats and oils, sugar rich foods or foods rich both in reducing sugars and proteins, KF is the preferred method.

Principle: Reduction of iodine ($I^{\circ} \rightarrow I^{-}$) to iodate by SO_2 in presence of H_2O(see pp. 130-1).

$2\ H_2O + SO_2 + I_2 \rightarrow 2HI + C_5H_2SO_4$

Without water in the medium, this redox reaction will not occur.(see Fig.8.6)

The basic reaction takes place in two stages:

1) $(C_5H_5N).I_2+(C_5H_5N).SO_2+(C_5H_5.N)+H_2O \rightarrow 2(C_5H_5N).HI+(C_5H_5N).SO_3$

2) $(C_5H_5N).SO_3+CH_3OH \rightarrow (C_5H_5NHSO_4CH_3)$

Even though the stoichiometry is not exact, at the turning point of the titration, for each mole of H_2O in sample, the amount of spent KF Reagent will contain:

1 mole of Iodine
1 mole of SO_2
3 moles pyridine
1 mole methanol.

So this is basically the composition of the KF Reagent. 1ml reagent corresponds to 3.5mg water.

The endpoint involves a change in Redox potential, which can automatically be detected with use of electrodes. There now are also automated KFTitrators by Merck. Ex.:For edible oil industry,where no water is desired in product, KF titration is used for automatic controls for any trace water.

CHEMICAL METHODS

Karl Fisher Method---Standard technique for low moisture foods.

Especially good for reducing sugars and protein-rich foods and good for foods with high volatile oils.

Theory: $2\,H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$

KARL FISHER METHOD

Karl Fisher Reagent:

Dissolve 132 g of Iodine + 425 ml of Pyridine + 425 ml of MeOH + 105 g of SO_2.

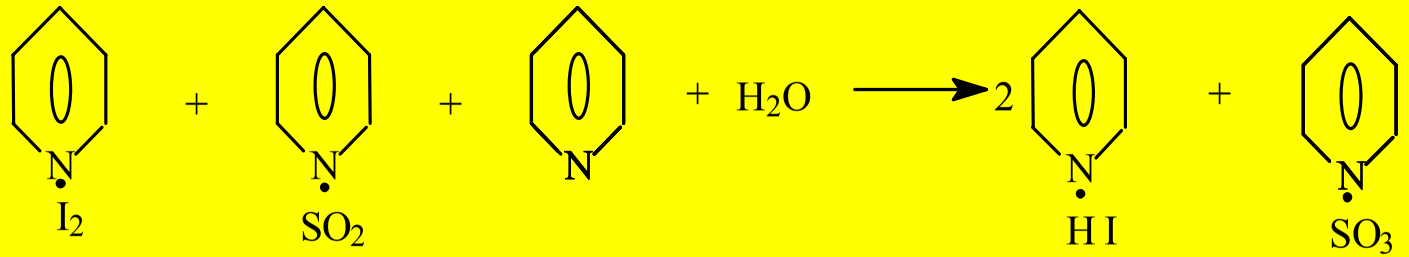
Titrate 120 mg of H_2O with Carl Fisher Reagent.

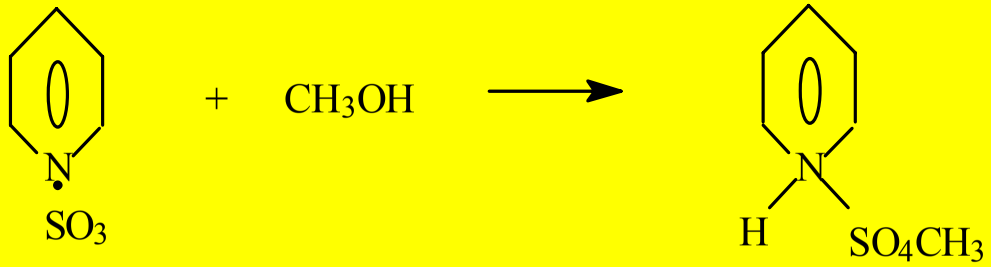
Calculated Concentration = mg H_2O/ml of Reagent

= 5 mg/ml of Reagent

% H_2O = Conc. x ml Reagent / mg of Sample x 100

KARL FISHER METHOD

1. 

2. 

Brown Mahogany Color

Method of choice for many low-moisture foods like dried fruits and vegetables, candies, chocolate, roasted coffee, oils and fats.

The method has been applied to intermediate moisture foods (bakery doughs, baked products, fat-rich cakes, and foods with high levels of volatile oils).

Methanol, sulfur dioxide, and pyridine are added in excess so that all water molecules react.
The amount of iodine reduced by water is titrated by KF reagent. The reagent has to be standardised against distilled water for finding its water-equivalence factor, KFReq(how much water 1 ml of KF reagent will correspond to).

Problems:

1. Extraction may not be complete or decomposition may take place during extraction. Therefore, found values will be too low.

2. Interference from:

a) Ascorbic acid which is oxidized by Karl Fischer reagents to dehydroascorbate and water(so titration measures both water and ascorbic acid).

b) Carbonyl compounds react with methanol to form acetals and release water, and found water values will be higher than the real situation.

c) Reaction with mercaptans, bicarbonates, and carbonates can cause fading endpoints.

d)polyunsaturated fatty acids will react with I, yielding high water values.

2. Generation of acetylene gas

$CaC_2 + H_2O \dashrightarrow CH{=}CH + CaO$

The amount of acetylene gas that is formed after reaction with water is measured by a monometer. This procedure has been used for determining water contents of powdered food products like cereals, flours, and cottage cheese.

3. Cobalt Chloride Paper:

$$CoCl_2 + H_2O \text{ ----------> } CoCl_2 * 6\ H_2O$$

(dry:blue) (wet:pink)

Filter papers are soaked in solution of $CoCl_2$ and dried. The sample is ground and a small quantity is spread on the paper. The sample is covered to allow color change.

Semiquantitative estimates of free water in food can be obtained by measuring the rate of color change on the filter paper. This method is used on high sugar foods such as raisins.

III.A METHODS Measuring Physical Properties:

Sometimes there is need for nondestructive analyses(i.e.plant breeders don't want to lose their very valuable samples).

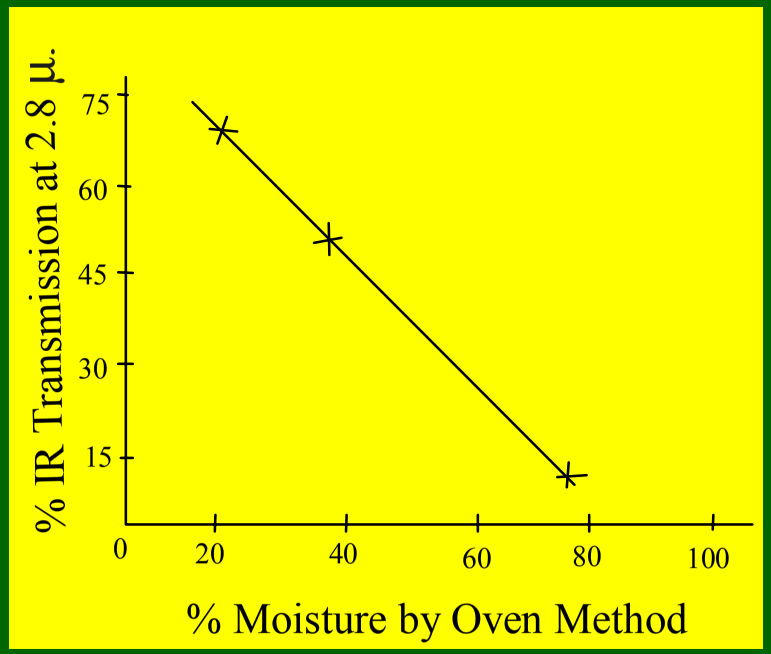
Examples of such nondestructive methods are spectroscopic methods like NMR (Nuclear magnetic Resonance), and Dielectrometry. However, these types of methods are not very specific, they need standardization (individual) where you have to prepare your own graphics using standards, so may be considered to be rather "empirical". Many parameters like the temperature of measurement affect measured values. Below is given a summary of these methods.

PHYSICAL METHODS

1. Infrared Method:

Absorption Method --- measuring the absorption of OH group at wavelength of 2.8 μ.

Common Method - 1 ppm (sensitivity)



*Spectroscopic methods - Near Infrared:

NIR →near ınfrared reflectence:

*Principle; Resonant frequency of protons in H_2O is different from that of protons in macromolecules.

•Used wavelengths are 3.0 and 6.1 um (fundamental vibration frequencies of water) 1.93 um (combination abs. band) and 1.45 um (first overtone of the OH stretching)

One advantage is that results do not need expert interpratation. Another is its excellent sensitivity – can measure down to few ppm. Also very rapid.

Disadvantage are very expensive equipment and very critical sample preparation step.

*Gas Chromatographic Methods: The water in sample can be extracted into methanol and analysed by GC, which is very good at separations – use a Poropack column (best for separation of polar materials. Water will easily be separated from methanol and measured using a universal detector (TCD:thermal conductivity detector)

- Quantification -A standard curve using different ratios of water to methanol should be prepared and results are extrapolated from this standard curve.
- Adv:Can run automated systems-rapidity
- Accurate/precise (limited to extraction)
- Little or no interferences
- Disadv:Cost of instrument,and expertise needed for reliable interpretations.

*Nuclear Magnetic Resonance

Principle: Hydrogen nucleus absorbs energy in specific radio frequency. While there are numerous forms (binding) of H nuclei, method can discriminate between what the H is bonded to e.g. OH.

- Works well for low moisture contents, but spectrum gets too complicated for high moisture products.
- Adv: Can determine/distinguish bound water – one of the few such methods,
  - Rapid (1 min), - Nondestructive since nonthermal, no decomposition,and accurate.
- Disadv: High cost and sophistication in operation

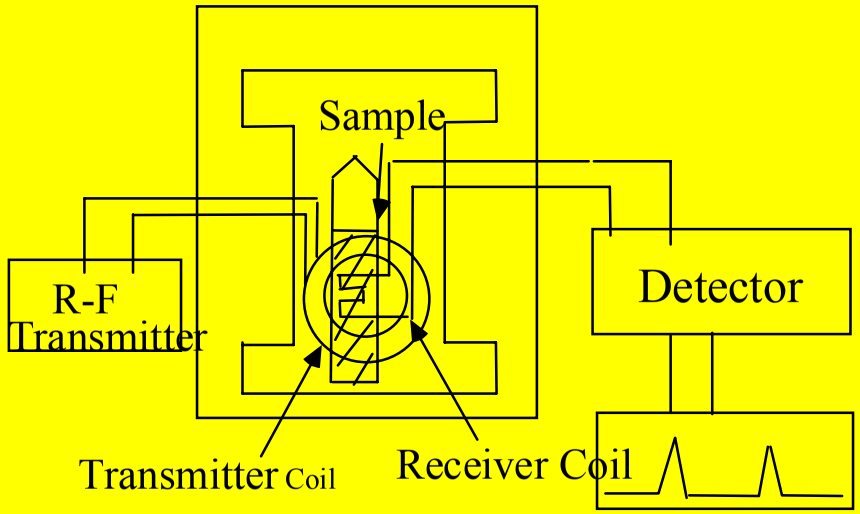
NUCLEAR MAGNETIC RESONANCE SPECTROMETER

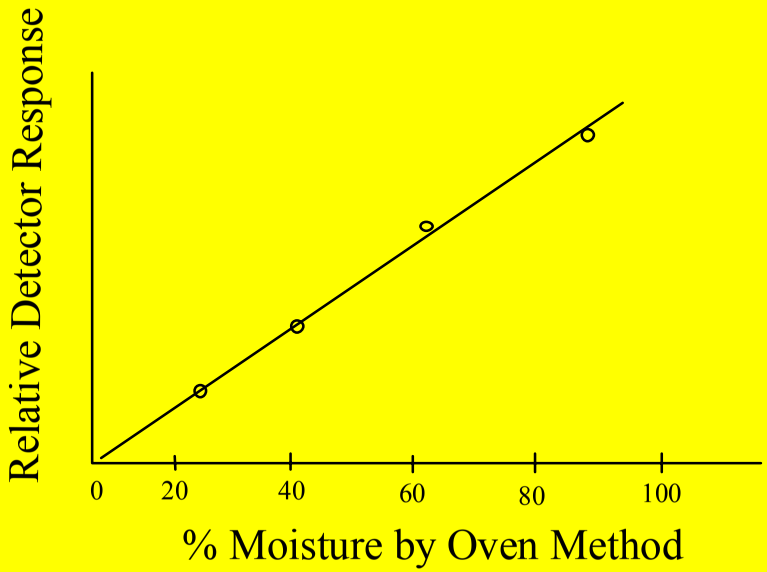
NMR: Measure the hydrogen nuclei

H2 nuclei of water will vibrate (spin-oriental) in a fixed magnetic field and proper radio frequency. Absorption of radio frequency by the hydrogen nucleus.

Rapid/Non-destructive/Accurate

Nuclear Magnetic Resonance Spectrometer





*Electrical Conductivity:

Empirical relationships have been developed between moisture content and electrical conductivity. Conductivity of sample depends on:

- Moisture content↑↑
- Salt content
- Packaging
-Temperature- Texture

Application: 20 g of prepared sample is put in a steel cup , a current is passsed through the vessel, and conductivity is read. The moisture content is to be extrapolated from the std curve to be prepared with different but known moisture contents.

Adv: speed;

Disadv:sample dimensions/packing in cell and other components will all influence the conductivity

Methods based on specific gravity and density

1. Specific gravity and density of liquid samples can be measured using a **pycnometer**, which is related to the water content of sample. There are tables that relate density or most commonly specific gravity to solids concentration ; but these should all be recorded at the same temp.
2. A **Westphal balance** can be used which is based on Archimedes' principle, "The same body will displace equal weights of all liquids in which it floats". WB will yield both density and specific gravity values , though specific gravity is the easiest to obtain. The balance has a sinker suspended on a thin wire that hangs from the end of the balance.

Using A and B where A = the weight of the sinker in air, B = the weight of the sinker in pure water, and C = the weight of the sinker in the liquid, water content of liquid sample can then be calculated.

Errors can be caused by surface tension on the wire and by air bubbles attached to the wire or sinker.

3. Specific gravity by **hydrometry:** This is the simplest way to determine specific gravity, again being based on Archimedes' principle. Concerns about this method include:

- cleanliness of the hydrometer
- temperature (liquid volume, therefore density will change with temperature),
-a large enough container should be chosen so that there is no physical interference from the container holding the fluid.

Some common hydrometers are:

A. Saccharometers
B. Balling
C. Brix
D. Baume' hydrometers[0° Baume = Pure water, 10 Baume' = 10% salt (NaCl)],
E. Lactometers

Example: **LACTOMETERS**:
Specific gravity of "normal" milk is 1.029-this corresponds to 29°in lactometer reading. So, to get specific gravity of milk, you divide lactometer degrees by 1000 and add 1. Total solids in milk can then be found according to the following equation:

$$\text{Total solids} = 0.25\,L + 1.2\,F$$

where L is the lactometer reading, and F is percent fat in the milk.

REFRACTOMETRY:

Principle: Optical density of solutions as well as the refraction will change with changing water contents.Some refractometers may read as RI (dimensionless) and some directly in % soluble solids(1°**Brix=RI of 1%w/w sucrose solution)**).

Refractive Index:

RI can vary between 1.300 and 1.700 at 20° C[with sodium D line (λ= 589 η m)].

RI also varies with:

-Temperature

-Concentration

-Wavelength of light (if other than Sodium D line)

III.B METHODS Based on Colligative Properties:

III.b.1.WATER ACTIVITY (aw)

Knowing only the water content of foods may not be enough. Another very important concept related to moisture is "water activity- aw", which is defined as:

Aw= (P) / (Po) = ERH/100

"The ratio of equilibrium vapour pressure of sample (P) to the equilibrium vapour pressure of pure water (Po) at that same temperature"

Methods for measuring aw are based on colligative(physicochemical) properties of water: When solutes are added to H_2O, vapour pressure ↓ osmotic pressure↑, freezing point↓, boiling point↑.

•Measurement of water activity in foods.

1. Directly measure Aw –

a. classical (manometric) measurement of the vapor pressure or by using hygrometers with a sensor containing hygroscopic material like LiCl, the conductivity of which will change according to the relative humidity in the chamber above sample, or psychrometers.

b. Dew point - mirrors

2.Measurement of ERH (equilibrium relative humidity)

Simplest apparatus uses salt-impregnated filter papers. Here the principle is : Salt will not dissolve H_2O unless surrounding humidity level rises to a point which is equal to the specific saturation moisture content of the salt (standard and constant values for each type of salt). Filter papers are dipped into various saturated solutions with known ERH levels, dried and affixed inside the upper lid of the petri dish;sample is placed in lower dish, covered with lid and equilibrated for 20 ghours at 20C. Aw of sample is between the wet paper of highesr aw and dry paper of lowest aw.

The vapor pressure (Aw) of water above a food is related to its moisture content. But the relationship is nonlinear for many food products and large errors can occur unless you linearize the data using a transformation. You can prepare an isotherm for the specific food but this will be time consuming, and hysteresis may lead to errors.

II.b.2. Freezing point elevation or depression:
When water is added to a food, there will be a freezing point depression , which can be measured and is valid for upper aw levels (>0.8).

Example:F.P. (freezing point) of unadultereted milk ≅0.55°C. Each 1% added water changes the freezing point of milk by .0055 ◦ C. Percent added water can thus be calculated using the equation:

One molal of any species decreases FP by 1.86°

$\Delta t(t_c - t_1) = -1.86 * \text{molal concentration}$

Where m: Molality of solution (moles solute/kg solvent)

Tc = Avg. freezing point of normal milk (-0.55C),

and T_1 = the observed freezing point

% added water = $100(Tc - T_1)/Tc$

REPORTING RESULTS (Ch.4, p.65-67)

The reference basis chosen is of utmost importance.There are the following alternatives:

1 AR(as received) or -as is basis: expressed on untreated samples(also sometimes as "fresh weight basis"(g/100g tissue).

2.OD(oven-dried) or dry matter basis: expressed on contents excluding water

Since moisture contents can vary greatly, it is best to report it in dry matter basis in order to be able to make comparisons.

3-Edible portion basis (Skinned eggs or Whole eggs) i.e. 100 gr of skinned eggs

4-Arbitrarily selected basis: See next 3 examples

Ex 1: In cereals $\rightarrow$ a reference point is 14% H_2O content is taken to express the nutrient contents

Ex 2: Quantity of amino acids can be expressed as mg per each 16 gr of N.

Ex.3: as ---- g/100 g of a specific nutrient – nutrients

5. Per serving – (g / serving)
6. ...../lot size –for manufacturing operations
7. In "standardized unit"s
   - RDI-recommended daily intakes (IU of vitamins),
   - ....activity in system (enzymes),
   -..... meq=O_2/g of product – (titrations)
8. "weight" or "volume" basis:

For example, ppm can denote both mg/kg-weightbasis(most common) or mg/L – volume basis. (air sampling or beverage formulations g/110 or g/100 L)

Calculations in converting from one basis to another basis:

Example: Sample composition is 10% H2O; 30% fat on (asis) basis. To calculate how much fat this will correspond to on "dry matter" basis:

$$Fat_{dm} = \frac{30 \ x100}{(100 - 10)} = 33.33$$

So the sample contains 33.33% fat on dry matter basis.

2. From % OD (oven dried) to AR (as received):

$$\%Y_{OD} = \frac{\%Y_{AR} \times 100}{(100 - \%\ loss_{OD})}$$

3. From AR to AM (arbitrary moisture basis):

$$\%Y = \%Y_{AR} \frac{(100 - \text{arbitrary moisture \%})}{100 - \%\ moisture_{AR}}$$

The “Units” used in expressing analytical results have to be SI units (metric).

List of commonly used SI units is given in your text-book on page 36-37.

The prefixes used denote the following :

giga : 10^{9} kilo : 10^{3} nano : 10^{-9}

micro : 10^{-6} mega : 10^{6}

Significant figures: Judgement of the number of meaningful digits in a result

- **Reported value should only contain significant digits(all known to be true, just the last one in doubt)**
- **64.72, 6.472,0.6472, 6.407 all hve 4 s.d.**
- **433.8+32.66=401.14→Rounded off→401.1(the number having the least significant figure dictates it.)**
- **Zeros ???**
- **Convert to exponential form: If zeros can be omited, then they are not significant:**
- **$7000 \rightarrow 7X10^3$: zeros not significant**
- **$7000.0 \rightarrow 7.000X10^3$:zeros significant**
- **Rounding up: <5:drop figure;**
- **>5:drop figure and increase previous number by 1**
- **Q-Value for rejection of results=X2-X1/W**

X1:questionable value,X2:next closest value, W:Total spread of values. Example: >0.76 if there are 4 observations

"EXPERT WITNESS"REPORTS:

In some countries, certificate of analysis by an expert witness is a legally valid document. In some others , the court is empowered to accept or to reject it. Report format should be preprinted for faster and more uniform processing.

The report should contain :

- proper sample identification (type, quantity, packaging, labelling etc.);
- analysis method used,
- results
- Interpretation of results.

Multivariate Analysis and Chemometrics

Insight & Understanding

These procedures are designed to extract useful information from large or complex data sets. Multivariate methods have broad application in many aspects of practical food science including microbiology, chemistry and engineering.

Experiment Design

Statistical experiment design techniques use experimental resources (time, materials, equipment) efficiently to collect data for development of models.

Modeling and Simulation

Models can be developed using regression or other methods and used to find true optima in quality or cost, or to seek acceptable compromises in performance of several factors.

These techniques have application in analytical method development and product and process optimization. They are particularly useful for generating process scale-up data, and often minimize surprises during transfer to industrial scale operation.

Composition/Property Relationships

Relationships between product constituents or ingredients and properties can be discerned, and in many cases controlled or optimized. The properties may include sensory (flavor, texture, turbidity, perceived color, etc.) or physical (firmness, light scattering, foam, etc.) properties or cost.

Structure/Function Relationships

Improving understanding of relationships between the structure of molecules (i.e., amino acid composition of peptides) and their biological (flavor) or physical behavior (foam, haze) can lead to improved ingredients and products.

Pattern Recognition procedures are useful for discerning which of a number of measurements can discriminate between classes of samples on a desired basis; the results can then be used to classify new samples. Applications include the identification of samples as to cultivar or growing area, or detection of adulteration.