Materials and Energy Balance

Materials Balance and Analysis

The equilibrium concentration of both products and reactants in a chemical reaction can be determined when the temperature, pressure, and equilibrium constant at that T and P is provided

Calculation of the concentration of the species in an iron blast furnace consisting of multiple reactions is possible by careful and detailed accounting of each element in each species taking place in all reactions

Material balance is the basic procedure that enables engineers specify all the amount of species without a knowledge of the complete system



If the composition and the concentrations of the reactants are known, the concentration of the products can be determined thanks to the principles of mass balance

The account of the raw materials is held routinely in every plant by using printed forms including the type of raw material and space to write the measured weights of input raw materials and their composition

The output section is reserved to write the measured or calculated quantities of products and their analyses

Material balances kept routinely in every plant serve as an accounting of the process and constitute valuable records of operation on the basis of which cost calculations can be made

The furnace charge has to be changed often in steelmaking practice due to changes in the specifications of the costume

Manipulations in charge proportions can be economically and accurately made based on the composition data

The operating variables like temperature and pressure in addition to composition can be altered in order to improve the efficiency of the process if only the exact variables of the system at the initial state is known by material balance

			METAL	TYPE	
ELEMENT	SYMBO L	Non-alloy Free cutting steel	Silicon- electrical steel	High- speed steel	Silico- manganese steel
Manganese	Mn				between 0.5% and 1.9%
Silicon	Si		between 0.6% and 6%		between 0.6% and 2.3%
Chromium	Cr	×	× ×	3-6%	
Carbon	с		not more than 0.08%	0.6% or more	not more than 0.7%
Aluminium	AI	2	can contain no more than 1%		
Molybdenu m	Мо			*	
Lead	Pb	0.1% or more	× ×		<i>2</i>
Sulphur	S	0.08% or more			
Tungsten (Wolfram)	W	2 S		*	
Selenium	Se	more than 0.05%			
Tellurium	Te	more than 0.01%			
Bismuth	Bi	more than 0.05%			
Vanadium	V	2	85 26	*	
Other Elements			may contain no other element in a proportion that would give the steel the characteristics of another		may contain no other element in a proportion that would give the steel the characteristics of another

In a commercial industrial operation it is difficult to make direct measurements on the process variables as a whole

The composition and concentration of reactant raw materials is conveniently measured, other process variables like the composition of flue gases may have to be estimated or calculated from the given data

The principles of general chemistry including the following stoichiometric principles enable us to calculate the missing parts of material balances:

- Conservation of mass
- Mass relations in metallurgical reactions
- Volume relations in metallurgical reaction
- Molar units
- Gas laws
- Excess reactants

Mass relations in metallurgical reactions

In extractive metallurgy processes, the accounting of the weight of products obtained from a given quantity of reactants is important

The simple way to determine the weight of the products is to make use of the atomic weights of elements appearing in a reaction

- 1. Write a correct chemical reaction describing the particular process $Fe_3O_4 + 4CO = 3Fe + 4CO_2$
- 2. Obtain the molecular weights of compounds appearing in reaction from atomic weights of elements

Atomic weights (g)	Molecular weights (g)
Iron: 56	Fe ₃ O ₄ : 3*56+4*16 = 232
Carbon: 12	CO: 12+16 = 28
Oxygen: 16	CO ₂ : 12+2*16 = 44

3. Calculate the relative weights of the reactants and products involved in reaction by multiplying the respective atomic or molecular weights with the stoichiometric coefficients

Number of moles Relative weights Fe₃O₄ + 4CO = 3Fe + 4CO₂ (1) (4) (3) (4) 232 4*28=112 3*56=168 4*44=176 344 = 344 Example – Calculate the weights of Fe_3O_4 and CO necessary to produce 150 kg of iron

 $Fe_{3}O_{4} + 4CO = 3Fe + 4CO_{2}$

Atomic weights (g) Iron: 56 Carbon: 12 Oxygen: 16 Molecular weights (g) Fe_3O_4 : 3*56+4*16 = 232 CO: 12+16 = 28 CO_2 : 12+2*16 = 44

Weight of
$$\text{Fe}_3 O_4 = \left(\frac{232}{168}\right) * 150 = 207 \text{ kg}$$

Weight of $\text{CO} = \left(\frac{4*28}{168}\right) * 150 = 100 \text{ kg}$
Weight of $\text{CO}_2 = \left(\frac{4*44}{168}\right) * 150 = 157 \text{ kg}$

Conservation of mass

The relationships between the quantities and analyses of the materials entering, leaving and participating in a process are obtained by using the law of conservation of mass

For any component X which may be chosen as an element or compound depending on the specific process, the generalized mass balance equation is written as

$$\sum m_R (\% x)_R = \sum m_P (\% x)_P \pm \Delta m_x$$

where m_R and m_P represent the masses of substances making up the reactants and products respectively, $(\% x)_R$ and $(\% x)_P$ are the weight percentage of X present in reactants and products, Δm_x represents an accumulation or depletion of X depending on its sign

Steady state process

Process yields a constant weight of outputs for a constant weight of input materials per unit time

 Δm_x for a steady state process is zero and calculations are simplified considerably Consider the continuous process operating at steady state: A + B + C = D + E + F

Explicit mass balance for x: Explicit mass balance for y: Explicit mass balance for z: $m_{A}(\%x)_{A} + m_{B}(\%x)_{B} + m_{C}(\%x)_{C} = m_{D}(\%x)_{D} + m_{E}(\%x)_{E} + m_{F}(\%x)_{F}$ $m_{A}(\%y)_{A} + m_{B}(\%y)_{B} + m_{C}(\%y)_{C} = m_{D}(\%y)_{D} + m_{E}(\%y)_{E} + m_{F}(\%y)_{F}$ $m_{A}(\%z)_{A} + m_{B}(\%z)_{B} + m_{C}(\%z)_{C} = m_{D}(\%z)_{D} + m_{E}(\%z)_{E} + m_{F}(\%z)_{F}$ Example – Make explicit mass balances for Fe, C and O in the following reaction: $Fe_3O_4 + 4CO = 3Fe + 4CO_2$

One mole excess CO is given to the furnace for each mole of magnetite

Fe balance:

$$m_{\text{Fe}_{3}\text{O}_{4}}(\%Fe)_{\text{Fe}_{3}\text{O}_{4}} + m_{\text{CO}}(\%Fe)_{\text{CO}} = m_{\text{Fe}}(\%Fe)_{\text{Fe}} + m_{\text{CO}_{2}}(\%Fe)_{\text{CO}_{2}}$$

$$232(\frac{168}{232}) + 5 * 28(0\%) = 3 * 56(100\%) + 4 * 44(0\%)$$

$$168 = 168$$

C balance:

$$m_{\text{Fe}_{3}\text{O}_{4}}(\%C)_{\text{Fe}_{3}\text{O}_{4}} + m_{\text{CO}}(\%C)_{\text{CO}} = m_{\text{Fe}}(\%C)_{\text{Fe}} + m_{\text{CO}_{2}}(\%C)_{\text{CO}_{2}} \pm \Delta m_{C}$$

232(0%) + 5 * 28 $\left(\frac{12}{28}\right)$ = 3 * 56(0%) + 4 * 44 $\left(\frac{12}{44}\right)$ + 12
60 = 48 + 12

O balance:

$$m_{\text{Fe}_{3}O_{4}}(\%0)_{\text{Fe}_{3}O_{4}} + m_{\text{CO}}(\%0)_{\text{CO}} = m_{\text{Fe}}(\%0)_{\text{Fe}} + m_{\text{CO}_{2}}(\%0)_{\text{CO}_{2}} \pm \Delta m_{C}$$

$$232(\frac{64}{232}) + 5 * 28\left(\frac{16}{28}\right) = 3 * 56(0\%) + 4 * 44\left(\frac{32}{44}\right) + 16$$

$$144 = 128 + 16$$

Volume relations in metallurgical reactions

The volume reactions between gaseous members of a chemical reaction are obtained from their stoichiometric coefficients similar to mass relations

This relation is based on the Avogadro's law which states that equal volumes of different **gases** will contain the same number of molecules under the same conditions of temperature and pressure

Example – Consider again the reduction of magnetite to metallic iron by carbon monoxide at constant temperature and pressure

 $Fe_3O_4(s) + 4CO(g) = 3Fe(s) + 4CO_2(g)$

4 liters of CO will produce 4 liters of CO₂

There is an important difference between the mass and volume relations: While the sum of the weights of products and reactants are equal, the sum of volumes may be different

Example -

$$CO_2(g) + C(s) = 2CO(g)$$

100 m³ 200 m³

Molar units

The coefficients preceding the formulas in reaction equations indicate the relative number of moles

Molar units used in material balance are gram-atom, kg-atom, g-mole and kg-mole

A gram-atom of an element is the mass in grams of this element in proportion to its atomic weight

 $gram - atom of an element = \frac{mass in grams}{atomic weight}$

Example – A gram-atom of carbon is 12 grams in mass, a kg-atom of carbon is 12 kilograms

A gram-mole of a compound is the mass in grams of this compound in proportion to its molecular weight

 $gram - mole \ of \ a \ molecule = \frac{mass \ in \ grams}{molecular \ weight}$

Example – A gram-mole of CO_2 is 44 grams in mass, a kg-mole of CO_2 is 44 kilograms

Gas laws

Extractive metallurgy processes always contain gaseous phases participating in the reactions

Gas laws provide valuable simplifications to mass balance problems in the case of missing data

Boyle's law - $P \propto \frac{1}{v}$ at constant T

Guy-Lussac's law - $V \propto T$ at constant P

Ideal gas law -
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = R$$

Useful deductions:

- One gram-mole of any gas at standard temperature and pressure (273 K, 1 atm) occupies 22.4 liters
- One kg-mole of any gas occupies 22.4 m³ at standard conditions
- $\bullet \quad \frac{V_T}{T} = \frac{V_{273}}{273}$

Example – Calculate the volume of air necessary to obtain blister copper in the Cu_2S converting process from a charge of 5000 kg

 $Cu_2S + O_2 = 2Cu + SO_2$

1 kg-mole Cu_2S consumes 1 kg-mole of O_2 to yield copper

5000 kg of charge equals $\frac{5000}{(2*64+32)} = 31.2$ kg-moles

31.2 kg-mole Cu_2S consumes 31.2 kg-mole of O_2

Volume of $O_2 = 31.2 * 22.4 = 700 \text{ m}^3$

Volume of air necessary = $700 * \frac{1}{0.21} = 3300 \text{ m}^3 \text{ at STP}$

Conducting the analysis at STP simplifies calculations and is suitable when exact gas temperatures are not known or when different gases at different temperatures are involved

The volume of gases under conditions different than STP can be calculated by the ideal gas law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Excess reactants

In many metallurgical processes the quantities of reactants supplied to the system are not in the exact proportions demanded by the reaction equation

More oxygen has to be supplied above the stoichiometric requirements in combustion, roasting or converting processes to prevent unreacted reactants

The amount by which a reactant is present in excess over the theoretically required quantity is expressed as the percentage excess of this reactant

% Excess air = $\frac{(Volume of total air-Volume of theoretical air)}{Volume of theoretical air} * 100$

Example – 25% excess CO is given to the system for each kg-mole of magnetite $Fe_3O_4 + 4CO = 3Fe + 4CO_2$

Material balance is the basic procedure that enables engineers specify all the amount of species without a knowledge of the complete system

Charge calculations enable engineers estimate the amount and ratio of the initial reactant charge of a furnace required to obtain the desired yield

The equilibrium concentration of both products and reactants in a chemical reaction can be determined when the temperature, pressure, and equilibrium constant at that T and P is provided

Knowledge on the initial or equilibrium state of a system is important since thermodynamic state properties do not depend on the path taken

Material balance should be supplemented with accurate material analysis results

Various types of photometers, spectrophotometers and other advanced instruments like ICP, XRF, XRD enable a rapid quantitative measurement of sample composition with high accuracies

Analyses of metallurgical interest

1. Ultimate analysis: Percentages of elements are reported. Instruments used: XRF, ICP-AES

Element	Weight %
0	46.60
Al	35.85
Са	3.63
•••	

2. Rational analysis: Percentages of compounds forming the sample are reported by gas analysis

Ultimate analysis can be combined with the information from XRD analysis to obtain rational Phases present in the sample: Al_2O_3 , CaO,...

Compound	Weight %
Al ₂ O ₃	80.45
CaO	5.72

3. Mineralogical analysis: Rational analysis given in terms of percent minerals making up sample
 Mineral Weight %
 Corundum 80.45

Limestone 5.72

4. Proximate analysis: Commercial specification of the results of standardized test Quantities reported in coal analysis: Fixed carbon, volatile matter, moisture, ash Compositon of various inputs and outputs should be determined in order to write material balance

A representative sample of the material is obtained by different methods depending on the state of the material

The precision of a weight measurement depends on the number of samples taken Its accuracy also depends on the sampling procedure

If the material being sampled is homogeneous, a single or very few samples may be enough to measure the weight accurately

On the other hand, a mixture (such as slag on top of liquid metal) may not be well-mixed and may require extensive sampling to improve the accuracy of the reported analysis

		Stag composition					
Heat	Sample Location	Fe	Cr	SiO ₂ CaO	MgO	A1203	Mn0
A	Charging Door	20.00	26.99	6.16 14.50	6.52	1.50	6.58
	Side Door	22.00	24.71	7.10 15.17	4.52	1.83	6.71
В	Charging Door	27.60	21.12	5.44 14.84	4.95	0.71	5.95
	Side Door	27.40	21.30	5.30 14.84	5.18	2.24	6.05
С	Charging Door	21.20	25.12	7.84 15.59	6.09	2.15	4.44
	Side Door	20.40	25.14	7.86 15.93	5.40	1.95	3.12
D	Charging Door	23.66	27.94	7.52 14.11	11.64	1.99	6.13
	Side Door	23.92	28.82	7.70 14.39	3.52	1.97	6.26
Е	Top of Slag	14.20	29.92	7.10 20.06	1.59	3.04	5.50
	8" below Top	14.60	30.25	6.74 19.41	1.30	2.97	5.50

Granular solids and lump ores (such as coal) present the biggest problems in sampling and require the use of carefully designed sampling procedures

The size of solid sample depends on 3 parameters:

- Particle size of the material
- Variability of the measured property from one particle to another
- Microstructural homogeneity of the material (valuable mineral grains may or may not be uniformly distributed)

Therefore theoretical prediction of the required sample size is impossible

A procedure for finding the sample weights based on sampling data of a known material: $W = kD^{a}$

where W is the sample weight, D is the maximum particle size in the sample, k is a constant depending on the material, a is a constant usually taken as 2

The only way to determine k is to have sampling data of the same material (weight of a material at one maximum size)

Example – A copper ore is known to give a satisfactory 100 g sample when the ore is crushed and ground to a maximum size of 1 mm. What size sample is required if the sampling of the ore is done from a crusher set at 12 mm opening?

Large piles of ore are needed to convert to composite samples to make accurate measurements by obtaining multiple parts

Example – The sampling procedure for coal from lots of 1000 tons or less is given in ASTM standards D492 and E105

	Particle Size of Coal Being Sampled							
	$5/8^{\rm H}$ and Under	5/8" to l" Inclusive	1" to 2" Inclusive	Over 2" to 6" Inclusive	Over 2" to 4" Inclusive	Over 4" to 6" Inclusive	Over 6" and bottom size 5/8" or over	0ver 6"
Under 8% Ash Min. No. of Cuts Min. Wt. of each Cut, 1bs. Min. Gross Sample Wt., 1bs.	15 2 30	15 4 60	15 6 90	15 10 150	15 10 150	15 15 225	35 30 1050	-35 20 700
<u>8 - 9.9% Ash</u> Min. No. of Cuts Min. Wt. of each Cut, lbs. Min. Gross Sample Wt., lbs	20 2 40	20 4 80	20 6 120	20 10 200	20 10 200	20 15 300	35 30 1050	35 20 700

Sample Sizes Required for Sampling Coal (From ASTM Standard D492)

Statistical certainty is provided by this procedure such that 95% of the composite samples will be within 10% of the true average composition Samples are taken

- by a single motion of the sampling instrument in such a way that the time for each sampling is the same
- in a random way such that every part of the pile has a probability of selection and the entire pile is represented proportionally in the gross sample

There are many sampling instruments for granular solids and the only criterion of selection is that each sample be truly representative of the pile or stream at that point or that instant of

time



Once the composite sample has been collected, it must be reduced to a size such that an analysis can be made

Example – ASTM D492 requires the gross coal sample to be crushed and screened so that 95% by weight will pass through a No. 4 sieve (5 mm) and 100% will pass a 10 mm round hole screen. Then sample is reduced to 27 kg by further crushing and screening to a sample of not less than 0.5 kg so that 95% will pass a No. 8 sieve (2.5 mm)

Sampling of liquids depend mainly on the mixedness of the liquid mixture and may require lengthy sampling procedures for heterogeneous liquids

Typically sampling spoons are plunged into liquid metal baths and withdrawn with a sample which is then poured into a metal chill mold

Other metal sampling devices that can be plunged deep into the metal with protective seals of caps that melt away and allow metal to be drawn into the sample mold



The number of samples from a metal bath that is required to obtain accurate accurate results also depends on the concentration and density of the element of interest

Example – Samples taken at the same time, from different locations in an electric arc furnce have varying compositions due to the heterogeneity of the metal

				and the same states				
		Metal Composition %						
Heat	Sample Location	C	Mn	Si	Ni	Cr		
A	Charging Door Side Door	.014	.20	.20 .20	13.32 13.56	2.08		
С	Charging Door Side Door	.04 .032	.20	.04	12.68 12.68	2.24		
D	Charging Door Side Door	.023 .024	.22	.030	11.75 11.68	4.28		
	Distance below the Interface							
	6"			.01	11.96	3.44		
F	6"			.02	12.40	3.44		
s:)	18" 27"			.02	12.28	3.44		

Metal and Slag Composition After Oxygen Blow (Carbon Boil) in a 15-foot Diameter Electric Arc Furnace

Similarly, alloy additions made to stationary baths may not properly disperse or elements reduced fro slags may be concentrated at the slag/metal interface

	and the second		
Heat	Depth into Metal Bath (Inches Below Slag Layer)	%Ni	%Cr
A	0 (Slag/Metal Interface) 6 12 <u>18</u>	6.88 6.88 7.12 (9.50)*	34.36 27.79 25.62 22.93 (18.08)*
В	0 (Slag/Metal Interface) 18 0 ^t (Interface) 6 ^t 18 ^t	5.28 15.16 3.44 10.04 15.60 (13.30)*	37:33 11.74 38.33 23.44 11.16 (17.24)*

Vertical Stratification Within the Metal Bath

* Average of bath after thorough stirring.

t Taken after five minutes of ineffective argon bubbling.

The type of sampler used for metals also has an effect on the accuracy of the analysis



PERCENT MANGANESE

Slag samples are often taken by spoon and poured onto clean concrete where the pancake is allowed to harden. It is then crushed for analysis

Care must be taken to check for entrained metallic particles and gas bubbles that may affect the density measurements adversely

Samples of the process gases are often taken for compositional analysis or particulate analysis Sampling for particulates is done with various methods, all of which depend on pulling the gas through a device which traps out the particles and measures the total gas flow at the same time

Example – ASTM standard 2006 recommends uisng a glass cloth filter to trap large relatively large particles, collecting them from about 2000 m3 of gas drawn through the sample over a 24 hour period

Other sample filters such as paper have to be used to trap very fine fumes, porous ceramic membranes for hot gases and filters of cellulose esters to collect colloids



For highest accuracy of particulate analysis, samples should be taken under isokinetic conditions (the velocity of the dust stream at the entrance to the probe = velocity upstream)

Direct weighing of charge materials or products is a routine procedure in many metallurgical procedures

There are a large variety of instruments used for weighing small or large batches:

- Belt weighers The weight passing a given location on a moving belt is obtained by multiplying the speed of belt and the force on the roller, measured by load cells
- Hopper weighers Feed hoppers, charging buckets, scale cars are weighed by load cells built into their supporting frame
- Platform weighers Stationary scales that are commonly used to weigh tons of ladles in steel mills or a few kg of alloying additions





 Crane weighers – Load cells are fitted to the spreader beam or located on the moving crab on large bridge cranes



• Roller converyor weighers - Slabs, ingots and other large mill products may be weighed while being transported via roller conveyors

This is done by active weigh scales where a section of the roller table acts as a platform scale



In processes involving molten slag and metal, mass cannot be easily measured directly

Density and volume data are obtained instead of weight of the material This requires an accurate measurement of density since the volume measurements are commonly inaccurate

 Liquid density – If the material is liquid at room temperature, a graduated cylinder and laboratory balance can give accurate values of density If the material is liquid in the process, but solid at room temperature, the solid sample density in combination with overall volume may be used for very inaccurate results Commonly, the density of the solid is determined and an assumption of the shrinkage upor

solidification is made

 Bulk density – The gross mass of a batch of granular solids / the volume of the container The most important aspect of the procedure that affects the accuracy of the measurement is to have a large enough sample box compared to the average particle size

$$\rho_{bulk} = (1 - \omega)\rho_o$$

where ho_o is the true density of the solid phase, ω is the void fraction

Example – ASTM standard D292-29 recommends using 60cm x 60cm x 60cm boxes for coke grains that are 12.5 cm or smaller in diameter, 30cm x 30cm x 30cm boxes for 2.5cm or smaller The weighing box is filled by a shovel from a height of 5 cm above the top of the box with no attempt to spread or arrange the coke

The accurate measurement of the temperature of process input and output materials is required in order to establish an energy balance A wide variety of temperature sensors are available

Practical Measurement Range of Temperature Sensors*

Sensor	Temperatur Low	e Range °C High
Thermocouples		
Copper-Constantan - ISA Code T	-300	+700
Chromel-Constantan ³ - ISA Code F	+32	+1400
Chromel-Alumel ⁴ - ISA Code K	+32	+2300
Platinum-Platinum/10% Rhodium5 - S	+32	+2700
Platinum-Platinum/13% Rhodium ⁵	+32	+2700
Iridium/Rhodium-Iridium	+1425	+36.00
Tungsten-Rhenium		+3600
Resistor Bylbs		
Platinym ⁷	- 325	+1000
Nickel ⁸	-40	+400
Copper	- 330	+250
Total Radiation Pyrometers ⁹		
High range	+1700	+1700
Intermediate range	+1000	+3400
Low intermediate range	+500	+1200
Low range	+100	+700
Spectracally Selective Pyrometers		
Optical or brightness pyrometer10	+1400	+7500
Two-color pyrometer 1	+1400	+6500
Filled System Thermometers		
Liquid-filled (SAMA Class 1A ¹³)	- 300	+600
Mercury-filled (Class V)	-38	+1000
Vapor-filled (Class II)	-432	+600
Gas-filled (Class III)	-450	+1400
Simetal Thermometers ¹²	-300	+1000
Pyrometric Cones	+1095	126.60
yromeer re cones	+1085	+3660
Surface-Applied Temperature-Sensitive		
types)	+100	+2500
() pc 3 /	+100	+2500

Temperature measurements in molten metals are made using disposable Pt-Pt/Rh or W-Re thermocouples contained in cardboard sleeves that fit over reusable steel bars

When making heat balance in industrial environments, the temperature of gas or air streams play a very important role

The measurement of the temperature of a gas is very different from a measurement in liquids and solids

The problem is the thermocouple sensor may not attain the same temperature as the gas

The thermocouple is usually enclosed in a metal protection tube which is connected to an opening in the wall of the duct, resulting in a temperature gradient through the tube The error in measurement depends on many parameters including the rate of flow of the gas, the length, diameter and materials of the tube and the thermocouple wires, and the temperature of the wall to which the tube is attached

Example – Thermocouple located in the wall of a flue with a hot gas stream may indicate temperatures 80K less when the actual gas temperature is 700K

Furthermore, it is not sufficient to measure the temperature of the gas at only one point, since the flow may be stratified The average of flow and temperature measurements made at multiple points should be used

to calculate the stream average heat flow

Analysis of processes also requires information about the mass-flow rates of gases There are a large variety of instruments for measuring flow in closed channels and ducts



Figure 3.7-7 Venturi meter



Measurement Characteristics of Process Flow Meters*

Туре	Pipe Size In.	Volume range	Accuracy	Remarks
Volumetric Meters				
Oscillating-piston positive-				
displacement.	1/2 to 2	3 to 120 gpm.	±0.20%	Repeatability=0.015%
Lobed-rotor	1% to 24	8 gpm, to 25,000 bbl./hr.	±0.20%	Repeatability 0.015%
Nutating-disk.	½ to 2	2 to 160 gom.	×1.00%	Receatability = 0.100%
Metering pump				
(proportioning)	Offline	Adjustable 4 to 100% of range	at 1.00%	Response=20 sec. full scale
Variable-Area Meters				
Plugged and ported cylinder	1 to 4		≈0.25%	Mainly for highly viscous fluids.
Tapered-tube rotameter with				
free bob	½ to 4	•••••••••••••••••••••••••••••••••••••••	∗0.5 to 2.0%	Generally superseded by guided float type.
Tapered-tube rotameter with				
center guide	½ to 4	••••••	±0.5 to 2.0%	Inductance bridge often used fo transmission.
Tapered-tube rotameter with				
beaded tube	up to 4		±0.5 to 2%	Enables viscosity-immune floats to be used without center guide.
Tapered-tube rotameter,				
metallic		••••••	2% of maximum bypass flow rate	 Measures bypass flow. Hence can be used on any pipe size containing ori fice or other differential-pressure producing primary flow device.
Velocity and Current Meters				
Vortex meters, liquid flow	1 to 10	6 to 60 gpm.	∞0.5%	Repeatability=0.1%
		to		Response:
		700 to 6,800 gpm.		1 & 2-in, meters∞ 300 millisec. 3 & 4-in, meters∞ 400 millisec. 6. 8 & 10-in, meters∞ 500 millisec.
Vortex meters, gas	1 to 10	750 std. cu. ft./hr. at 20 psig. to	* 1.0%	Response: 1 & 2-in, meters=300 millisec.
		150,000 std, cu. ft./hr. at 1.500 osig.		3 & 4-in, meters ≈ 400 millisec. 6, 8 & 10-in, meters ≈ 500 millisec.
		to		
		1.2 million std. cu. ft./hr. at 20 psig.		
		to 25 million std. cu. ft./hr. at 1 500 psig		
Vortex mass-flow meter, gas	1 to 10	5 to 25,000 lb./min.	×0.1% over 5:1 range ∗0.3% over	Response=1 sec.
			25:1 range	
elocity and Current Meters Turbine meter with mag-			-	
netic signal pickup Turbine meter (viscosity	1 to 10	6 to 7.200 gpm.	±0.25%	Repeatability===0.02%
compensated)	6 to 16	600 to 15,000 bb!./hr.	±0.15%	Reapeatability = + 0.015%
Electromagnetic meter		0.1 to 250 million gal./day	= 1.0%	Responds almost instantaneously to
				changes in flow rate.

*D. M. Considine, Chemical Engineering, Jan. 29, 1968, p. 84.

Sometimes it is necessary to measure and record pressures in systems where a gas phase is involved the process e.g. Metal ore reduction by CO gas In metallurgical processes this rarely involves pressures outside 10-6 to 10 atm

A sensing device having some form of elastic element is used for pressures above 5 atm, like helixes, spirals, etc.

For lower pressures manometers and bells are commonly used

Manometers may utilize mercury, water or oil as the fluid, depending on the range of P



Once a significant sample has been obtained, an accurate chemical analysis must be made The technique used determines the accuracy of the results and depends on the physical state and nature (metallic, oxide, silicate, etc.) of the material as well as on the level of concentratio of the element of interest

	Chemical Analyses	Sample	Preparation Time	Analytical Time
x-ray diffraction Gravimetric analysis Volumetric analysis	Emission Spectroscopy	Solid Disk (Compacted powder)	Minutes	Fast (seconds)
ir absorption	Atomic Absorbtion	Solution	Depends on sample-slow if solid, fast if solution.	Fast
	Colorimetric Analysis	Solution	0	Moderate
Colorimetric analysis	X-Ray Fluorescence	Solid- powder	Minutes	Fast (if auto- mated)
Emission spectrography	X-Ray Diffraction	Solid- powder	Minutes	Slow
Atomic absorption	Gravimetric	Variable	Hours	Slow
Gas chramatanranky	Volumetric	Solution	Hours	Slow
<u> </u>	Fire Assaying	Powder	Hours	Slow (hours)
	Gas Chromatography	Gas	None	Moderate (minutes)
1ppb 10 ppb 100 ppb 1 ppm 10 ppm 0.01 % 0.1 % 1 % 10 % 10C %	Infrared Absorbtion	Gas, liquid, solid	None, if gas or liquid	Fast
	Flame Photometry	Solution	16	Fast

Sample Forms and Analytical Times for Various Analytical Techniques

ICP-AE spectrometry – the fastest and most convenient method for metals Atomic emission spectroscopy uses quantitative measurement of the optical emission from excited atoms to determine the concentration of a solution Atoms are energized into the excitation region where they are de-solvated, vaporized, and atomized by a flame, discharge, or plasma (Inductively **C**oupled **P**lasma)



High-temperature atomization source provides sufficient energy to promote the atoms into high energy levels

The atoms decay back to lower levels by emitting light

Light emitted due to transitions between distinct atomic energy levels are recorded as spectra The spectra of samples containing many elements can be very crowded, and spectral separation of nearby atomic transitions requires a high-resolution spectrometer





XRF spectrometry – Requires finely ground powder sample When a material is hit with X-rays, fluorescent X-Rays are analyzed in order to gain information on the elemental composition



An energy dispersive detection system directly measures the different energies of the emitted X-Rays from the sample

An XRF spectrum is generated by counting and plotting the relative numbers of X-Rays at each energy





X-ray Diffraction – Requires finely fround powder sample Analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions Crystalline substances and spacing of planes in a crystal lattice act as three-dimensional diffraction gratings for X-ray wavelengths

X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, and directed toward the sample

The interaction of the incident rays with the sample produces constructive interference and a diffracted ray when conditions satisfy Bragg's Law





Atomic absorbtion spectroscopy

The technique measures the absorption of spectral energy characteristics by metallic atoms The fraction of the spectra absorbed is directly proportional to the concentration of the atoms Spectra are generated by using hollow cathodes made of the metal of interest, so a different cathode must be used for each element

The absorbing atoms whose concentration is determined are dissolved in a liquid which is their vaporized in a flame in the path of the spectra

Relatively free of inter-element interactions and the resulting need for corrections



Detection Detection Limits Element λ Limits Element λ 3092Å 1.0 ppm Мо 3133 0.1 ppm A1 2176 2.0 Nd 4634 10.0 Sb 0.1 Ni 2320 0.2 1936 As 3349 Nb 20.0 Ba 5535 0.1 2476 0.5 0.1 Pd Be 2349 Ρt 2659 1.0 Bi 2231 250. 0.01 0.05 Κ 7665 В 2496 4951 10.0 Ca 0.1 Pr 4427 3460 15.0 8521 0.1 Re Cs 3435 0.1 Rh Cr Co 3579 0.1 7800 0:18 2407 0.1 Rb Ru 3499 Cu 3247 1.0 4297 10.0 Sm 1.0 Dy 4212 Sc 3912 1.0 2.0 Er 4008 1.0 4594 20.0 Se 1961 Eu Si 2516 0.8 Gd 3684 1.0 3281 0.01 2874 2.0 Ag Ga 5890 0.01 Ge 2652 1.0 Na Sr 4607 0.1 10.0 Au 2428 4714 10.0 2.0 Ta Ηf 3072 0.5 Тe 2143 Нο 4104 0.1 0.4 0.1 Th 3776 In 3040 2354 0.5 2483 75. Sn Fe 1.0 Ti 3643 0.01 La 3928 4009 1.0 0.03 Ч Рb 2170 U 3515 100. 0.001 Li 6707 ۷ 1.0 3184 2852 0.05 Ma 2.0 Y 3988 Mn 2795 1.0 2139 0.01 2537 Zn Нq Zr 3601 50.0

Detection Limits for Atomic Absorption Analysis (Using Nitrous Oxide-Acetylene Flame)* The oxygen content of flue gas is an important indicator of combustion efficiency It is often monitored on a continuous basis by passing the process gas through a thermal conductivity cell with a heated filament on either side of the stream This method makes use of the strong paramagnetic susceptibility of oxygen One filament is surrounded by a magnetic field so that the oxygen in the gas sample is drawn to that side, cooling the filament

The resulting difference in resistivity of the filament is proportional to the oxygen content of the gas



Gas analysis

Orsat apparatus is used to analyze gases in terms of volume percentages of molecular species present on a dry and dust-free basis

Mole percentages which are equivalent to the ratios of partial pressures of gaseous components to total pressure are also used interchangeably

Orsat apparatus consists of a measuring burette to take about 100 cm³ of gas and a number of bulbs attached

Pyrogallol solution is used to determine the oxygen content, KOH solution for CO_2 content, CuCl, HCl solution for CO content. Other bulbs can be added for hydrocarbon contents

This apparatus, being movable, can be transported to a boiler house or similar place and the analysis of waste gas made there without the delay

Orsat apparatus gives the percentages on a dry basis since it is saturated with water

A similar apparatus exists for the determination of sulfur gases in roasting