Measurement Techniques

A Layman's Guide to the Origins, Concepts and Uses of Density, Refractive Index, Conductivity and pH

M Mohammadi

Unilever

1993

SETTING THE SCENE

In the following pages you will find a **layman's** guide to the measurement techniques and tools used in the Liquids-Processing laboratory. The guide has at least two purposes. First it provides an introductory document to the subject that will enrich your experience and make these cold tools more fascinating and fun to work with: in this it serves as a **Teach-In**. Second, it helps in the induction and training of newcomers to the section as it also includes many unique uses which have evolved from our (heavy duty) Liquids programme (a list of which is given in the Appendix). In this it serves to show that fundamental research can be done by these simple, nearly extinct techniques.

Let me explain my approach. Each of the four modules begins with a **History**. I believe that when the history of a subject unfolds before us we grow fond of it and come to terms with it. Much is to be learned from this history. We discern, for example, the making of the West as an economic power from the mid-1700s (what historians call the **Western Miracle**) mainly because of the faster growth of its science and technology and its capacity to translate scientific knowledge into economic productivity. The idea of repeating that miracle, though in a much smaller scale, crosses the mind of every incurable optimist in these difficult times!

With history comes **people**. This Teach-in teems with people and their ideas. One finds the brief description of their careers inspirational. After history comes the **Concept**, where things are defined, and then **How Measured** gives some insight into the physics behind the instrument. The **Uses**, where applications are listed, precedes the **Process/on-line** versions of the tool and then how to **Care** for the instruments and experiments.
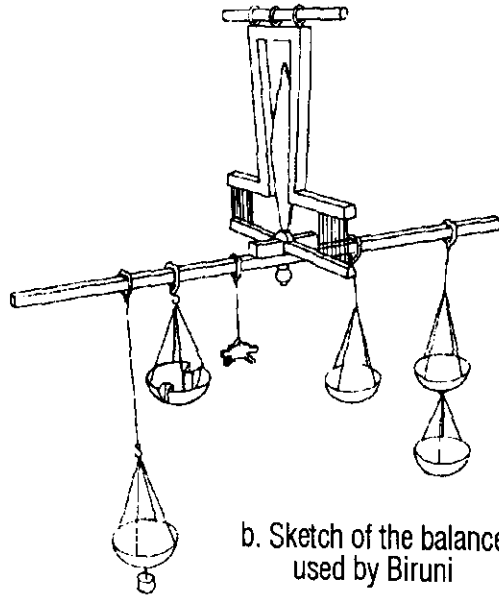
Each module ends with a **Quiz**. These I have designed for fun and one learns a great deal more by doing them. A Chinese proverb goes: "I hear, I forget. I see, I remember. I do, I understand."

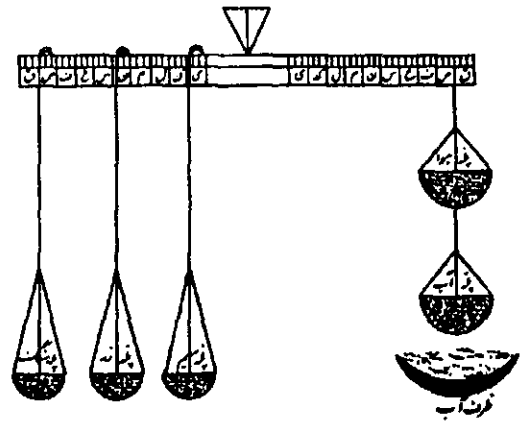I think this **Teach-In** provides the motivation and stimulus for us to explore new frontiers of application.
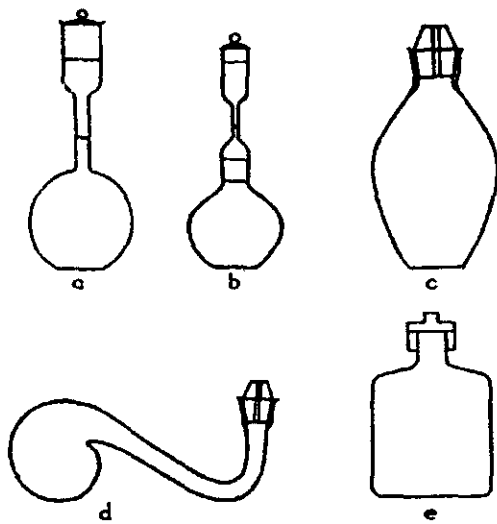
DENSITY
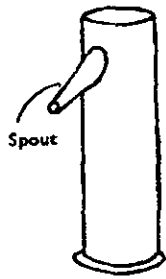
a: Eureka can

b. Sketch of the balance used by Biruni

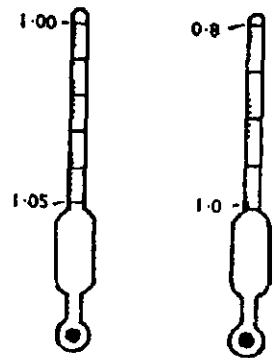c. The balance of al-Khazini

d. Specific Gravity Bottles

a b c d e

e. Hydrometers

Cream
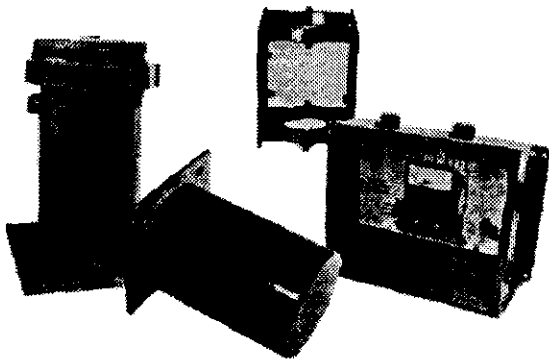
Milk

Skimmed milk
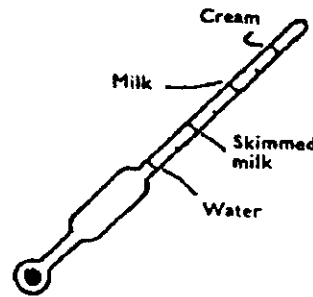
Water

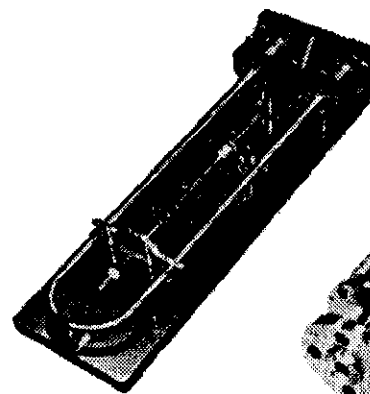For testing milk

1·00
1·05
For liquids denser than water

0·8
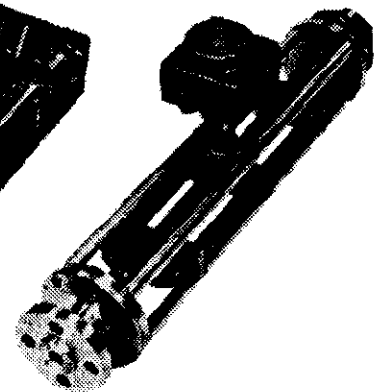1·0
For liquids less dense than water

Process Density Meters

f. Model 3600 density analyser

g. Series FD800 density meter

h. Gravitrol density meter

CHAPTER 1 - DENSITY

1.1 *History*

Our first record of density dates back to **Archimedes** (287-212 BC). **Plutarch**, the historian, in his book **Marcellus** gave an account of Archimedes' inventions (e.g. the **compound pulley**, by which he moved a ship and its crew single-handed, and his **water snail** designed for irrigation in Egypt which is still in use). Archimedes wrote many books including,

- **"On Floating Bodies"** (where he defined density),
- **"Elements of Mechanics"**,
- **"Optics and Catoptrics"**,
- **"On the Spheres and Cylinders"** (where he gave us $4\,\pi r^2$ and $4/3\,\pi r^3$ for the surface and volume of a sphere respectively),
- **"On the Measurement of Circle"** (where he worked out the value of π, $3\,10/71 < \pi < 3\,1/7$ accurate to two decimal places, decimal places were non-existent then which explains the use of fractions),
- **"Sandreckoner"** (where he described a system to express large numbers, and calculated the number of sand particles to fill the universe 10^{63}).

The story goes that Hieron II, the king of Syracuse, did not trust his goldsmith and asked Archimedes to determine the purity of his new crown - alloying silver and gold must have been rife at the time. Archimedes realised that by measuring the **density** (weight divided by volume) of the crown he could crack the problem because he already knew the densities of pure gold and silver.

The problem was to measure, without melting, the **volume** of the crown which had an odd and irregular shape. He hit upon the idea one day while taking a bath and uttered the famous cry; **"Eureka"**. The volume of the displaced water when the crown was completely submerged gave him the volume of the crown. This novel method of measuring the volume of irregular shapes by the **Eureka can**, Fig. a, has been in use throughout the ages ever since.

Muslims over a millennium later preserved the Greek heritage by translating it into Arabic. They improved upon Archimedes' work by devoting a great deal of effort to the development of the **balance**, a scientific instrument for density measurement. **Mohammad Biruni** (973-1050), (Persian chemist, astrologist, geologist, mathematician, mineralogist, physicist, and inventor, to whom science and technology is indebted for bringing **zero** from **India**) designed ingenious balances for density measurement (one of his is sketches shown in Fig. b). In one of his books (he wrote 146 volumes), **"Kitab al-jawahir"** (The book of Elements), he gave accurate densities, even by today's standards, for eight metals, fifteen minerals, six liquids and ice and water at different temperatures.

Omar **Khayyam** and others wrote treatises on the subject but the most renowned works were **"Kitab Mizan Al-hikmah"** (The Book of the Balance of Wisdom) and **Risala Fil-alat** (Treatise on Instruments) by **Mansur al-Khazini** (1070-1130), originally a slave boy of Byzantine origin, a Persian astronomer, mathematician and inventor of waterlocks who knew of the change in the viscosity of liquids with temperature. He perfected the balance, and gave formulae for the percentage of gold in alloys from their densities, Fig. c shows one of his balances.

The Latin West received its knowledge of Archimedes from these Arabic translations in the 12th century.

1.2 *What is Density?*

The density (**d**) of a substance is its mass or weight (**W**) divided by its volume (**V**),

$$d = \frac{W}{V}$$

it therefore has a **unit** of g/cm^3 or kg/m^3. Density depends on temperature because of the temperature dependency of volume. Here are some densities you (or captain Scott!) may have encountered.

	Density g/cm^3	Temperature °C
water	0.9982	10
water (H_2O)	0.9999 (max. density at 3.98°C)	4
heavy water (D_2O)	1.1059	"
milk		
full fat	1.029	25
semi-skimmed	1.030	"
skimmed	1.033	"
coffee		
white with	1.022	25
white without	1.006	"
black without	1.001	"
Earth	5.515	"
Sun	1.41	?
Neutron star	200000000000000.	?
Intergalactic gas	0.000000000000000000000000000000002	?

1.3 *Specific gravity scales*

Arising from a lack of communication between various scientific and industrial communities a number of different **specific gravity** or relative density scales (density at a specific temperature compared to the density of water at the same temperature) were invented in the early days. These included:

- **API** or **A**merican **P**etroleum **I**nstitute scale, as a standard for petroleum products in US,
- **Balling** scale [after **Karl Balling** 1868, a German chemist] in the brewing industry to estimate percent wort but also used to indicate weight percent of dissolved solids and sugar liquors,
- **Brix** scale [after **Adolf Brix** 1870, a German chemist and inventor] used exclusively by the sugar industry representing weight percent of sucrose,
- **Baume'** scale [after **Antoiny Baume'** 1804, a French chemist] for acids, light and heavy liquids,
- **Quevenne** scale [after **Theodore Quevenne**, 19th century French pharmacist] for milk testing which represents an abbreviation of specific gravity (20°C Quevenne equals d = 1.020),
- **Richter, Sikes,** and **Tralles** [after **Johann Tralles** 1822, a German physicist] an alcoholometer scales indicating the percent of alcohol by weight (or by volume),
- **Twaddle** scale [after **William Twaddell** 1840, a Scottish inventor] came about to simplify the measurement of industrial liquids heavier than water.

Two scales relevant to us in industry are **Twaddle**, for our raw materials (e.g. potassium hydroxide), and **Brix** on our refractometers,

Brix = % weight pure sucrose dissolved in water at 60 F (17.5°C)

Specific gravity = (Degree Twaddle) x 0.005 + 1.000

Surprisingly the Brix on refractometers corresponds to the percentage dissolved of most salts and even dispersed rinse conditioners.

1.4 *How is density measured?*

Due to the great importance of density as a physical parameter, many techniques have evolved for its measurement (including an unusual microscopic one where the **striation** of one liquid flowing through another gives density). However the traditional density measurement techniques for liquids were based on:

- the weighing principle or **pycnometry** [pycno = dense] by the density bottle, Fig. d.
- the buoyancy principle or **hydrometry** [hydro = water] by using a graduated glass bottle that floats upright in a liquid and the sinking depth gives the density, Fig. e. It is called hydrometry because it was first used to measure the quality of water. Hydrometers were

described as early as the third century AD. **Robert Boyle**, the epoch-making chemist used hydrometers frequently for measuring the density of gold and its alloys. **Lavoisier** designed accurate hydrometers for analyzing the content of **spa waters** in France. In the **pH** module we will learn more about Boyle and Lavoisier.

More recent methods include:

- the **vibration** principle where the vibration damping of a "U" **tube** enables automatic density measurements to be made. The front cover and Fig. g depict two versions of such a density meter. We used the Paar U-tube meter to obtain the densities of milk and coffee in the table above.

1.5 *Process density meters*

Due to the technological importance of density a vast number of **in-line** or process density meters exist in the market. These work on the above and other principles (such as **radiation adsorption** or **gamma-ray** in Fig. f), Figs. f-h. Only the radiation adsorption types are non-contacting and can thus be mounted outside the process line.

1.6 *Uses of density*

The following list summarises but a few of the more common uses of density;

- **purity** as in Archimedes' crown case, or in mining where one assumes additivity of volumes in order to find the content of one component. For a two-component mixture we have,
  V (total) = V_1 + V_2 (see **QUIZ** No. 1).
- **concentration** measurement as the Twaddle of our liquid raw materials (for instance potassium hydroxide and citric acid), or Brix in **sugar industries** and **soft drinks**, or **alcohol** in **beverages** (**Q.** 5,15),
- **volume change** on mixing due to chemical reactions. For example in mixing water and alcohol or neutralising LAS acid with alkalines volume contraction takes place which results in a mixture which is denser than expected,
- **phase volume** or volume occupied by different components of a mixture.
  For example 15% by weight zeolite in Marilyn occupies only 10% of space because of its relatively high density (**QUIZ** question No. 14),
- density is also a **parameter** in many scientific **formulae** (as those you learned in the **scale-up** teach-in). For example density enters into the formula that gives the rate of creaming of fat particles in milk or settling of solids in water. The sign of the density difference determines if particles go up or down when you centrifuge a sample, or if you can pump a number of grades of oil in the same pipeline for hundreds of miles without getting them mixed !
- **bulk density**, density of a powder measured by a **density cup** tells us about the lightness or the "fluffiness" of the powder, its flow properties, its dustiness, and the ease of its incorporation into liquids,

- **bulk density** also tells us about the structure of powders i.e. whether the particles are bound together (forming compact or loose units) or are free to flow. Recently we developed this technique for the "taming" and characterisation of zeolites for heavy duty liquids,

- **bulk density** is also a critical parameter in the manufacturing of **ceramics**,

- **density** and **refractive index** often correlate and this fact has found many uses as discussed in the next module (QUIZ Question No. 11). **Newton** for example, investigated this aspect using the formula:

$$\frac{(RI^2 - 1)}{d} = Constant$$

- accurate **density** can be obtained from the measurement of **refractive index** using the above expression for simple liquids.

1.7 Care

Accurate measurement of density becomes very important in some applications (in combination with refractive index for phase-volume determination and particle sizing). The greatest pitfall and source of error in its measurement is the presence of **bubbles** and **air pockets**. Deaeration for some materials is almost impossible when the U-tube or density bottle is used (thick gels and rinse conditioners, soft solids like cationic raw materials). Deaeration by centrifugation (using the centrifuge tube as a density bottle) offers a simple solution with an accuracy penalty (stemming from the inaccuracy of reading the volume off a tube). New measurement techniques **(Helium Pycnometry** where the helium gas penetrates voids) offer a greater scope in these cases.
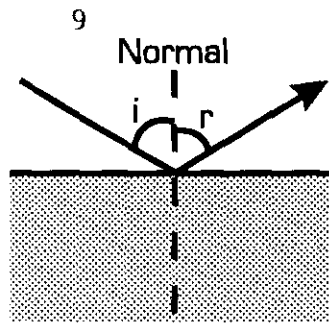
Care should be exercised in using the U-tube meters for fast-settling **slurries** (dispersions of solids in liquids) and melts which solidify fast, as incorrect readings result (probably caused by the non-uniformity in density). The U-tube meters are practically maintenance-free and need no **calibration**. It is important to quote the temperature at which the density is measured. Density meters do not usually correct for temperature.
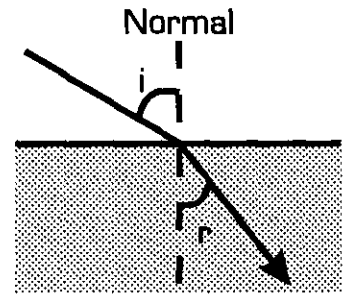
1.8 Quiz No. 1

1. Which one is heavier, a pound of feathers or a pound of iron?
2. How did Archimedes work out the purity of the crown? What was his assumption? If d (gold) = 19.3 and d (silver) = 10.5 and the crown weighed 1 kg and displaced 100 g water what happened to the goldsmith?
3. What is the densest metal on Earth?
4. Balsa wood is the lightest wood; it is used for supertankers and sound-damping in high-speed trains (d = 0.060 g/cm^3). A solid has been invented that is lighter (SEAGEL) than balsa (d = 0.040). How is it done and can a solid float in air?

5. Work out the concentration of sugar in the coffee-with from its density if d (sugar) = 1.588 g/cm^3?

6. Is there a density limit below which powders become difficult to disperse into liquids?

7. Which product is more prone to creaming, a HDL or a RC?

8. Which is denser, a saturated or an unsaturated fatty acid?

9. What is the density difference between once-distilled and many-times-distilled demin. water? Why is heavy water denser than normal water?

10. Use the density of water at 4°C to calculate the density of heavy water (D$_2$O). Compare your value with the experimental one in the table above.

11. If the density of a liquid at 20°C = 0.952 g/cm^3 and its RI = 1.3465 what is its density at -20°C if its RI = 1.3501?

12. Is sloping water possible by having higher density in one side (of a lake or canal) by suspending magnetic particles in the denser water for example (would be useful for water-skiing and lockless canals)?

13. What is the densest planet in the solar system?

14. Work out the volume fractions (phase volumes) of gold and silver in the Archimedes' crown.

15. From the densities of milk samples in the table above work out the fat content of whole milk if d (fat) = 0.93 g/cm^3 at 25°C.

16. What is the density of blood? What is the density of blood plasma? If the volume fraction of plasma is 0.55, what is the average density of the particulate materials of blood (platelets, red and white blood cells etc)?
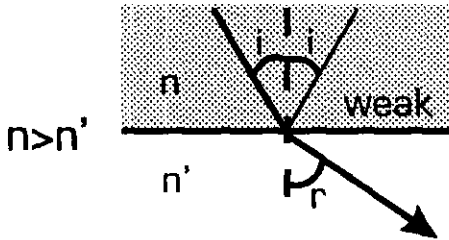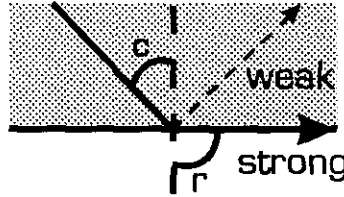
Refractive Index

Normal
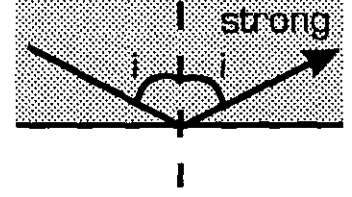
i r

a) Reflection

Normal

i

r

b) Refraction

n > n'

n

i i

weak

n'

r

c) Refraction

c

weak

r

strong

d) The Critical Case

strong

i i

e) Total Internal Reflection

θ

f. Internal Reflection

Sample

B*

Lens

A*

Photo-Diodes

A

A'

B

Light

Light Source

Prism
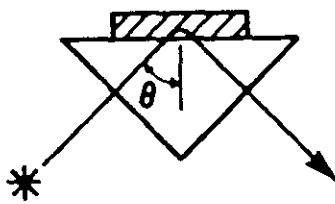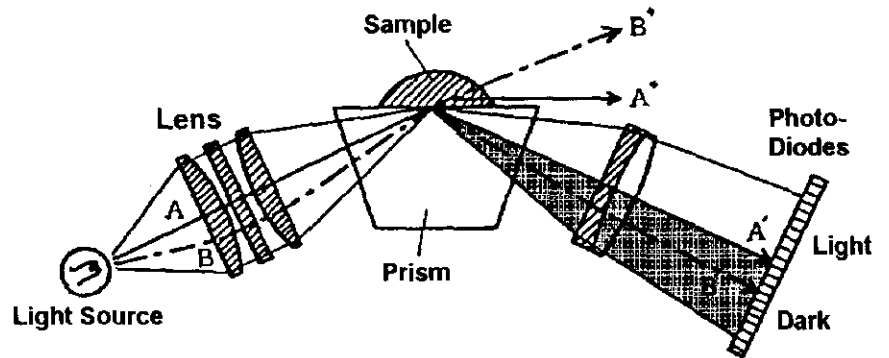
Dark

g. Automatic sensing of dark-light line
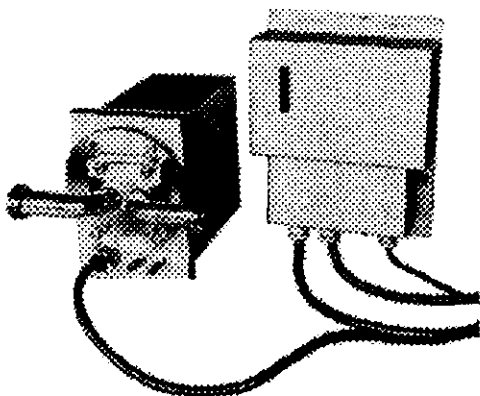
Measuring Head
& Alarm Unit

Control Unit PRM100

h.

Drive motor

Light source

Collimating lens

Helical scanner

Direction of beam travel

Focusing lens

Light Dark

Solar cell

Sapphire prism

Thermistor probe

Process liquid

Refracted angle
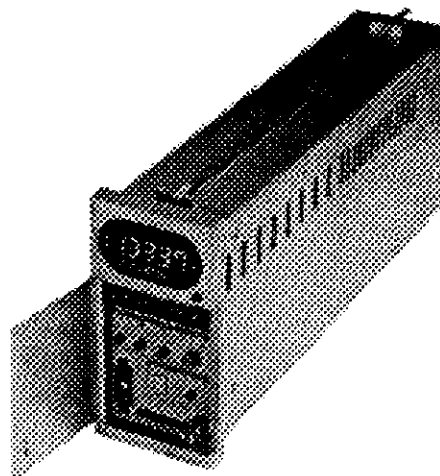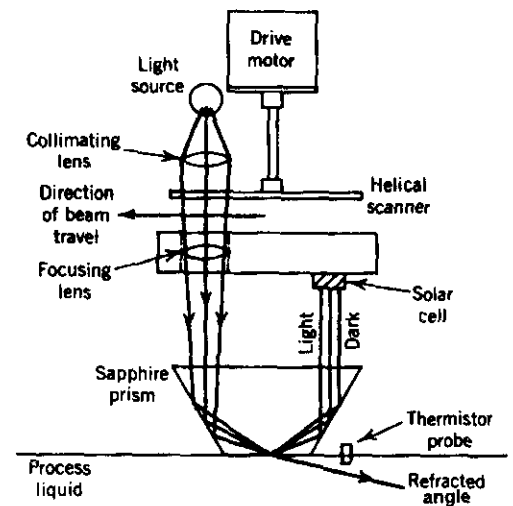
i. Model SSR-72 Process Refractometer

Process Refractometers

CHAPTER 2 - REFRACTIVE INDEX

2.1 *History*

The scientific study of **light** dates back at least to **Euclid** who wrote his "**Elements**" in 300 BC on **plane** and **solid geometry** and gave us **Euclidean geometry**. This book contains an amazing 467 theorems, all deduced from a few axioms such as 'the whole is greater than any part', or, 'if equal parts be added to equals the sums are equal' (got it?).

Through Euclidean geometry man obtained his first grip of the subject of light. From the simple observation that light travels in a straight line (ie the **shortest path**) he discovered the famous **law of reflection** (known in those days as **Catoptrics**). That is, the reflected light from a surface takes a direction that the angle of incidence, i, equals the angle of reflection, r, see Fig. a. He could not show this by experiment for lack of precision instruments but he, nevertheless, had the foresight and courage of conviction to formulate his law. We see that the representation of a ray of light by a straight line created the science of **optics**. Euclid was the first one to observe that a ray of light **bends** when it passes from one medium (less dense) to another (denser one), Fig. b. The bending of light is called **refraction** and explains why a straw or a spoon in a glass of water looks broken or why ponds or swimming pools appear shallower than they are (careful when you jump in!).

The problem of refraction posed a real challenge to **Ptolemy** (100-170 AD), the Alexandrian mathematician and astronomer born in Ptolemias in upper Egypt. In order to explain the bending of light from stars near the earth's atmosphere, he devised ingenious optical tools and made extensive measurements of **i** and **r**. He found them to be related (at small angles i/r was a constant) but the exact relationship eluded him. The **law** of **refraction** in which **refractive index** appears defied discovery for a few more centuries.

Ptolemy's renowned book, the "**Almagest**" (the great compilation), was translated into Arabic around AD 800 as a source book on optics and astronomy. **Ibn al-Hytham** (965-1040 AD), the great Egyptian scientist, known in the west as **Alhazem** and the **father of optics** (he studied the eye, vision, spherical mirrors, and the thickness of the atmosphere and he invented water clocks), followed up Ptolemy's work on refraction in his "**Kitab al-Manazir**" (the book of Optics) but he too failed to discover the law. In the process he developed the 'rectangle of velocities' technique which was used by **Newton** and **Snel** in the solution of this problem. The lack of an appropriate mathematical tool was the reason for the failures.

The background work by **Indian** scientists paved the way for the invention of **trigonometry** (**sine** and **cosine**) by Muslims. **Al Buzjani** in 9th century in his famous book "**Almagest**", named after Ptolemy's book, formulated **sine, cosine, tangent** and **cotangent** (**secant** was his invention also and not **Copernicus** as is usually believed) . Buzjani completed trigonometry

as a new independent science but it was again **Biruni** (mentioned earlier for his work on density) who wrote the most masterly work on the subject and popularised it. The trigonometry ideas were incorporated into Ptolemy's optical and astronomical theories by **Al-Battani**, (858-929), one of the greatest astronomers and the founder of modern astronomy whose book, **Kitab al Zij**, (Opus Astronomicum) greatly influenced the west (Copernicus, Kepler, Galileo and Delambre mention him fairly often in their works).

Ptolemy's Almagest (like the work of most Greek masters) became known in western Europe through a Latin translation of the Arabic copy by Gerard of Cremona in 1175.

In 1621 **Willebrord Snel** (1580-1626), Dutch astronomer, mathematician, physicist and translator, studied law but ended up as a professor of mathematics (he worked out π to 35 decimal places) at Leiden University, and it was he who discovered the law of refraction. It emerged after years of observation and experimentation on the shallow pond problem. The manuscript of his work was lost but commented on by **Huggens**.

2.2 *What is Refractive Index?*

Snel found that it was not the ratio of the angles of **incidence i** and **reflection r** but the ratio of their sines that was a **constant.** That is,

$$\frac{sine\ i}{sine\ r} = n \qquad \text{Snell's Law or the Law of Refraction}$$

This constant **n** was called the **index of refraction,** or **RI**. Being the ratio of two numbers **RI** has no units. The equation shows that the greater the **RI** (the **denser** the second medium) the greater the bending of light towards the normal (the greater is **r**). Because **RI** depends on density it also depends on temperature. **RI** also depends on the **wavelength** (λ) of light. That is why in the rainbow red light bends more than violet. The standard λ in our lab. equipment is the **sodium yellow light,** $\lambda = 0.5893$ μm. The table below gives the **RI** values of a few familiar materials.

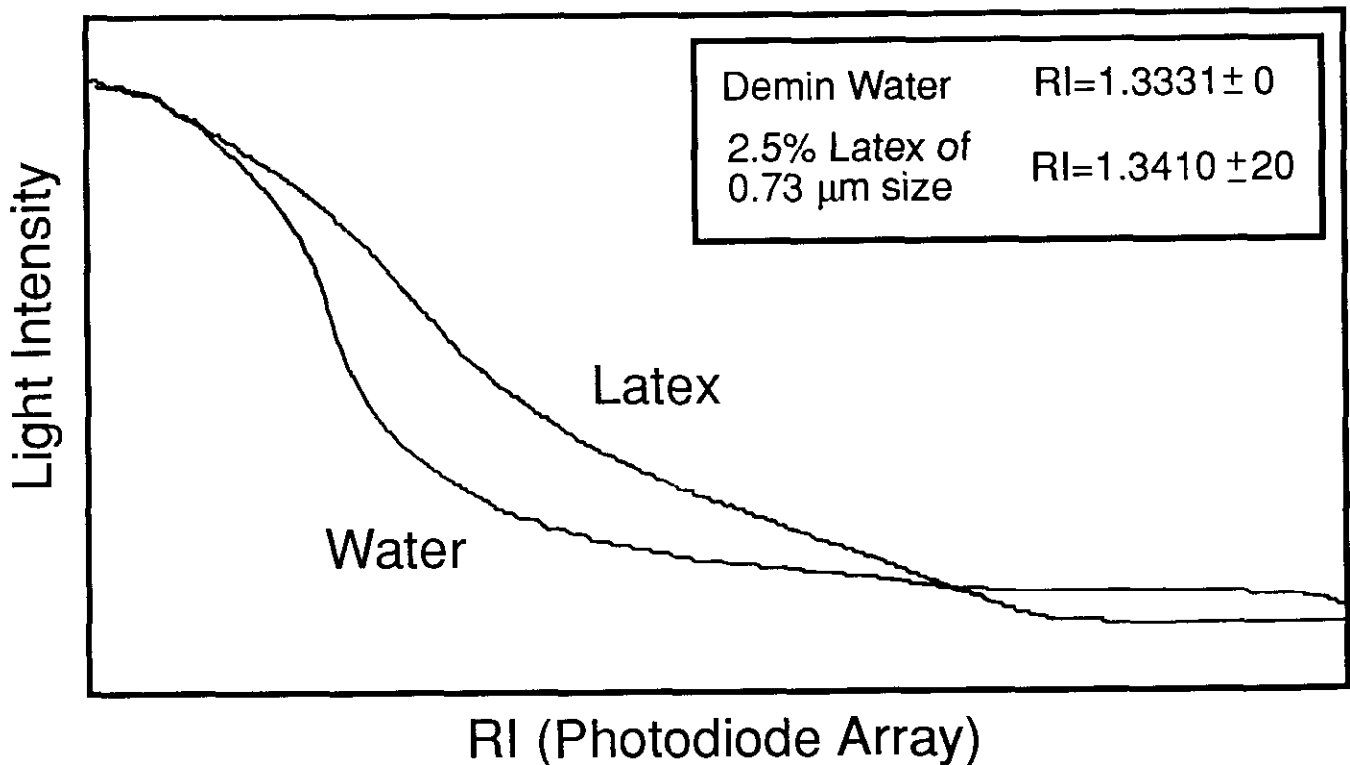|	RI (BRIX) $\pm$ SD at 20°C, λ = 0.5893 μm
Air	1.0003
water	1.3333 (0.0%)
coffee	
white-with	1.3431 (6.9%)
white-without	1.3369 (2.8%)
black-without	1.3346 (1.1%
milk	
full-fat	1.3482 $\pm$ 0.0002 (10.3%)
full-fat homogenised	1.3530 $\pm$ 0.0005 (13.4%)
semi-skimmed	1.3500 $\pm$ 0 (11.4%)
skimmed	1.3482 $\pm$ 0 (10.3%)
glycerol	1.4729
glass	1.5 to 1.9
diamond	2.434
rinse conditioner (5%)	
good process	1.3429 $\pm$ 0 (6.1%)
bad process	1.3407 $\pm$ 0 (5.3%)
Marilyn	
stable	1.4330 $\pm$ 0.0002
unstable	1.4251 $\pm$ 0.0008

The **Brix** concentration scale indicates the significance of the decimal places in **RI**. From the **RI** values the fat content of the milk or the sugar content of the coffee can be estimated (Q. 9 and 18).

2.3   *How is RI measured?*

An instrument which measures **RI** is called a **refractometer** because it measures the extent of refraction. For liquids, almost all models available nowadays work on the basis of the **critical angle principle** (see Figs. c-e) where a light source illuminates a prism on the surface of which the liquid sample is spread. At the critical angle we have a **total internal reflection** of the light rays where the surface behaves as a perfect mirror, see Fig. e. A similar situation occurs when one looks for example into a glass of water from above. At a certain angle the glass wall becomes a mirror.   However one can see ones fingers through this mirrored surface by nearly touching the glass. This indicates that the light in fact escapes outside the glass and then changes its "mind" and returns to create the mirror effect, Fig. f (quite magical!).

Periscopes, binoculars (using two prisms to work as mirrors), and refractometers (for RI measurement) exploit this principle. The reflected light under total internal reflection creates a **dark-light** region, see Fig. g. The exact location of the **demarcation** line between the dark and light regions corresponds to an angle which gives the RI of the liquid if the RI of the prism is known. The location of the demarcation line can be found visually as in the **Abbe** refractometer or electronically as in our Lab. RX1000 machine which contains 5000 photo-diodes arranged on a line for this purpose, shown in Fig. g.

Note that the concept of refractive index belongs to clear liquids rather than milky ones (those with suspended particles, like milk, creams, and emulsions). For milky liquids the demarcation "line" is not a line but a **fuzzy band**. The accurate identification of the dark-light border under such conditions becomes extremely difficult. The new automatic refractometers seem to be far superior at this than the naked eye. Still in these situations repeat RI readings of the same sample could be widely different necessitating an averaging procedure. In extreme cases on **OUT OF RANGE** or **UNABLE TO READ** message indicates the machine's frustration with the fuzziness or lack of a sharp demarcation line. This situation sets the limit to the accuracy of measured RI though the machine has a precision of $\pm$ 0.0001, but the milkiness of the sample may not allow anything better than $\pm$ 0.005. The profiles below, from our **Differentiating Refractometer** developed in collaboration with UMIST, illustrate how the light intensity across the photo diode array spreads out and loses its sharp demarcation in going from water to a 2.5% polystyrene latex of 0.73 μm in size.

| Demin Water | RI=1.3331 $\pm$ 0 |
| 2.5% Latex of 0.73 μm size | RI=1.3410 $\pm$ 20 |

Latex

Water

Light Intensity

RI (Photodiode Array)

2.4 Process refractometers

Numerous **in-line** refractometers exist in the market, covering the RI range of 1.32 - 1.7, see Figs. h and i. The first process refractometers appeared in 1952, though as bench analytical tools they were the oldest in use in many industries including;

- **food** (for sugar concentration of jam, sauce, fruit juice, beverage, chocolate, and marzipan),
- **paper/pulp,**
- **petroleum** (gasoline octane rating, phenol manufacture, aromatics and production), and,
- **chemical** (monitoring phosphoric acid, sulphuric acid, brine, glycerine, glycol, edible oils, and caustic soda production).

2.5 Uses

Refractive index is one of the most fundamental property of matter. Our imagination sets the limits to its applications. The following presents but a limited list of its uses for;

- **purity** of liquids, as every compound has its own unique RI (raw material discrimination, for example),
- **concentration** of mixtures (of liquids or a liquid and a soluble solid) from the fact that **RI** (mixture) = **RI₁** ϕ_1 + **RI₂** ϕ_2, ie volume additivity rule where ϕ is the volume fraction or phase volume.
- **chemical structure** of compounds from the **molar refraction (R_m)** equation,

$$R_m = \frac{(RI^2 - 1)}{(RI^2 + 2)} \frac{M}{d}$$

where **M** stands for molecular weight and **d** for density.

No where has the technique been so profusely used as in **Unilever** (URPSL and URVL) for;

- **water** content of active phases,
- **fat** content of potato chips,
- **chemical** interactions,
- **hydrogenation** of oil (**iodine value**),
- **lipids** of the surface of skin,
- **perfume** toleration of formulations,
- **discrimination** of raw materials,
- **density** of aerated clear liquids and also density at different temperatures,
- **solubility** of salts in HDLs
- **creaming** of emulsions,
- **flocculation** of droplets or particles,
- **mixing** efficiency,
- **phase volume** measurement when conductivity does not work as in some RCs,
- **particle sizing** in HDLs.

Refractive index lends itself to **particle sizing**. A brief description of this application is in order here. This novel use of RI has been overlooked in the science of refractometry elsewhere mainly due to the lack of hardware and the meaning of RI for milky liquids. The graph below goes some way in clarifying the concept.
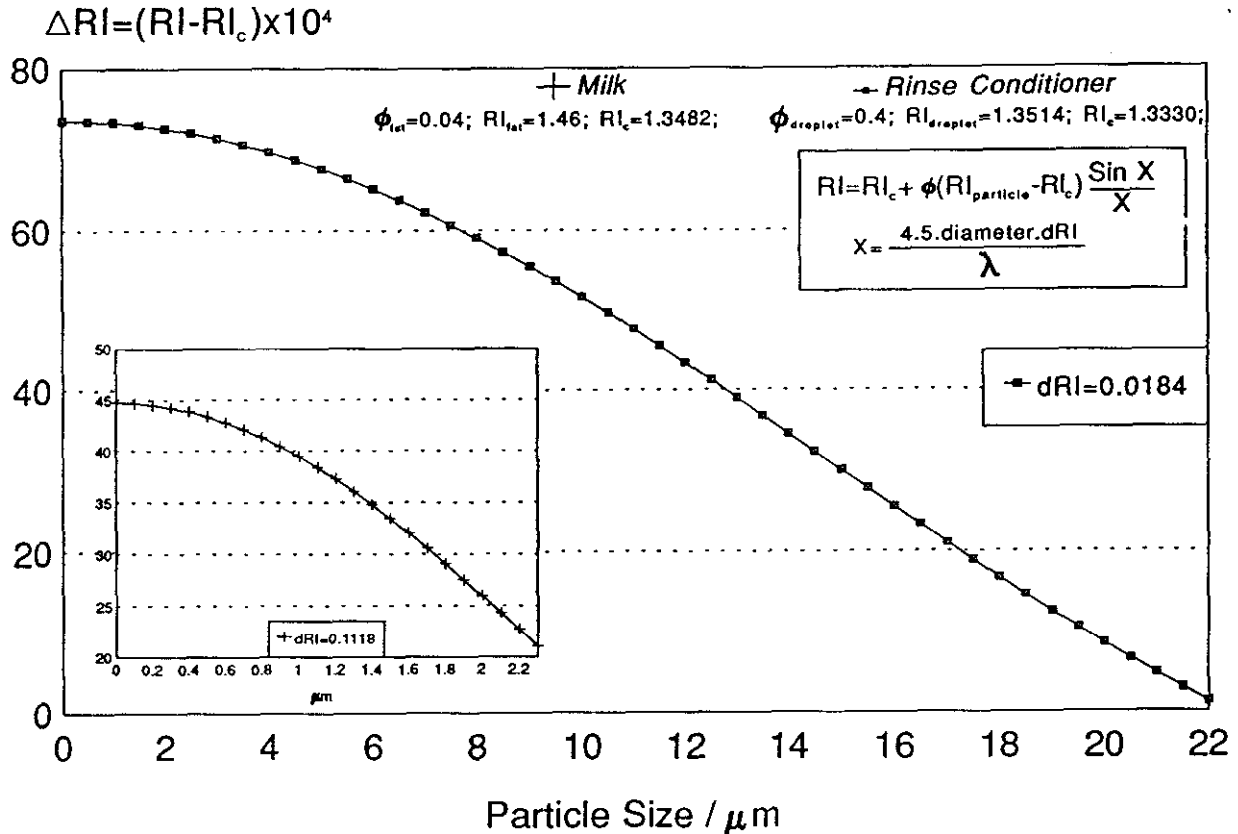
We see that particles (solids, fat globules, or droplets) beyond a certain size do not contribute to the **RI** of the sample, that is the particle size at which $\Delta R = 0$ (about 22 μm for the rinse conditioner and 3.5 μm for fat). The particle size threshold at which this happens depends on how close the **RI** of the particle is to that of the surrounding liquid, ie the **RI matching** factor or **dRI** in the graph. Clearly this idea is a new lease of life for RI in areas where particle size changes occur (in **homogenisation** or **milling** operations, or **flocculation**, namely, particle enlargement). When **dRI** is large extensive light scattering occurs resulting in **OUT OF RANGE** responses as explained before. New refractometers with improved optics cope with out of range cases very well (Bellingham and Stanley RFM340 refractometer, for example).

2.6 Care

Refractometers are extremely robust and abuse-friendly except for the prism surface (made of sapphire). This surface must retain its polish. Surface scratching causes light scattering which ruins the sharpness of the demarcation line and hence the accuracy. The surface should not be touched with metallic or glass rods and should be cleaned with soft tissues (kitchen towel has been recommended instead of Kleenex as even that seems to scratch the sapphire; sapphire means the scratching stone, its Moh's hardness is one unit less than that of diamond!).

Once calibrated initially, refractometers need no further **calibration**. In this regard they are very convenient. Similar to density, temperature control is important for RI measurement. The standard temperature for RI is 20°C. The RX1000 instrument also gives a **temperature-corrected** reading (to 20°C, based on sugar solution so inapplicable to HDLs except probably for the water-electrolyte satge before active addition).

2.7 Quiz No. 2

1. Which appears shallower, a pond filled with sea water or one filled with rain water?
2. Where is a magnifying glass more powerful, under water or in the air?
3. Whose blood has a higher RI, a vegetarian or an omnivorous person? Which is healthier, the high RI or the low RI?
4. Which do you expect to have a higher RI, methyl alcohol (CH_3OH) or water (H_2O)?
5. Why do you think diamond has the highest RI in the Table (Germanium has the highest RI of 4.00) ?
6. What is the highest RI liquid?
7. Write the volume additivity equation of RI for the whole milk using the densities from Chapter 1 to work out the phase volumes of fat and the skimmed milk (as its continuous phase), assume that d (fat) = 0.93 g/cm^3.
8. Compare the density and RI of the milk samples, how do you explain the results? Does the proportionality of density and RI hold for these samples and why?
9. What is the fat content of the whole and semi-skimmed milk samples? Work these out from density values and compare them with those from RI.
10. Which creams faster, a whole milk sample of high RI or one of low RI?
11. Which has the highest RI, a batch-processed RC with post-shear or without post-shear (homogenisation) and why?
12. Do you see any upper or lower limit for RI?
13. Are negative RI values possible? Why?
14. How do you explain the standard deviations in the RI reading of the full fat milk samples compared to that for skimmed, or the two RC samples?
15. Which one shows a higher RI, a saturated fatty acid or an unsaturated one? How do you suggest RI can indicate the iodine value of oils?

16. What is the critical angle for a ray of light in water, assuming that RI = 1.3330 for water.

17. For a dispersion of particles with RI (particle) = 1.4500 in water at what size particles cease to contribute to RI of the dispersion?

18. What is the sugar content of the coffee-with in the table? Compare this with that obtained from density calculations from Chapter 1.

19. Work out the RI of the particulate matter of blood from the RI values of Plasma and blood if ϕ (plasma) = 0.55.

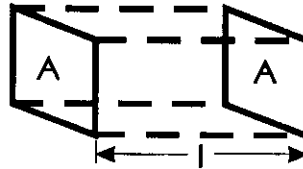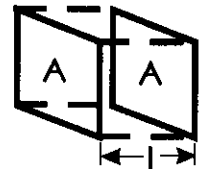# Electrical Conductivity
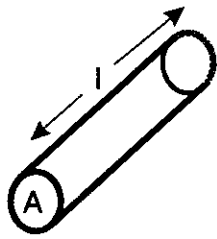
a. wire resistance $\alpha \frac{l}{A}$
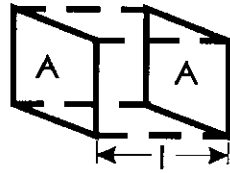
$A = 1\ cm^2$
$l = 1\ cm$
$C = k$
$\theta = 1.0\ cm^{-1}$

$A = 1\ cm^2$
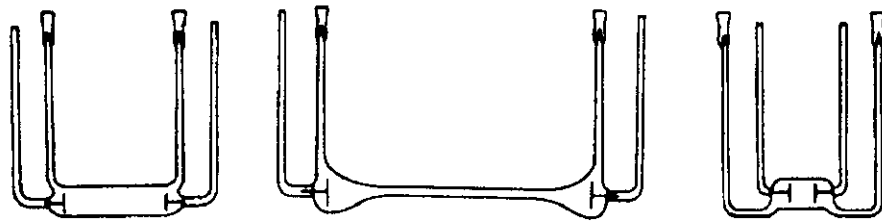$l = 10\ cm$
$C = 0.1\ k$
$\theta = 10\ cm^{-1}$
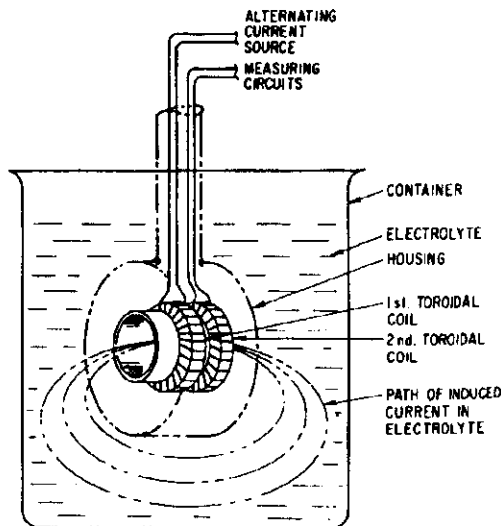
$A = 1\ cm^2$
$l = 0.1\ cm$
$C = 10\ k$
$\theta = 0.1\ cm^{-1}$

b. Cells with different cell constants (θ)

c. Precision Conductivity Cells for medium, high & low (specific) conductivities

ALTERNATING CURRENT SOURCE
MEASURING CIRCUITS

CONTAINER
ELECTROLYTE
HOUSING
Ist TOROIDAL COIL
2nd. TOROIDAL COIL
PATH OF INDUCED CURRENT IN ELECTROLYTE

d. Inductive electrolyte conductivity measuring circuit
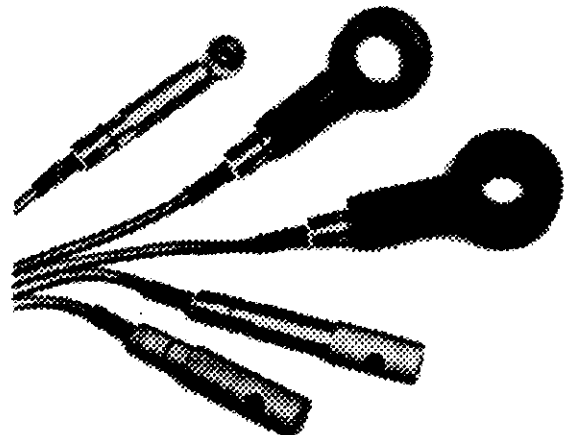
e. Foxboro electrodeless conductivity sensors

Process Conductivity Probes

f. Beckman electrodeless conductivity cells

g. Beckamn electrode type conductivity cells

CHAPTER 3 - CONDUCTIVITY

3.1 History

The science of **electricity** and **electrical conductance** began in 1658 with
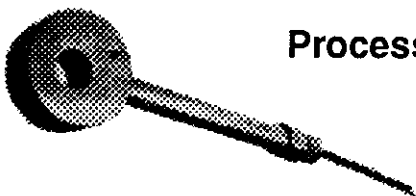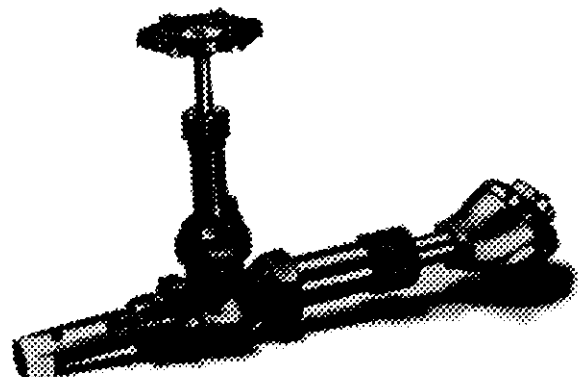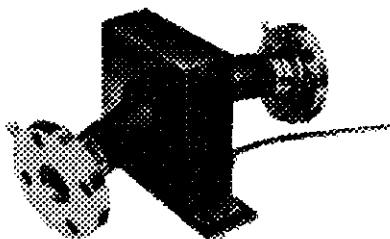**Jan Swammerdan** (1637-1680). A Dutch naturalist and the most accurate microscopist known to science, he was the first to observe and describe the red blood cell. He also created a system of classification for insects (in his book **A General History of Insects**, dubbed the **Bible of Nature**). He showed a **frog's muscle** contracted when the nerve leading to it was joined to a **silver wire** and the circuit was completed with a **copper wire**.

His publication of this effect in 1739 went unnoticed. In 1760 **Sulzer**, sandwiching his tongue between a lead and a silver plate, noticed a peculiar taste when **metals** came into contact. However it was the work of **Luigi Galvani** (1737-1798), Italian physician and physicist who studied the nature and effect of **electricity** in **animal tissue**, which provided publicity and momentum for the subject. He believed in **animal electricity** and tried to prove the existence of the "**animal electric fluid**". This idea was rejected by the "**metallic electricity**" advocate the Italian physicist **Allessandro Volta** (1745-1827).

This animal-metallic electricity conflict provided a major stimulus for Volta who finally invented the first source of continuous current, the **Voltaic battery**. Volta gave a demonstration of his battery before **Napoleon** who made him a Count and Senator in the kingdom of Lombardy (science paid!). The **volt**, a unit of electromotive force that drives current (see later), was named in his honour in 1881. The eponym "galvanize" from Galvani's work was coined by Volta. Thanks to both of them we have cruelty-free torch lights and Walkmans which are not charged with a piece of loin from our butcher.

The best detectors of the new phenomenon of electricity were frog's muscle, tongue or tongue and eye combination. Until in 1820 **Hans Christian Oersted** (1777-1851), the Danish physicist and chemist who prepared metallic **aluminium** in 1825, discovered that an **electric current** produced a **magnetic field**. This led to the construction of the "**magnetic needle**" or the **galvanometer** for detection of electricity. This discovery in turn helped **Gerge Simon Ohm** (1789-1854), German physicist, to discover his famous **Ohm's Law** (see later). His paper on this law was so badly received that Ohm resigned his post at Colonge University as a professor of mathematics.

On these foundations the structure of electricity and **electrochemistry** were erected by **Michael Faraday** (1791-1867), English physicist and chemist, who started as a bookkeeper, but went on to invent the **electric motor**, and **dynamo**. He liquified **chlorine** (1823), isolated **benzene** (1825), and discovered the phenomenon of **electromagnetic induction** (current from a change in magnetic field).

Unlike his contemporaries Faraday was not convinced that electricity was a **material fluid** that flowed through wires like water through pipes. Similar to **wires (metallic conductors** of electricity) some liquids (solutions of acids bases and salts) could conduct electricity. Faraday called these liquids **electrolytic** conductors or **electrolytes.**

Faraday spent eight years on extensive experiments (which cost him his health) to validate his theory. His premise was that the electricity threw the **neutral** dissolved **molecules** (salts, acids, bases) of an electrolyte into a state of **tension** (his **electrotonic** state). Under such tension the neutral molecules were divided into two **oppositely charged** parts. He called these charged parts **ions.** The **negatively** charged fragment called **anion** was of non-metallic nature (like the chloride ion (Cl^-) when table salt or sodium chloride is dissolved) whilst the **positively** charged fragment called **cation** was metallic like sodium ion (Na^+) of table salt.

This explained the electrolysis effect (or electrodeposition) where the passage of electricity or current from a battery caused positive ions to move towards the negative pole and vice versa. There they could be released (electrolysis of water into hydrogen and oxygen gases for example) or deposited (electroplating).

Faraday's **ions** therefore explained why some aqueous liquids could have electrical conductivity. In 1884 **Svante Arrhenius** (1859-1927), the Swedish physicist and chemist defended his Ph.D. thesis on the theory of **electrolytic dissociation** at University of Uppsala. He speculated that electrolytes are in an **ionic state** even when there is no current flowing through them. For example, he believed that acids in water **ionize** into hydrogen ion (H^+) and bases into hydroxyl ion (OH^-) and the more H^+ is there the more acidic the water (see the next module). This was considered outrageous by the pundits and his thesis was awarded a forth class (a bare pass). In 1903 Arrhenius won the **Nobel Prize** for chemistry in recognition of his theory of electrolytic dissociation.

Arrhenius is one of the founders of modern physical chemistry. His other less known works include Cosmic physics on the pressure of light rays (the **panspermic** theory of transport of living spores and seeds through interstellar space). The concept nowadays runs the Russians solar sail project for interplanetary transport. In 1892 he published **"on the influence of carbonic acid in the air upon the temperature of ground"** where he gave a theory for the glacial periods and other climatic changes, based on the ability of carbon dioxide to absorb the infrared radiation emitted from the earth surface. Does it ring a bell? He predicted the **Green House** effect but it fell on deaf ears.

3.2 What is conductivity?

As mentioned above the conduction of electricity in electrolytes occurs as a result of migration of ions (all ions, anions and cations) to the **electrodes** or poles of opposite charge. This ability to pass electric current is called **conductivity**. The higher the current the higher the conductivity. Electrolytes, like metallic conductors, obey **Ohm's** law, **V = RxI**. Namely if two electrodes are immersed in an electrolyte and a _voltage_ (V) applied across them the **current** (I) that flows through it inversely relates to the **resistance** (R) of the electrolyte. The inverse of resistance is called **conductance** (K). To understand the unit of conductivity we recall that the resistance of a wire of cross-section area A and length l, Fig. a, is;

$$R = r\frac{l}{A} \qquad \text{so that its conductance becomes} \qquad K = k\frac{A}{l}$$

where **r** is the specific resistance (**resistivity**) of the wire and depends on the metal of the wire. The unit of resistance is **Ohm** (in honour of Ohm) and **r** in **Ohm-cm** as can be seen from the above equation. Likewise the standard unit of conductance is **1/Ohm** (or **Mho**) and that of specific conductance **k** (**conductivity**) is **Mho/cm**. Mho/cm, in honour of **Ernnst Werner von Siemens** (1816-1892), German inventor and physicist, is now called **Siemens/cm** or **S/cm**.

It is worth mentioning here that Siemens founded the Siemens Brothers company in London (1847) which manufactured and laid cables and designed the "**Faraday**"; the first cable laying ship that laid the Atlantic cable in 10 years. Even more dramatic was the construction of the **Indo-European telegraph** line by his company linking London to Calcutta in 1870. Siemens was a business man who believed 'a **nation would never gain and maintain international status if it did not excel in research and based its science and technology upon it**'.

Let us return to the more immediate problem of **k** measurement. It is independent of A and l (the **cell** size between electrodes) and is a characteristic of the solution only. Note that l/A (in cm^{-1}) is called the **cell constant**. By placing the electrodes at different distances from each other the size of the cell can be varied, Fig b. This enables the manufacturers to cope with the measurement of different conductivities. For example for very low conductivities a low cell constant and for high ones a high cell constant is needed, Fig. c.

Our cells have a cell constant of 1.0 cm^{-1}.

Conductivity depends strongly on temperature. Therefore the solution temperature must be noted (other temperature related issues are dealt with in **CARE**). Here are some illustrative conductivity **k** values;

|	Conductivity/μScm^{-1} at 25°C
ultra pure water	0.05 - 0.1
demin water	0.1 - 0.9
coffee	
white-with	1579
white-without	1689
black-without	1339
1% solutions of	
sodium chloride	17600
hydrochloric acid (HCl)	103000
caustic soda (NaOH)	532000
LAS acid	0.38
17 nonionic	0.03
milk	
whole homogenised	4480
semi-skimmed	4540
skimmed	4650

3.3 How is conductivity measured?

For measuring conductivity we need a **cell** and a **meter**. Conductivity is traditionally measured by placing two electrodes in contact with the electrolyte. The space between the electrodes or the cell isolates some volume of the solution and an electric circuit (meter) measures the conductance (actually the resistance) which is then converted to conductivity by using the cell constant.

In practice instead of a simple **direct** current (**dc**) an **alternating** current (**ac**) is applied across electrodes. This prevents the electrolysis effects, called **polarisation**, from taking place (opposite ions surround opposite electrodes and interfere with the true conductivity measurement). An alternating current reduces the polarisation. The **ac frequency** is about 10 kHz in precision lab meters.

Other interesting methods of conductivity measurement include;

1. **electrical induction** (another discovery by Faraday) where there is no contacting electrode involved. This type is the most suitable for in-line applications allowing different cell designs to cope with very high conductivities, Figs. d and e.

2. **4-pin electrode** which can be mounted flat on a surface as we made for the **Haake Minimixer** cup,
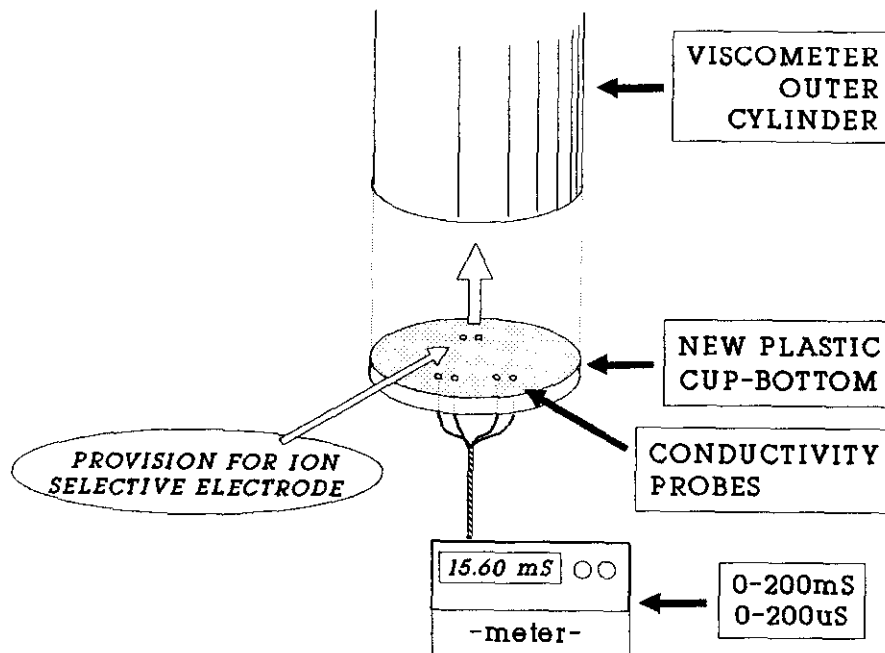
3.4 *Process conductometers*

Conductometry is one of the oldest **in-line** analytical techniques. Hence a wide range of equipments have been commercially available, Figs. f and g. These come in cell constants ranging from 0.001 to 100 cm⁻¹ (for ultra pure water and steam to extremely conductive melts and acids) and also capable of standing high temperatures and pressures. The electrodes are made of platinum, titanium or graphite. Our in-line pilot plant probes are of the conductive type (introduced by Simon Holbrook). In the Lab. we have been using a probe with graphite electrodes and an epoxy body since three years ago (the WTW probe-meter system).

3.5 *Uses*

Conductivity provides one of the most convenient and precise analytical tools to technologists and scientists. The scope of its use is limited only by our imagination. Conductivity measurement has served such diverse fields as,

. **concrete,**
. **sea water** (salinity for oceanographers),
. **suntan lotion,**

- **magma**, and **molten salts** (for production of material like aluminium and other metals),
- **geothermal waters** (spa water, and geothermal steam for electricity generation),
- **semiconductors**,
- **water purity** (Q. 1, 3 and 6) and even **water colour** (Q. 11),
- **environmental** monitoring, and,
- **dairy industries** (for milk adulteration, udder infection, fat and protein content).

Its use in Research has been extensive (but not exhaustive) for,

- **chemical reactions** (synthesis of zeolite from metal oxide and SiO_2 for which because of the high conductivity an inductive probe was used),
- **dissolution rate** of salts,
- **crystallisation** studies,
- **dispersion rate** of powders and HDL liquids (in washing machines, and batch mixing studies),
- **rate** of release from **encapsulated** systems,
- **phase inversion** of emulsions when oil droplets in water convert to water droplets in oil,
- **critical micelle concentration** (at which conductivity shows a step change with increase in concentration of the active) of detergent actives like LAS or sodium LAS and fabric softeners,
- **exchange** of potassium ions with sodium ions by zeolite in **Marilyn**,
- **phase volume** measurement in HDLs using **Bruggeman** equation,

$$\phi = 1 - \frac{(k - k_p)}{(k_c - k_p)} (\frac{k_c}{k})^{\frac{1}{3}}$$

where k, k_c, k_p, and ϕ are the conductivities of the sample, the continuous phase, and the particles and the phase volume (Q.5 and 6),

- **phase volume** of RCs can not be determined using the Bruggeman approach unless salt concentration is $\geq 0.1\%$ ($CaCl_2$). Below this salt level k depends also on droplet size as they are conductive (Q. 10).

Organic or **non-aqueous** liquids (like our **Mercure** formulation) have very low conductivities due to the low solubility of salts in the non-ionic. There are therefore fewer applications in organic media (for example potassium bromide, KBr, and aluminium bromide, Al_2Br_6, in toluene with $k = 6$ µS/cm is used for aluminum electroplating).

However we have used conductivity in our non-aqueous liquid programme for

- **chemical reaction** between LAS acid and detergent salts in Mercure like soda ash and calcium oxide,
- **water contamination** as conductivity increases with water content of these liquids, and,
- **concentration** of ionic species in organic solvents.

3.6 *Care*

Conductivity measurement is not as care free as density or RI. Conductivity probes suffer from constant change under our usage condition and **need calibration** preferably on a **daily** basis. This involves conductivity reading of a standard **KCl** solution of a conductivity which is near to that of the test sample. In this way the drift in the probe's behaviour can be monitored to allow absolute conductivity determination.

The robust graphite probe-meter system (WTW) currently in use in our lab. does not allow cell constant adjustment. It also lacks a **temperature knob** because it automatically corrects for temperature. Namely the conductivities other than at 25°C are scaled to that temperature using the **temperature coefficient** of a KCl solution. This does not apply to our systems. Consequently all readings especially those for calibration need to be done at the standard 25°C. For accurate and comparable processing work the use of a meter with a temperature adjustment is recommended (Q. 13).

3.7 *Quiz No. 3*

1. Where does the finite conductivity value of absolutely pure water come from?
2. Which is more conductive in a traffic jam, a motor bike or a car? (use this concept to answer Q. 7)
3. Why is the conductivity of the coffee white-with lower than that of white-without? Why is the conductivity of white without greater than that of black?
4. Why do you think the conductivity of strong acids, bases, and salts goes through a maximum as their concentration increases?
5. Use the Bruggeman equation to work out the fat content of the whole milk? Compare your calculation with those from density and RI, you found in previous chapters.
6. Work out the volume content of sugar in the white with coffee from the Bruggeman equation. Compare this with those from RI and d, from previous chapters.
7. Potassium salts have a greater conductivity compared to similar sodium salts at equal concentration. can you explain this ?
8. **Walden's product** (conductivity x viscosity = constant) introduced in 1906 relates to the conductivity of an **ion** at **infinite dilution** and the viscosity of the solvent. However people have used it for all cases. Can we use it to rank the viscosities of the milk samples?
9. Do you see a connection between Walden' rule and that of the Bruggeman?
10. Why does Bruggeman expression not work for low salt rinse conditioners?
11. How do you explain the fact that Water Authorities use conductivity for the colour of water. What is the connection?
12. Which way does the conductivity go if potassium ions are exchanged for sodium in a solution?

13. Work out a scheme to convert your process conductivity profile measured at different temperatures above 25°C to that at 25°C.

14. What are the conductivities of blood and blood plasma? Work out the phase volume of the particulate matter in blood using Bruggeman's equation.
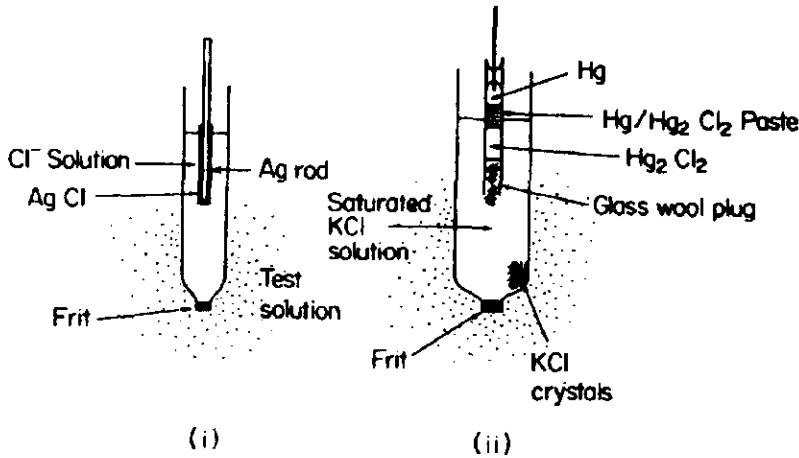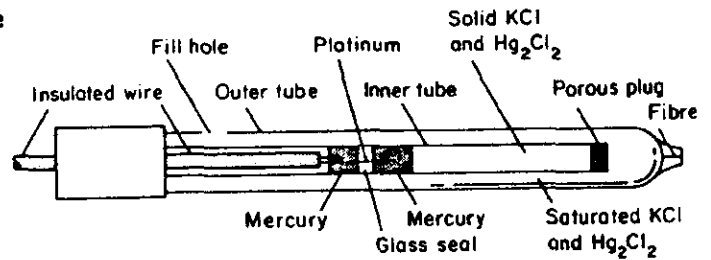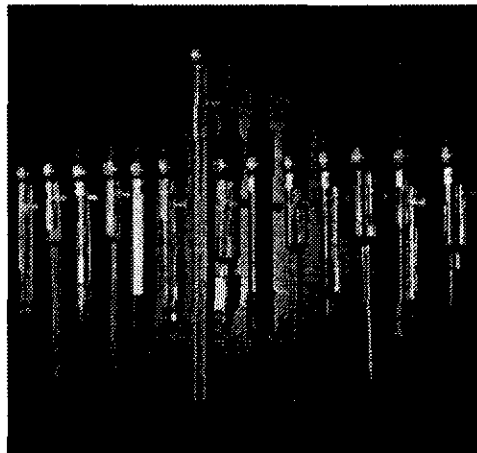
pH
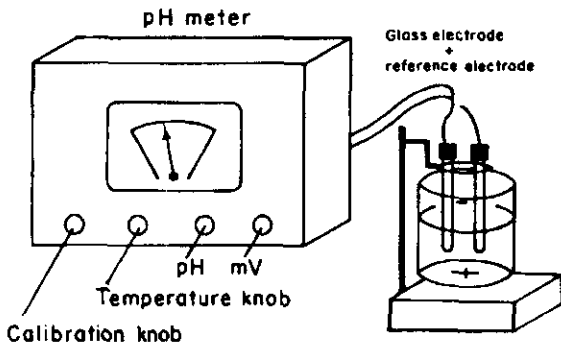
a. pH Meter
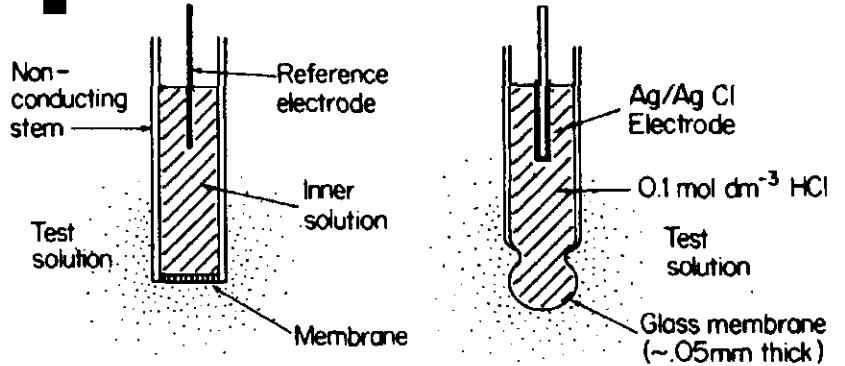
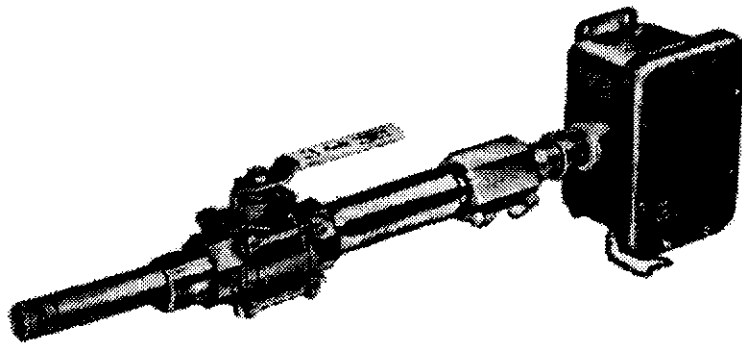b. Membrane electrodes (i) General construction
(ii) Glass electrode

c. Reference electrodes
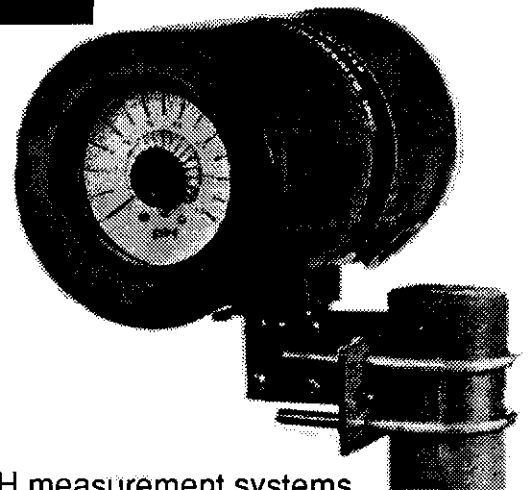(i) silver/silver chloride
(ii) calomel

d. A commercial version of a
saturated calomel electrode

e. Some commercial combination
pH electrodes

f. 7774-1-1 Mounting,
Electrode Inserted Through Valve

g. GLI pH measurement systems

CHAPTER 4 - pH

4.1 *History*

This last chapter deals with **acids, alkalis,** and their **strength.** Although acids and alkalis are ancient, ideas about their definition are quite recent.

The 8th century was the golden age of chemistry or **alchemy. Jabir Ibn Hayyan** (721-815), the Persian chemist, known in the West as **Geber** and the father of chemistry laid its foundations as a science. In one of his books (2000 are ascribed to him!) called the "**Invention of Perfection**" he clearly described the production of **nitric acid.** Another great chemist, philosopher, and physician of that period **Mohammad Razi** (854-935), or **Rhazes** who strongly influenced the Latin West, in his "**Secret of Secrets**", a chemistry laboratory manual, described **sulphuric acid.** These two acids form the backbone of Chemical Industries.

Geber in his work defined acids as '**solvative waters**'. Progress in the definition of acids was made possible by **Robert Boyle** (1627-1691), the Anglo-Irish natural philosopher, physicist, chemist, theologian and Parliamentarian. He was one of the founders of Royal Society and discovered **hydrogen, phosphoric acid** (1680), and the famous **Boyle's Law** (that volume of a gas varies inversely with its pressure). The colour changes observed in the course of chemical reactions always fascinated him. In two books, "**Sceptical Chemist**" and "**Experiments and Considerations Touching Colour**" he described various ways of producing colour changes and used these to classify and identify chemicals. Boyle claimed in these books to be the first to realise that all acids turned the **blue syrup of violets** red (this was known for a few acids only) and all alkalis turn it green. This left him with three classes of compounds, **acids, alkalis,** and those that were "**neither**". At this time acids were imagined as particles having needle-like points which enabled them to penetrate into pores of metals.

The **oxygen theory** of acids by **Antoine Lavoisier** (1748-1794), French chemist, geologist, economist, social reformer, and physiologist who died at the guillotine, paved the way for further progress. His discoveries include the role of **oxygen** in **combustion,** and the **gaseous** nature of the atmosphere (which was known as **aeriform fluid;** the word **gas** was invented at this time). Lavoisier's teacher (**Rouette**) had confirmed that **salts** were combinations of an acid with certain substances that served as a "**base**" (hence base for alkali). He had also shown that certain salts were **neutral** (i.e. neither). Following this salt idea Lavoisier thought acids must also come from a **universal acid.** By 1772 he was convinced that air entered into the composition of acids. In an important article in 1779 he said that oxygen (known at that time as the **pure part of air**) was the universal acid or the acidifiable principle. According to this oxygen theory non-metallic elements like carbon were converted into acids by burning, namely CO_2 into carbonic acid H_2CO_3 and hence all acids contained oxygen.

This led to some confusion as acids were known that contained no oxygen but Lavoisier explained those away. **Humphry Davy** (1778-1829), English chemist inventor and poet (a friend of Coleridge), who learned chemistry from Lavoisier's book proved his oxygen theory wrong. Davy is famous for the **Davy Lamp** which he invented to prevent explosions in **coal** mines caused by **methane gas** in Newcastle-upon-Tyne area (the first gas-coal conflict, the second being the recent dash for gas!). His work on Volta's battery, where he replaced one of the metals with carbon, led to the invention of the **carbon arc**. He discovered the anaesthetic effect of **nitrous oxide**, electrolysed water into **oxygen** and **hydrogen**, produced **potassium** (the name given to it by him, its chemical symbol **K** is from its Arabic name kalium from alkali) for the first time from potash by electrolysis, isolated for the first time **magnesium, calcium, strontium, barium, boron**, and **carbon**. His electrolytic work with **Faraday** led him to realise that oxygen was not a constitute of all acids. His hydrochloric acid, HCl, and hydrocyanic acid, HCN, were the critical proof. This ushered in an era when acidity was associated with **hydrogen**.

The acid-base concepts were revolving around experiments carried out in water. In such an **aqueous** environment, **Arrhenius's acid-base theory** (1887) grew out of his electrolytic dissociation work (as detailed in the previous chapter). According to this theory a compound can be considered as an acid only if in **water** it generates through dissociation **hydrogen ion** (H^+) and as a base if it gives **hydroxyl ion** (OH^-). From this came the concept of **neutral** or neutralisation as an interaction between H^+ and OH^- to generate water H_2O and a **salt**.

Viewed with a general acid-base definition in mind, Arrhenius's theory was a step backward (see later) nevertheless from it emerged a quantitative scale for the strength of acids and bases; ie the **pH** scale.

4.2   What is pH (power of Hydrogen)?

The concentration of hydrogen ion chemists found in solutions usually ranged from 1 to 10^{-14} g/litre. To avoid having to deal with such cumbersome numbers **Soren Peter Sorensen** (1868-1939), a Danish chemist who later became interested in proteins and the effect of acidity on their precipitation, introduced the concept of **pH** in 1909 during his investigation of potentiometry (see later) methods for hydrogen ion determination. He used the concept of **logarithm** (log) to translate hydrogen ion concentrations into numbers between 0 and 14 by;

pH = - log [H^+]

where the square brackets [ ] symbolises **concentration** for chemists and **p** (lower case) stands for **power**. Since in pure water they found that [H^+] = [OH^+] = 10^{-7} (at 25°C,) then according to the above definition; **pH = 7   pOH = 7   and   pH + pOH = 14.**

Pure water being considered as **neutral** (neither acidic nor basic or alkaline) therefore gave us the definition of **neutrality (at 25°C); neutrality is pH = 7** so that, **acidity is pH < 7** and **basicity is pH > 7.**

The table below graduates some common values of **pH**.

pH table

Left labels	pH	Right labels
hydrochloric acid 1N →	0	
sulphuric acid (1N) →		
sulphuric acid 0,1N →	1	
oxalid acid 0,1N →		
citric acid 0,1N →	2	coca cola / lemon
acetic acid 1N →		apple
acetic acid 0,1N →	3	acid (natural)
acetic acid 0,01N →		orange / sherry
hydrogen sulphide 0,1N →	4	tomato / beer
carbonic acid (satureted) →	5	
		cheese
	6	salmon
		whole milk
	7	hair shampoo / drinking water / blood plasma / eggs
	8	
sodium carbonate →		gin
borax 0,1N →	9	
	10	
aqueous ammonia 0,01N →		liquid soap
aqueous ammonia 0,1N →	11	
potassium hydroxide 0,01N →	12	soda
potassium hydroxide 0,1N →	13	
potassium hydroxide 1N →	14	soft soap

The normal **pH** range is 0-14 but this does not mean that **pH** values outside this limit cannot exist. For instance strong alkaline or acid solutions can have **pH > 14** or **pH < 0**;

    LAS ACID   **pH = - 2.6**

    potassium hydroxide KOH (50%)   **pH = 16.4**

Later on we explain how these were measured.

Also note the importance of temperature on $[H^+]$ in pure water;

temperature (deg C)	0	10	20	25	30	40	50
$[H^+]$ in units of 10^{-7}	0.35	0.54	0.82	1.00	1.21	1.71	2.34

We see that the condition of neutrality changes with temperature. It is for example incorrect to judge the acidity or alkalinity of blood at the blood temperature of 37°C with **pH = 7** at 25°C.

4.3 How is pH measured?

Some consider **pH** and conductivity to be similar. In fact they differ greatly. Conductivity measures the concentration of all the ions present in a solution whereas **pH** reads the content of **hydrogen ions** only. For **pH** measurement we need an **electrode** which can **sense** hydrogen ions only (a **hydrogen selective electrode**). For conductivity we measure resistance, for **pH** we measure **voltage** or **potential** (like in a battery). Methods of **pH** measurement fall into two classes, **colorimetry** and **potentiometry**.

4.4 pH by colorimetry

This is the old method of using natural **indicators** (syrup of violets) such as **red cabbage, mushrooms, lichens,** or **flowers**. Red cabbage is red in acids but blue or violet in a neutral medium and green in a strong alkaline solution. Mushrooms whiten when treated with vinegar but turn brown in alkalis.

Litmus which turns red in acids and blue in alkalis or **pH paper** form the basis of colorimetry. Litmus (Old Norse, litr = colour + mosi = moss) is a mixture of organic colours obtained from several species of lichen that grow in the Netherlands. Lichens also provide the colours of Harris Tweed. **pH paper** is a paper impregnated with suitable dyes with colour codes to give pH values with at least ± 1 unit accuracy.

4.5 pH by potentiometry

This is the most accurate and universal way for pH determination. In spite of the deceptive simplicity offered by pH meters today the underlying theory of potentiometry is quite complex. In conductivity measurement we apply a potential (a voltage) across two electrical

connections (**electrodes**) and **measure resistance**. In pH measurements we still need **two electrodes** but we measure a tiny **potential** (hence **potentiometry**) that gets built up across the electrodes. The sensitivity of the **hydrogen-selective electrode** to H^+ causes the potential build up.

The potential across the electrode depends on how the electrode responds to $[H^+]$ and also on the second electrode (called the **reference** electrode because it only provides a fixed potential independent of the solution). Therefore a **potential meter** and a **pair of electrodes** comprise a **pH meter**, see Fig. a.

The important point about pH meters to notice is that they actually measure the potential (and display it as milliVolt or **mV**; remember Volta?). Then by **calibration** this voltage is converted into **pH**. Therefore without calibration the readings have little meaning (see also **CARE** for more details). **pH** values greater than 14 and less than zero would not usually be displayed by pH meters. To measure the pH values of LAS acid and KOH with the Lab-based **Corning 240 pH Meter** we read the **mV** (instead of pH) for three **buffers** and plotted their pH against their **mV** as shown below.
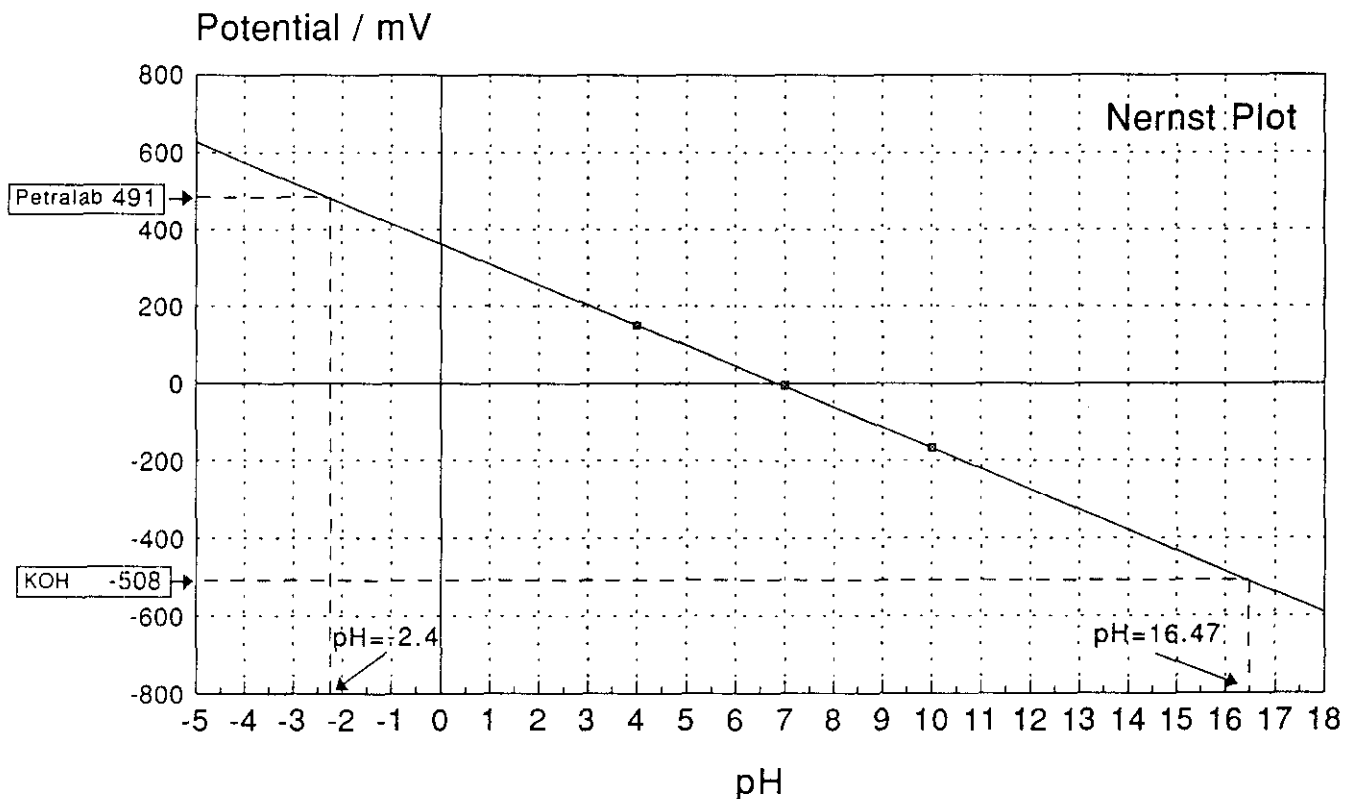
From this graph by **extrapolation**,the equivalent pH values of LAS and KOH were estimated. This type of graph is called a **Nernst** plot after **Werman Walter Nernst** (1864-1941), German physicist who turned chemist and together with Arrhenius and Ostwald founded the science of **physical chemistry** at University of Leipzig (they were called the **Ioner** group). Nernst had an unparalleled theoretical command of physical chemistry. He wanted to be a poet and had a lifelong infatuation with Shakespeare. His crowning achievement was in **thermodynamics** (the **third law of thermodynamics** or Nernst heat theorem 1906) for which he received the Nobel Prize for chemistry in 1920.

4.6   The glass electrode

In 1906, **Cremer** discovered that certain glasses (the soft soda glass) responded to hydrogen ion concentration.   Soft soda glass consists of 72% silicone dioxide (SiO_2), 22% sodium oxide (Na_2O) and 6% calcium oxide (CaO). It was easily worked into a thin wall ball **(membrane)** the interior of which was filled with a fixed concentration of HCl and an electrode for the electrical contact with the reference electrode; see Fig. b.

The glass electrode was not uniquely selective to H^+ but responded to **sodium** ions as well if present at high concentrations. The glass electrode had a poor response in the two extreme ends of the pH scale at below 1 and above 13 (called **acid** and **alkaline errors**). We use below the Nernst plot to indicate these errors;

Glass electrode response
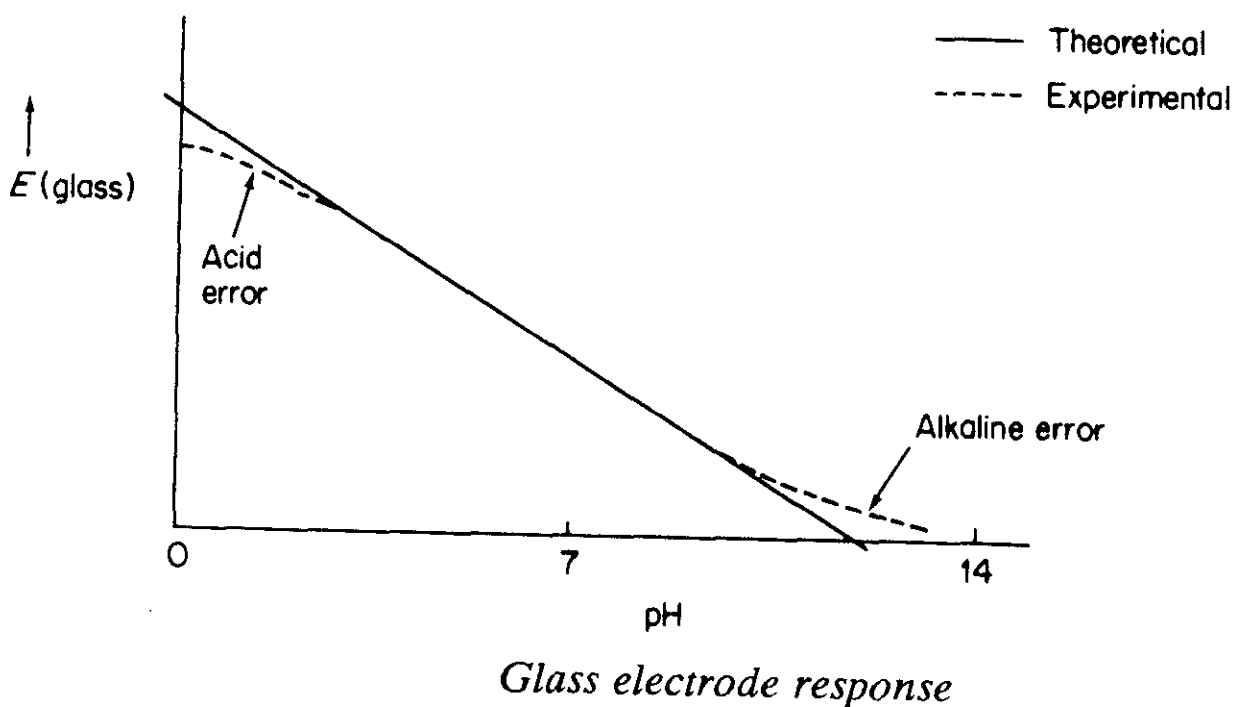
The alkaline error was greater for sodium (Na^+) and Lithium (Li^+) ions compared to potassium (K^+). Glasses doped with a small amount of **aluminium oxide** (Al_2O_3) or **boron oxide** (B_2O_3) increased the alkaline error. This led to the birth of glasses sensitive to Na^+ (or other ions; **ion-selective electrodes** for pX metry where X stands for other ions). By replacing calcium with barium or strontium the alkaline or sodium error drops. Most new full-range pH electrodes incorporate these new types of glass with very little alkaline error. The best way to find out whether an electrode is well-behaved is to plot its Nernst response using buffers covering the pH range of 1 to 13.

New H^+ sensitive materials are constantly being invented or discovered. One is the oxide film on some stainless steels which respond in a Nerstian way to $[H^+]$ from pH 1 to 13.

4.7 The reference electrode

Figs. c and d depict the anatomy of two common reference electrodes used with a glass electrode to enable **pH** measurement. Their design is based on **Nernst** discovery that the combination of a metal with an **insoluble salt** of that metal in a salt solution maintains a **constant potential** at a given temperature. New pH electrodes combine the reference and the glass electrodes in one (**combination** electrode), see Fig. e for a variety of such designs.

4.8 The tail of two pH scales

The **pH scale** of 0 to 14 belongs to **water** (H_2O) as the medium or **solvent**. In a **non-aqueous** "universe" things are very different. For example, acetic acid is a weak acid in water but a strong one in ammonia (NH_3). The work of **Paul Walden** (Pavel Ivanovich Valden, 1863-1957), Germano-Russian (Latvian) physical chemist who introduced the **Walden Rule** (conductivity x viscosity = constant), on the **electrochemistry** of **non-aqueous** solutions led to the resolution of these inconsistencies in the acid-base theory (the details of which is beyond the scope of this document).

We are interested here in the problem of measuring $[H^+]$ in a **non-aqueous** or **organic** environment where neither pH paper nor glass electrode works properly. This is because the organic solvent **attacks the** sensitive glass surface (see later). In other words it is the water that makes the glass electrode sensitive to H^+. The solvent attack is known as the **solvent effect** as well (and can actually be exploited to measure the alcohol content of beverages by ion-selective electrodes as we have reviewed the area in an R report). Looking back at the **pH** value of LAS acid in comparison to its conductivity one can see a discrepancy. The **k** value is extremely low (showing no ionic activity) whereas the **pH** indicates a large H^+ activity. This low **pH** value could be a manifestation of the solvent effect rather than a high H^+ activity (hence caution must be practised in the measurement and interpretation of **pH** in organic media).

Here are a few **pH** measurements (at 25°C) on Mercure; our non-aqueous HDL which contains non-ionic and lots of alkaline solids.

Non-ionic A7	pH = 7.55
Mercure	pH = 9.66
Mercure + 5% water	pH = 10.46
Mercure + 10% water	pH = 11.04
Mercure + 15% water	pH = 11.02

4.9 *Process pH meters*

Many industries rely on **pH** measurement for quality control (see **USES**). A wide range of commercial industrial **pH** meters are now available to suit every need. The continuous **in-line pH** measurement has not been straightforward and has become a reality by innovative technologies. The problem lies in the glass electrode itself. The potential generation due to [H⁺] takes place at its surface. Therefore its cleanliness is vital for its performance. Periodical **cleaning** (by brushing, ultrasonic, chemicals, or manual) and **calibration** is essential. The **fouling** and **poisoning** of the reference electrode in the process liquid is another problem which has been solved in process **pH** systems. See Figs. f and g. for examples.

4.10 *Uses*

Industrial uses of pH include **sugar refining, pulp** and **paper, food** and **beverage** processing, **metal plating, fermentation** process, **fertiliser** and **drug** manufacture, **mining, dyeing** and **cosmetics** industry, **corrosion** inhibition, and **effluent** and **water** treatment.

pH has biological and everyday life significance. Living organisms thrive at a particular **pH** (azaleas, rhododendrons, and conifers like acidic soil for best performance). The **pH of blood** is very critical, one unit change and death becomes inevitable (**buffers** in the blood stabilise its **pH**).

Scientific and laboratory uses are many, including, reaction **end-point determination**, **neutralisation**, and monitoring of changes which involve hydrogen ion concentration. The **pH** of our HDLs, because of their influence on the fabric is very important (see the Appendix for more applications).

4.11 *Care*

The pH and ion-selective electrodes need great care for meaningful measurements. As was mentioned before this is due to the surface of the glass electrode. This surface is almost "alive". Water absorbs at the surface changing it chemically to create a **gel-layer** of 0.01 to 0.04 µm in thickness. The formation and maintenance of this gel is essential, see below

Glass surface I-Si-O-M + Water (H2O) ---> Glass surface I-Si-O-H + MOH (metal in water) gel

where M = metal ion (which leaches out of glass).

We now see that the electrode is "aquatic" and dies in a non-aqueous environment. Organic solvents or media which damage this gel induce a response which has little to do with the real **pH** of the system.

The glass electrode needs good conditioning in water before use. New, dry electrodes need at least 24 hours soaking in water or 0.1 molar HCl solution before use for the formation of the gel. Implicit in this is the limited life time of the glass electrode because of its fatigue.

The drift in the **pH** response usually experienced with glass electrodes stems from the variation in the gel and ageing (fatigue) of the glass which necessitate regular **calibration** with pH **buffers**.

Correction for **temperature** is also important. The temperature dependency is rather complex. There are **two sources** for the temperature effect; the **Nernst** equation, see **Question** 13) and the change in the **dissociation** of hydrogen ion with temperature. Instruments may correct for both effects. The instrument manual must be consulted for correction of the temperature effect.

4.12 *Quiz*
1. What is the vital chemical compound represented by H I J K L M N O ?
2. If you were a farmer how would you neutralise your acidic land?
3. What is the definition of an acid ? Can you think of a better definition?
4. Which ion is denser H^+ or OH^- ? Which is more conductive? Which is more basic?
5. Speculate on how indicators change colour with pH.
6. Is there any connection between 7 in the pH scale and 7 in the Scriptures (seven days and seven heavens)?
7. What is the pH of our gastric juice? What is the pH of the dental plaque which is believed to causes tooth decay?
8. The pH of lemon juice is 2.2 what does it mean in terms of H^+ level?
9. Why is the pH of LAS acid below 0? If this is a clue to its high $[H^+]$ why then its conductivity is almost zero?
10. Is pH measurement meaningful for margarine which is a water-in-oil emulsion ? How about oil in water emulsions like Marilyn or ALBA?

11. Which one is more acidic compared to water at 25°C, steam or ice-cold water? If you were to measure pH of ice-cream how would you express your results (what would you use for the neutrality of water)?

12. How would you report a pH measurement during processing where the temperature (and chemicals) changes from say 80 to 25°C. How do you correct for the temperature? How do you then define acidity or basicity (neutrality) under the varying temperature condition?

13. Read the slope of Nernst plot and work out the famous Nernst equation
    $E = A - Slope \times pH$ or $E = E_0 + (constant) \times \log [H^+]$.

14. What is the significant of pH measurement in high salt (Na^+ and K^+) solutions?

15. Is pH a reality or it is here because it has been a historical development and we are now stuck with it? Is there a better way of expressing pH?

16. Which is more acidic H^+ or D^+?

ACKNOWLEDGEMENT

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