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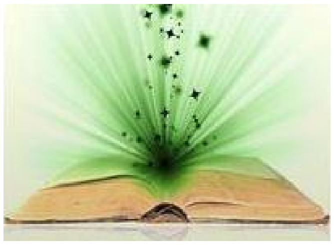

ANALYTICAL METHODS – AN OVERVIEW

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ABSTRACT

"Science represents the accumulated and systematized knowledge of natural phenomena, while technology involves the exploitation of scientific discovery for practical applications that satisfy human needs through creating conditions for industrial activities, jobs, markets etc., aimed at improving the quality of life".

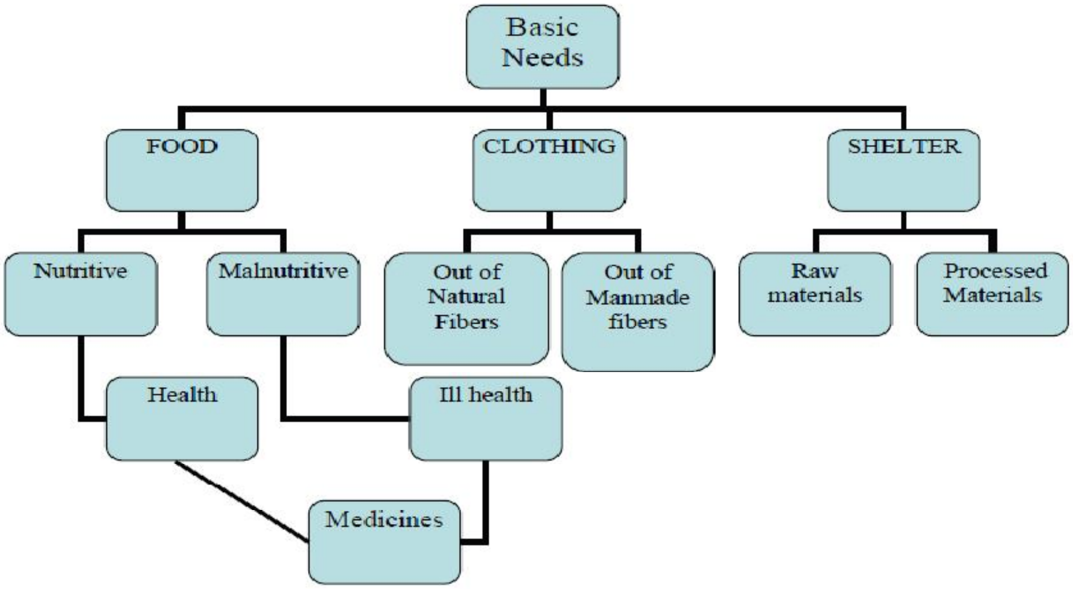
Keywords: Analytical Method

INTRODUCTION

Everyone that has lived through 20th century witnessed fast and rapid changes that took place during the period, a few of which are in the fields of telecommunications, computers, transport systems, space research, drugs and medicines. None can deny that all these and many more developments in different fields are due to science and technology. "Science broadly considered is incomparably the most successful enterprise human beings have ever engaged upon" said Peter Medawar, Nobel laureate in Physiology. (1960).

"Science represents the accumulated and systematized knowledge of natural phenomena, while technology involves the exploitation of scientific discovery for practical applications that satisfy human needs through creating conditions for industrial activities, jobs, markets etc., aimed at improving the quality of life.[1]. In other words, science sows the seeds for improvement of the quality of human life while technology yields the fruits. Science is the hub to the wheel that is technology. Man has close association with materials like neutraceuticals, pharmaceuticals, weather resistant building materials and weather compatible dress materials. Fig.1 depicts the basic needs of man.

Figure-1



“We, chemists, extend the natural world all the time with tremendous effect”. [2]. Chemistry, which is essentially concerned with the structure and composition of materials, plays an important role on the way we live. The industry draws this essence for improving the standard of contemporary living.

The structure is concerned with the energy link among the constituent parts of the matter while the composition is related to the mass part. Burrowing a little deeper, perturbation in either the energy part or the mass part of the constituents is useful in the science of Analytical Chemistry.

a. Modification in the energy part is useful in the field of instrumental methods of analysis as probes and detectors.

b. Modification in the mass part is helpful in the field of production of more useful materials.

Prior to 20th century the attitude of chemists hovered round absolute clean product and neat constituent analysis with little attention to the real matrix. Modern 21st century attitude is towards quality assurance with the result that chemical analysis had been looked down as a tool only and never looked upon as a full fledged discipline even though it got metamorphosed to Analytical Chemistry. This leads us to understand the connection between tools and concepts in just the same way as that exists between experiments and ideas. Experiments lead to ideas. Ideas in turn lead to experiments.

“The effect of a concept – driven revolution is to explain old things in new ways. The effect of tool – driven revolution is to discover new things that have to be explained” [3]. Nevertheless, rapid developments in the mass – mass interactions and energy – mass interactions led to tremendous developments towards more sophistification in the trend of readability, repeatability and realisability of the end result. But then analytical chemistry did not lag behind. Rapid developments took place both in the methods and measurements to suit the modern requirements of improved limits of readability, quality of reproducibility and greater degree of realisability.

Study of chemical analysis gradually changed from single objective {Robert Boyle, (1654)] intent to multiple objective goal; from specificity to selectivity; from a single element to multi element in a single run; from a single variate to multi variate; from macro- to semi micro- to micro- to nano- to pico- level readability and from a single discipline study to multi discipline study of the constituents in the material. In other words, second half of 20th century witnessed the emergence of analytical chemistry from that of simple chemical analytical tool to the 3rd millennium computer aided sophisticated science. More simply it has evolved from test tube to push button operation.

The approach to chemical analysis is well expounded by Laitinen.
"First step in chemical analysis is the definition of goal. Problems may involve:
(a) Control of a manufacturing process; (b) gypsy moth devastation;
(c) fluoridation of drinking water supply; (d) monitoring the motor oil for engine wear etc.
To solve the analytical problems facing him, a chemist must be prepared to use any part of chemical information and tools at his disposal. This includes knowledge not only of methods for measuring chemical and physical properties of atoms, ions and molecules but also of modern methods of separation, sampling, measurement and handling of statistical data"[4]. But it should be realized that the 3rd millennium problems are far more intricate than those envisaged by Laitinen. Such problems are many. A few representative examples, all from "Chemistry – Today and Tomorrow"[5] may throw more light.
1. Medicine: "We don't have effective anti – viral medicine. Where is the compound that can cure flu?"
2. Food: "Do we have food chemicals that are safe and effective?"
3. Environment: "We need to get chemical products such as refrigerants and pesticides that last the right time but not longer."
4. Biology: "The chemistry of life is fairly understood in biology, but understanding the chemistry of brain is a new challenge."
In the laboratory, physical sciences controlled experiments can be carried out to verify the theoretical model by measuring theoretically predicted parameters. But in the geological, geophysical, forensic, life and environmental sciences it is much difficult to carry out well controlled experiments and analyses in much the same way as with experiments in the physical sciences. Lower readability limit alone is not the solution to the problem of realisability and repeatability.

1. Readability is the least detection limit and is dependent on the constituent level.
2. Repeatability or reproducibility reflects the robustness of the result and is dependent on operational factors which in turn depend on analyst, method and measurement.
3. Realisability corresponds to the degree of approachability to the ideal or true or practically closer to the true value. Periodical attention to the standardization with respect to materials and methods helps towards increase in the confidence of reliability of the result. (Fig.2)
The steps in analysis (or analytical operations) are: (i) Sampling, (ii) Dissolution (where the sample can be disintegrated), (iii) Deriving the analyte sample solution or analyte matrix, (iv) Analyte evaluation or determination or measurement and (v) Accuracy assessment in terms of error analysis. Each one of these steps has an operational protocol so as to lead to the final result.

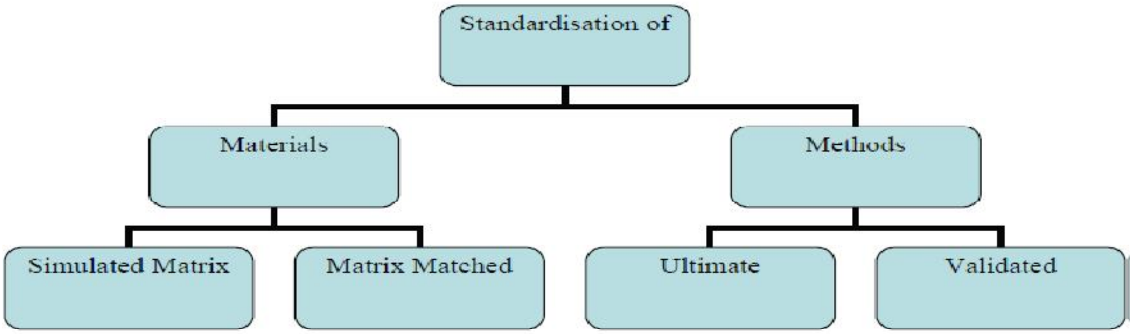


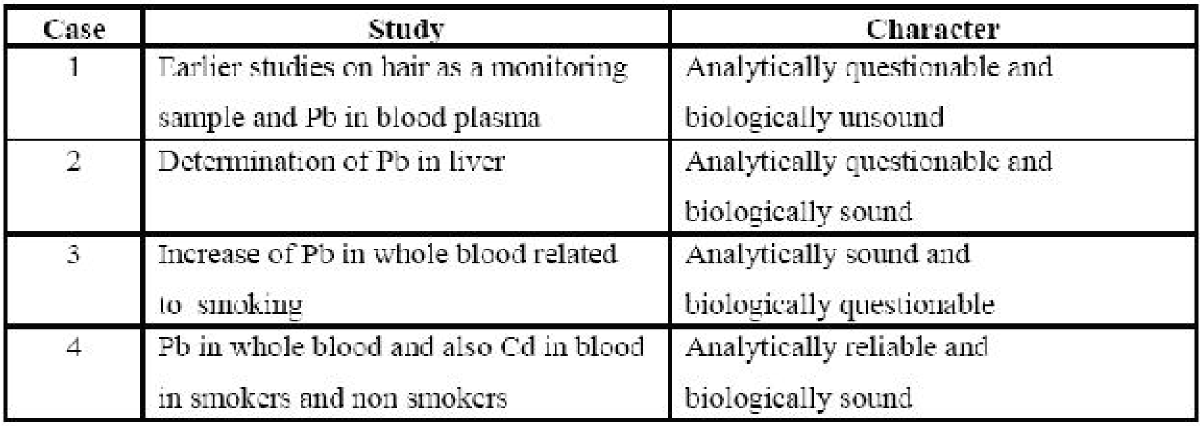
Figure-2

1. Sampling

The purpose of sampling is to obtain a representative portion of the bulk material to be analyzed in such a manner that the result obtained on the derived portion closely matches the bulk. Sampling procedure depends on the state of the material, (gas, liquid, or solid) and the matrix (geological, metal or alloy, vegetative, biological, atmosphere, hydrosphere, macromolecular etc,). The basic principle involved in sampling seems to rely on the idea that the more homogeneous the matrix the easier is the sampling procedure.

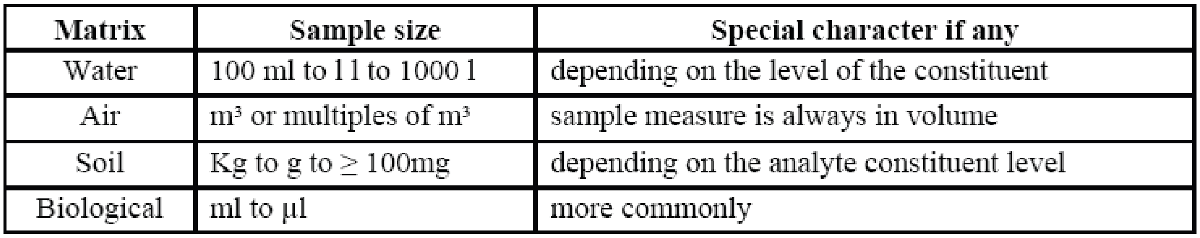
Soundness in the selection of the sample also needs proper attention along with the analytical technique. This aspect is highlighted in Table.1, while Table 2 draws attention to the sample size. Skewed perception of a single disciplinary attention to a multidisciplinary problem is presented in Table.1

Table.1. Example – Determination of Lead (Pb) in tissues and body fluids [6].



Case	Study	Character
1	Earlier studies on hair as a monitoring sample and Pb in blood plasma	Analytically questionable and biologically unsound
2	Determination of Pb in liver	Analytically questionable and biologically sound
3	Increase of Pb in whole blood related to smoking	Analytically sound and biologically questionable
4	Pb in whole blood and also Cd in blood in smokers and non smokers	Analytically reliable and biologically sound

Table.2. Sample size in different matrices (especially relevant to environmental analysis).



Matrix	Sample size	Special character if any
Water	100 ml to 1 l to 1000 l	depending on the level of the constituent
Air	m^3 or multiples of m^3	sample measure is always in volume
Soil	Kg to g to ≥ 100mg	depending on the analyte constituent level
Biological	ml to μl	more commonly

2. Dissolution

Dissolution also is dependent on the nature of the material. Fig.3 is a broad outline of the methods for bringing the sample into solution for the next operation.

Fusion and dissolution is usually carried out on a hot plate or on a burner. But then this is tedious and time consuming, taking in general 4 hours, counterbalancing the gain of time of analysis with multichannel direct current plasma, inductively coupled plasma atomic emission, and mass spectrometry, which are capable of measuring 20 to 60 elements at parts per billion levels within one minute’s time. This problem received due attention and the time consumption is reduced substantially to the extent of 50% with the microwave heating technique replacing the hot plate heating method.

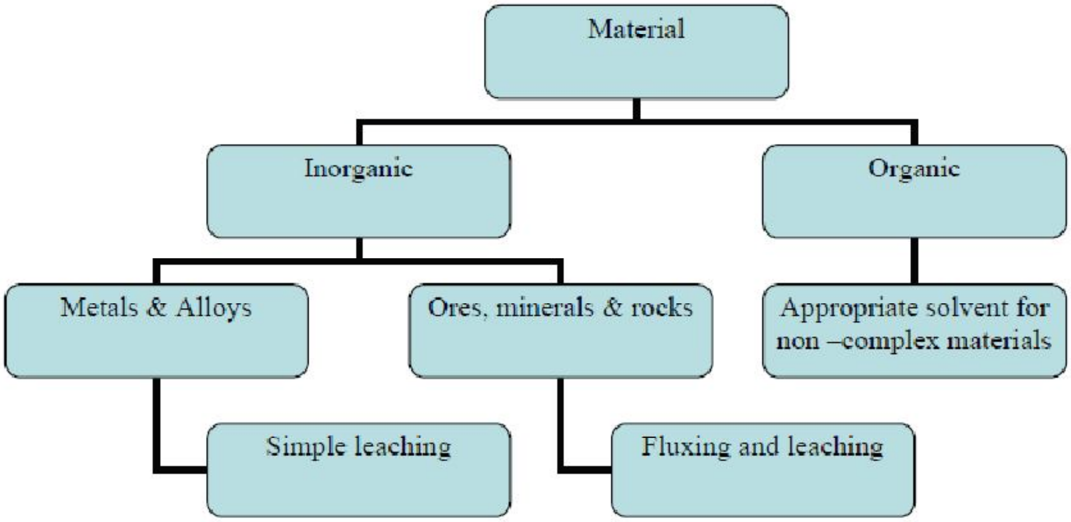


Figure-3

3. Deriving the analyte sample solution

Fig.4 illustrates general guidelines.

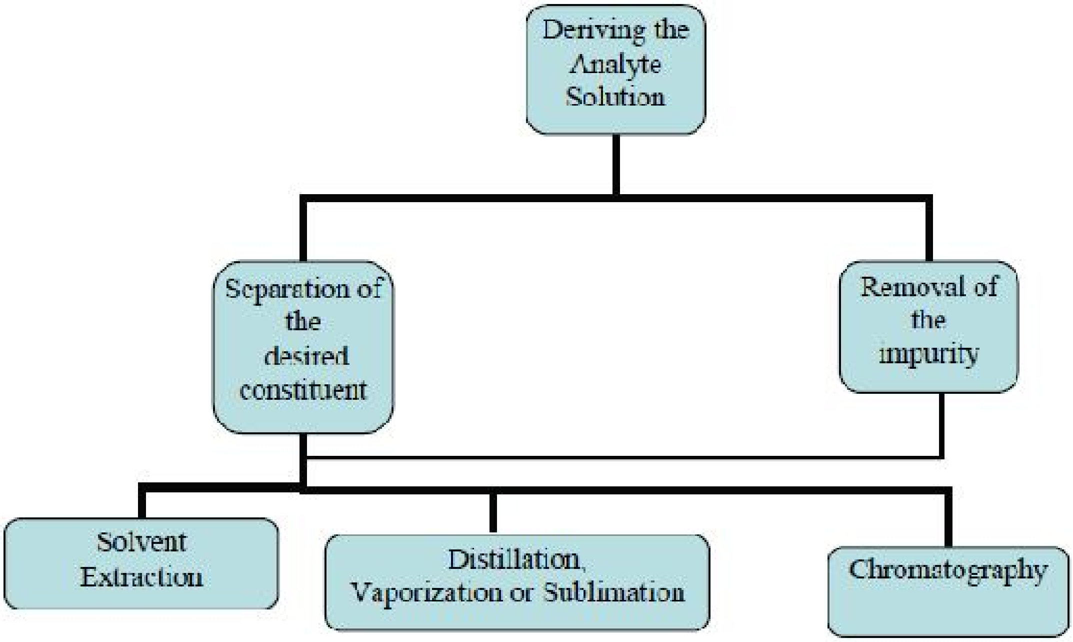


Figure-4

4. Evaluation or measurement step

The next step is conversion to measurable form. This depends on the choice of the measuring technique. For example, if the constituent is to be evaluated based on the optical property it should be transformed to the colored form, if it is not already colored. The categories of different techniques/methods are shown in Fig.5.0 and its subordinates.

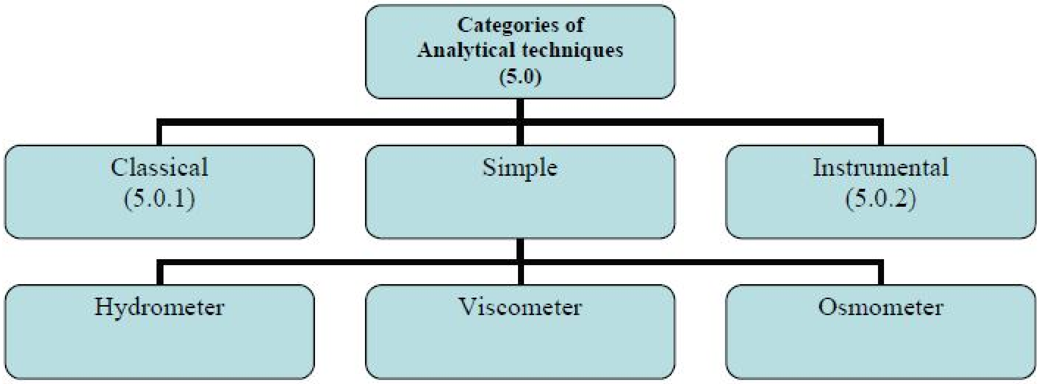


Figure-5.0

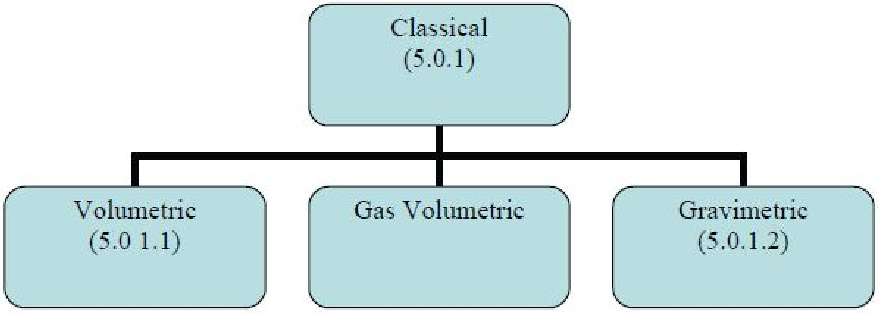


Figure-5.0.1

Are these developments in instrumental methods so fantastic as to lead to a situation that "our modern chemistry graduate students cannot solve acid-base equilibrium problems and would have no idea of how to detect the presence of toxic levels of tin and mercury in drinking water without a $200000/- MS spectrometer and a technician to run it"? [7]

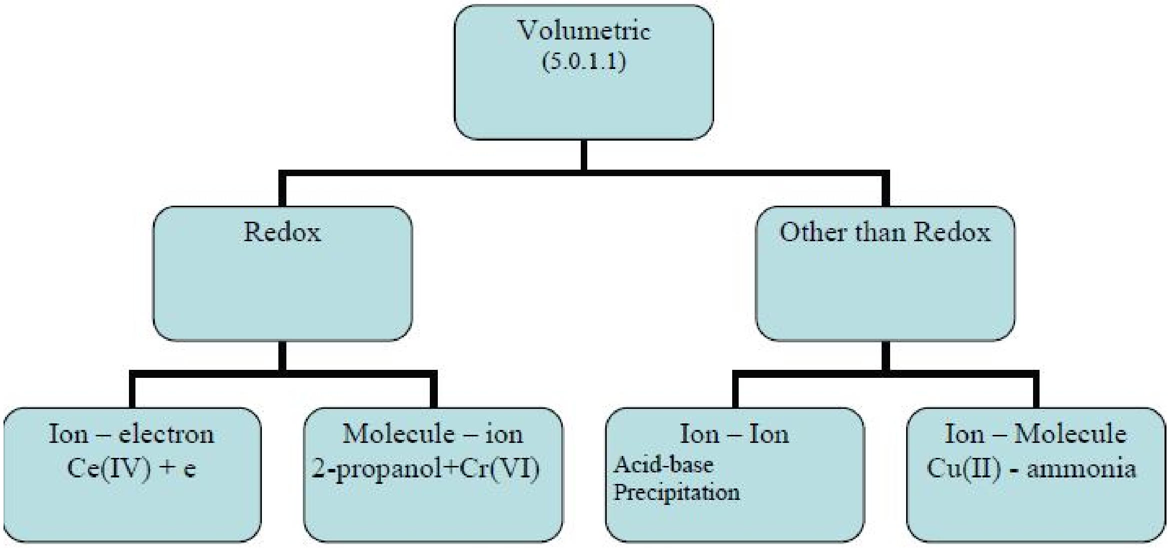


Figure-5.0.1.1

Against this backdrop it becomes relevant to know the significance of classical methods and the instrumental methods. Although the instrumental methods are preferred by the analyst, classical methods still hold the ground to serve as absolute and primary reference methods. Classical methods of analysis are the ultimate key to measurement traceability, accreditation and good laboratory practices (GLP).

Efforts are continuously being made to develop better reference materials and methodologies in order to achieve better harmonization of standards and reliable systems of testing and certification.

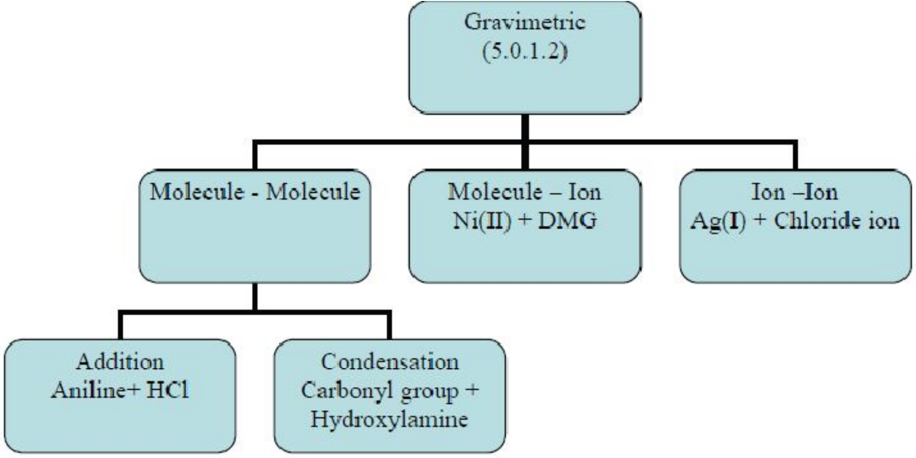


Figure-5.0.1.2

(Late) Prof.G.Gopala Rao made quite substantial contributions in this area for which he got the global recognition.

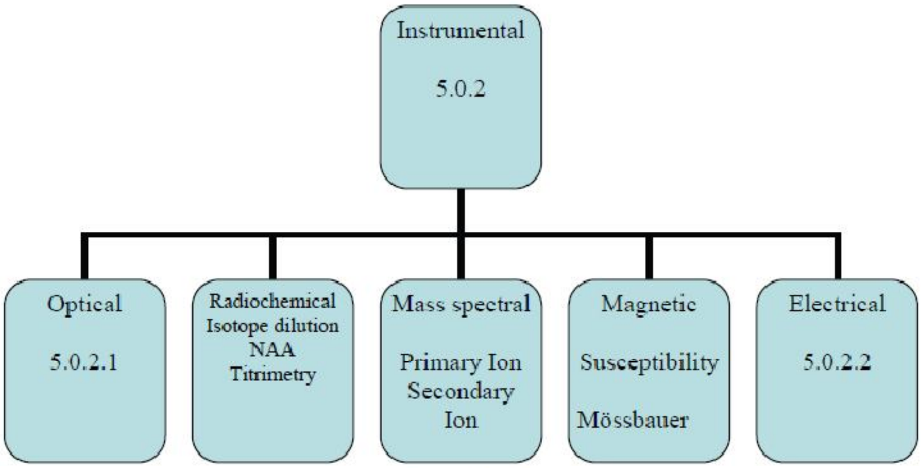


Figure-5.0.2

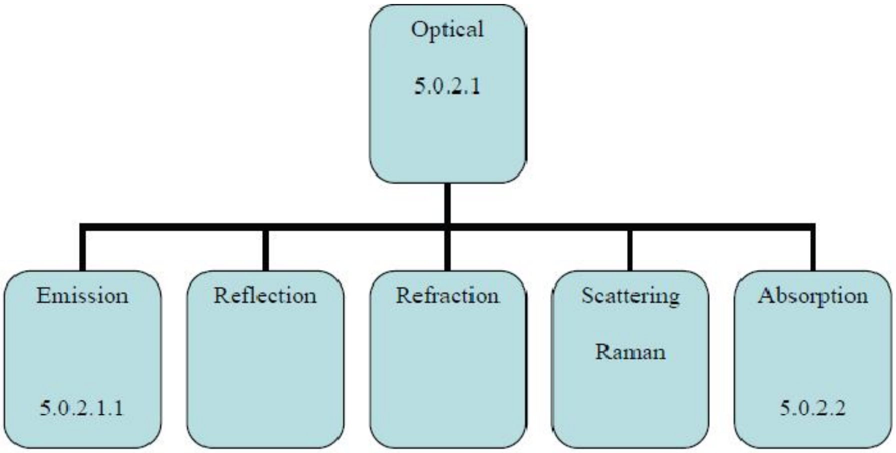


Figure-5.0.2.1

But classical methods have some limitations: (a) they are time consuming, (b) they are not useful for automation, nor are they useful for on line inspection. A comparison between classical and instrumental methods is given in **Table.3.**

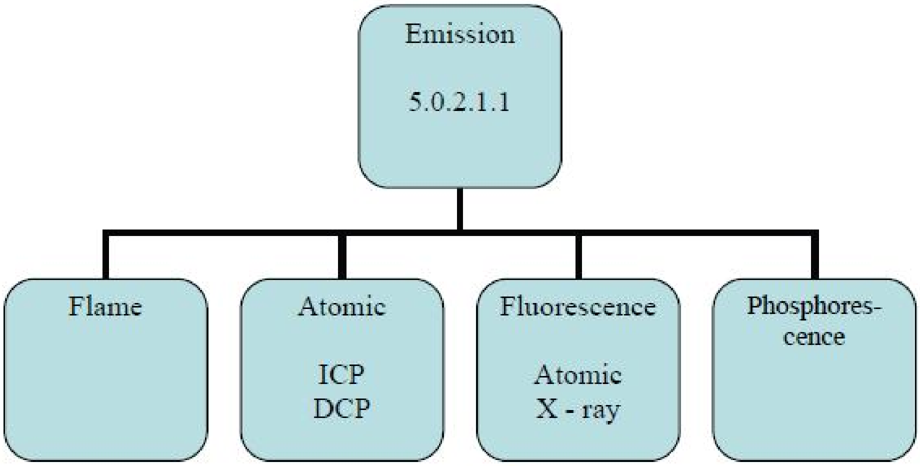


Figure-5.0.2.1.1

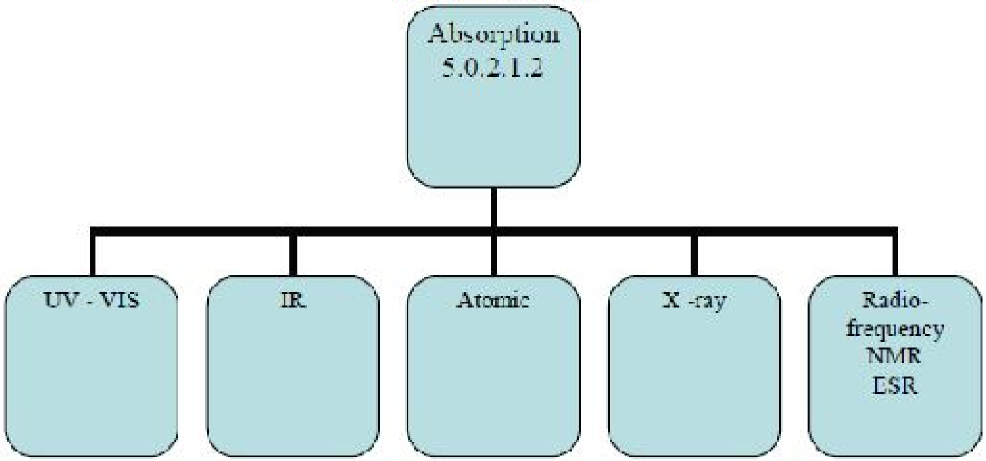


Figure 5.0.2.1.2

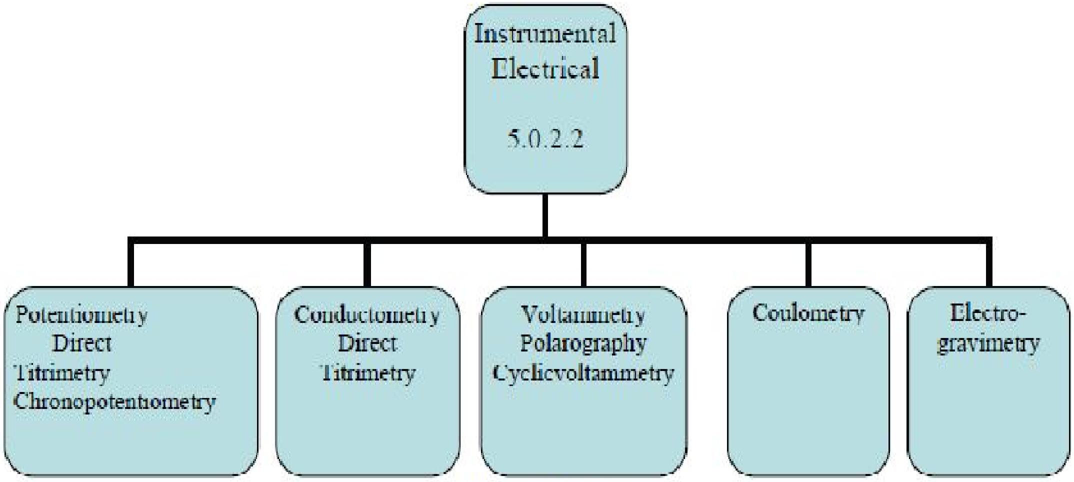
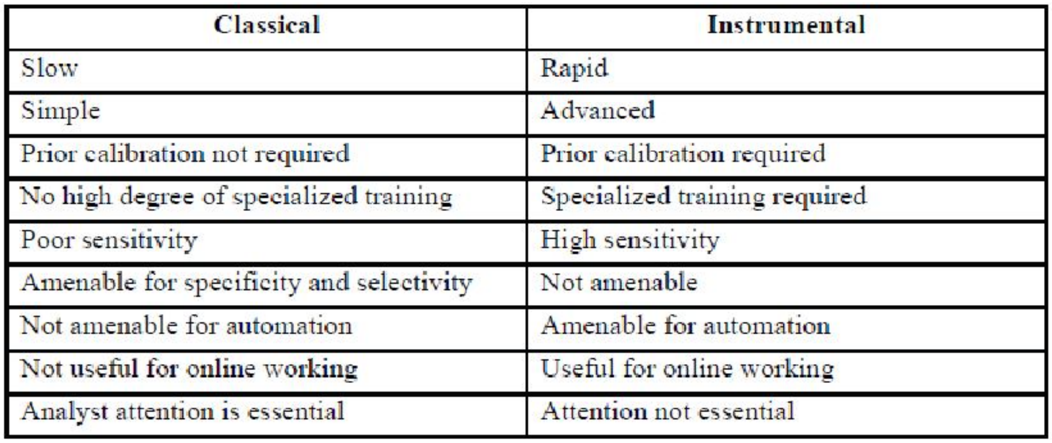


Figure-5.0.2.2

Table.3.



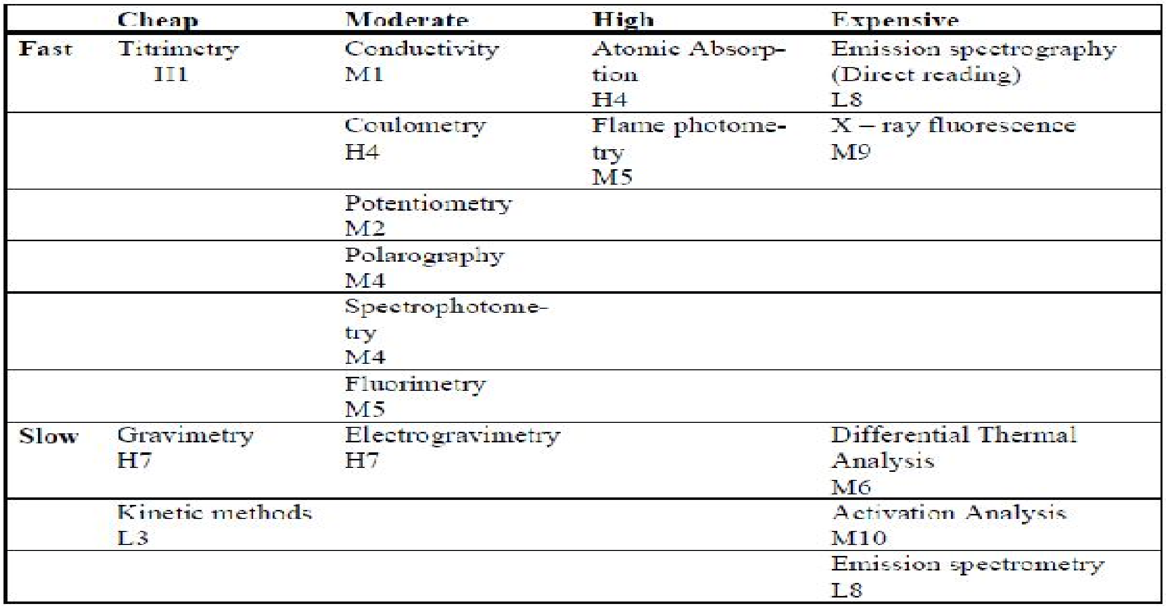
Classical	Instrumental
Slow	Rapid
Simple	Advanced
Prior calibration not required	Prior calibration required
No high degree of specialized training	Specialized training required
Poor sensitivity	High sensitivity
Amenable for specificity and selectivity	Not amenable
Not amenable for automation	Amenable for automation
Not useful for online working	Useful for online working
Analyst attention is essential	Attention not essential

With the information that is presented herein one question arises - how can I decide which of the several alternative techniques (methods) should be chosen for any particular situation? In other words what are the factors that need to be considered in the choice of the analysis technique? The answer depends, among others, upon the following [8] :-

1. Kind of sample: whether alloy, ionic solution, ore, gas, soil, biological, geological, environmental, organic, polymeric, macromolecular etc,.
2. Nature and approximate quantity of the desired constituent
3. Nature and approximate quantity of the impurity
4. Type of information required - % desired constituent; % total impurities; absence of specific contaminant.
5. Required precision
6. Speed within which the analysis is to be completed
7. Whether the analysis is for process control or for on line inspection
8. Availability of the equipment
9. Cost factor
10. Personal preference.

General perspectives concerning the techniques with respect to speed, cost, accuracy, and the lowest detectable level are presented in **Table.4**

Table.4

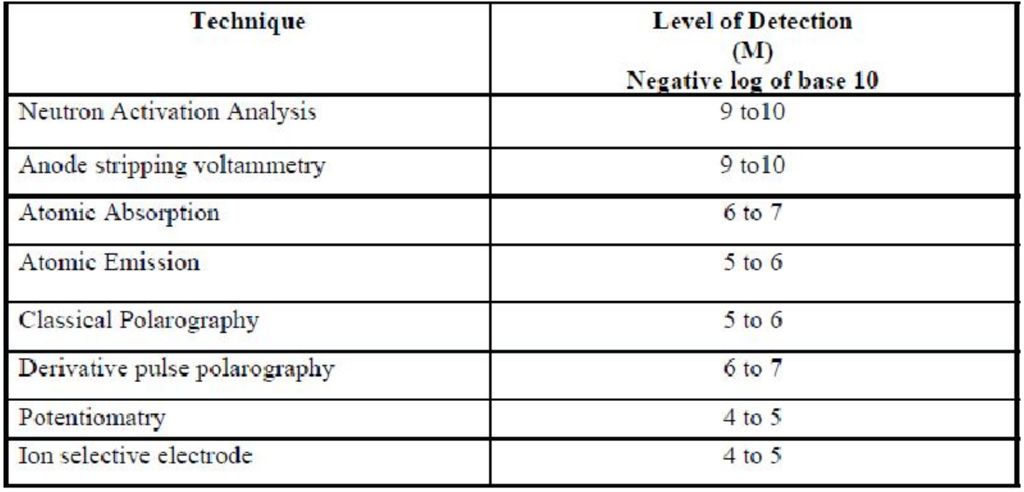


	Cheap	Moderate	High	Expensive
Fast	Titrimetry H1	Conductivity M1	Atomic Absorption H4	Emission spectrography (Direct reading) L8
		Coulometry H4	Flame photometry M5	X – ray fluorescence M9
		Potentiometry M2		
		Polarography M4		
		Spectrophotometry M4		
		Fluorimetry M5		
Slow	Gravimetry H7	Electrogravimetry H7		Differential Thermal Analysis M6
	Kinetic methods L3			Activation Analysis M10
				Emission spectrometry L8

Accuracy is indicated by: H-High- (error – not less than 1%)
M-Medium-(error – 1 to 5%)
L- Low-(error – not less than 5%)

Lowest limit of detection:
1- cg per cubic decimetre; 2- mg per cubic decimetre; 3- µg per cubic decimetre
4- mg per cubic decimeter;5- µg per cubic decimetre; 6- mg actual weight
7- mg actual weight (macro analysis); 8- parts per billion; 9- 0.001 per cent
10- parts per billion
Source: Arthur I Vogel [9].
An alternative look at techniques and levels is shown in Table.5**.**

Table.5 Detection Limits of Typical Instrumental Methods

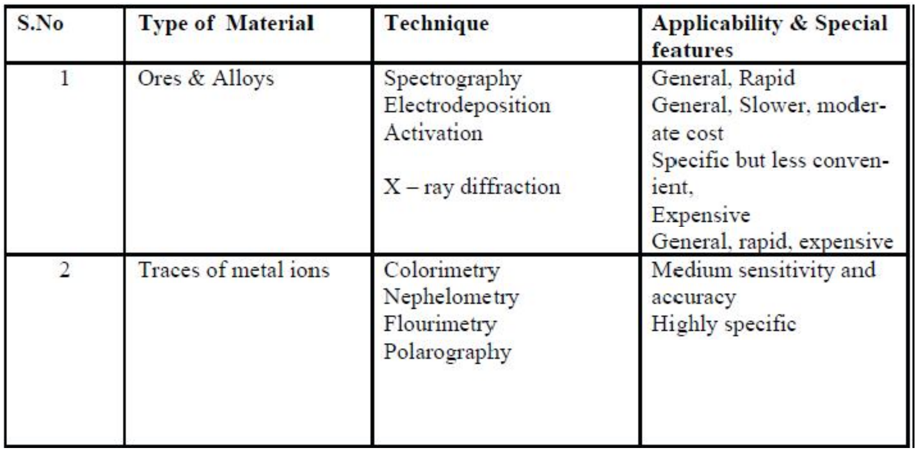


Technique	Level of Detection (M) Negative log of base 10
Neutron Activation Analysis	9 to10
Anode stripping voltammetry	9 to10
Atomic Absorption	6 to 7
Atomic Emission	5 to 6
Classical Polarography	5 to 6
Derivative pulse polarography	6 to 7
Potentiomatry	4 to 5
Ion selective electrode	4 to 5

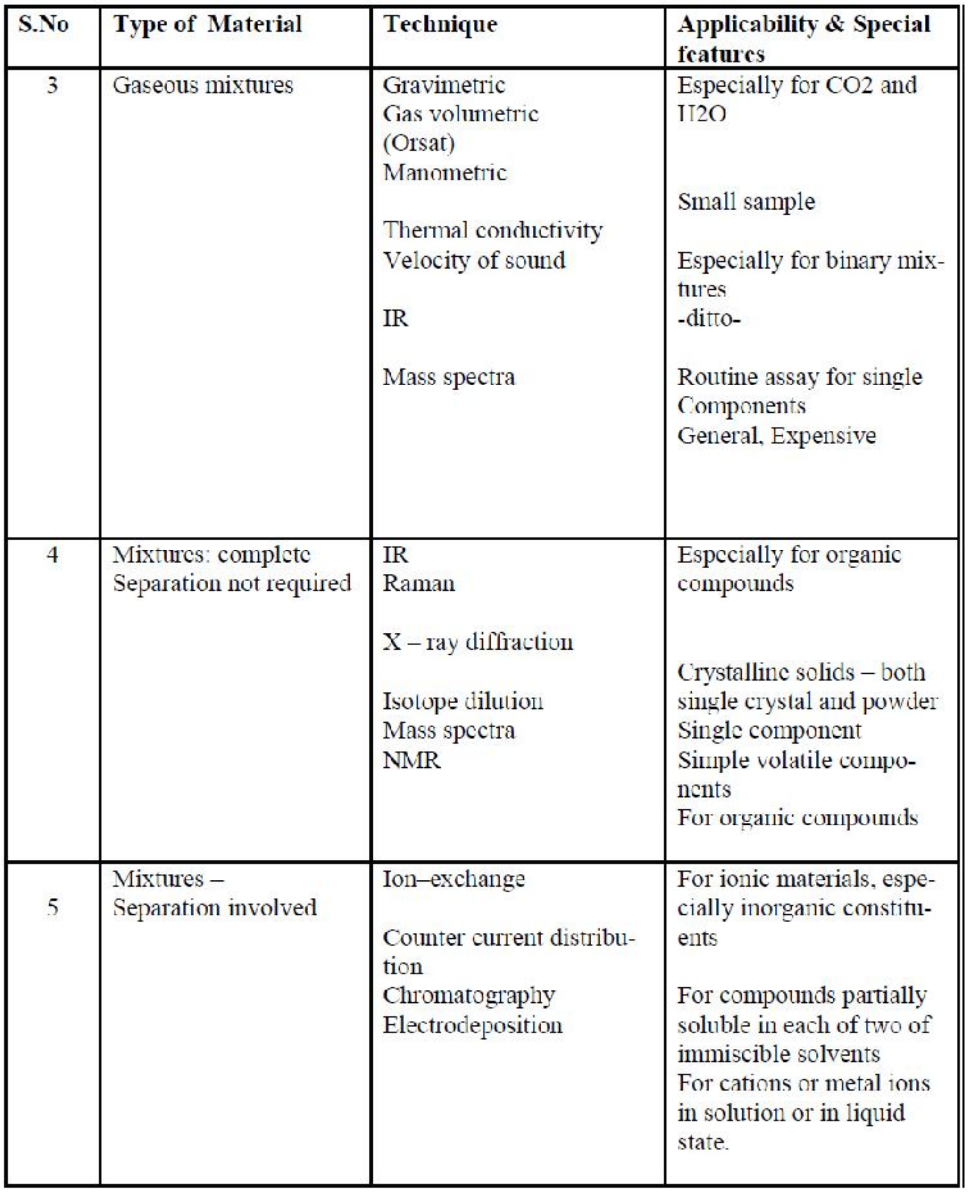
Source: A.K.DE[10].

Table.6 is a collection of materials, applicable technique and special features of the technique [8].

Table.6



S.No	Type of Material	Technique	Applicability & Special features
1	Ores & Alloys	Spectrography Electrodeposition Activation X – ray diffraction	General, Rapid General, Slower, moderate cost Specific but less convenient, Expensive General, rapid, expensive
2	Traces of metal ions	Colorimetry Nephelometry Flourimetry Polarography	Medium sensitivity and accuracy Highly specific



S.No	Type of Material	Technique	Applicability & Special features
3	Gaseous mixtures	Gravimetric Gas volumetric (Orsat) Manometric Thermal conductivity Velocity of sound IR Mass spectra	Especially for CO_2 and H_2O Small sample Especially for binary mixtures -ditto- Routine assay for single Components General, Expensive
4	Mixtures: complete Separation not required	IR Raman X – ray diffraction Isotope dilution Mass spectra NMR	Especially for organic compounds Crystalline solids – both single crystal and powder Single component Simple volatile components For organic compounds
5	Mixtures – Separation involved	Ion–exchange Counter current distribution Chromatography Electrodeposition	For ionic materials, especially inorganic constituents For compounds partially soluble in each of two of immiscible solvents For cations or metal ions in solution or in liquid state.

The article is intended to give an overall and a bird's eye picture of the analytical operations and in depth information is definitely and decidedly out of the scope. The main intent of the presentation is to put before the novice the gamut of chemical analysis at his finger tips.

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