APPENDICES

Appendix A

SUZ-4 Synthesis Conditions and Autoclave Reactors

Appendix Table A1 Chemical of Al^{3+} and Si^{4+}sources for each experiments.

Experiment No.	Al^{3+} source	Si^{4+} source
1-3	Sodium aluminate ($NaAlO_2$) (53% Al_2O_3 ,40-45% Na_2O)	Sodium silicate ($Na_2Si_3O_7$) (29% SiO_2, 40-45% Na_2O)
4	Al $(NO_3)_3.9H_2O$ (98%)	SiO_2 pure (98%)
5	Al_2O_3 (99.88%)	SiO_2 pure (98%)
6	Al (99.7%)	SiO_2 pure (98%)
7	Al (99.7%)	Carb-osil M-5 (98%SiO_2)
8-17	Al (99.7%)	Ludox AS-40 (Silica colloidal 40%SiO_2)
M1-M5	Al (99.7%)	Ludox AS-40 (Silica colloidal 40%SiO_2)
M1S-M5S	Al (99.7%)	Ludox AS-40 (Silica colloidal 40%SiO_2)

Note:

Experiment

No. 1-17: Synthesis using stainless steel autoclave-Pressure reactor Parr 300 ml, Model 4561, USA

No. M1-M5 and M1S-M5S :Synthesis using 390ml Teflon-lined home-made design stainless steel autoclave with circulating air drying oven (Forced convection BINDER GmbH Model FP240, Germany)

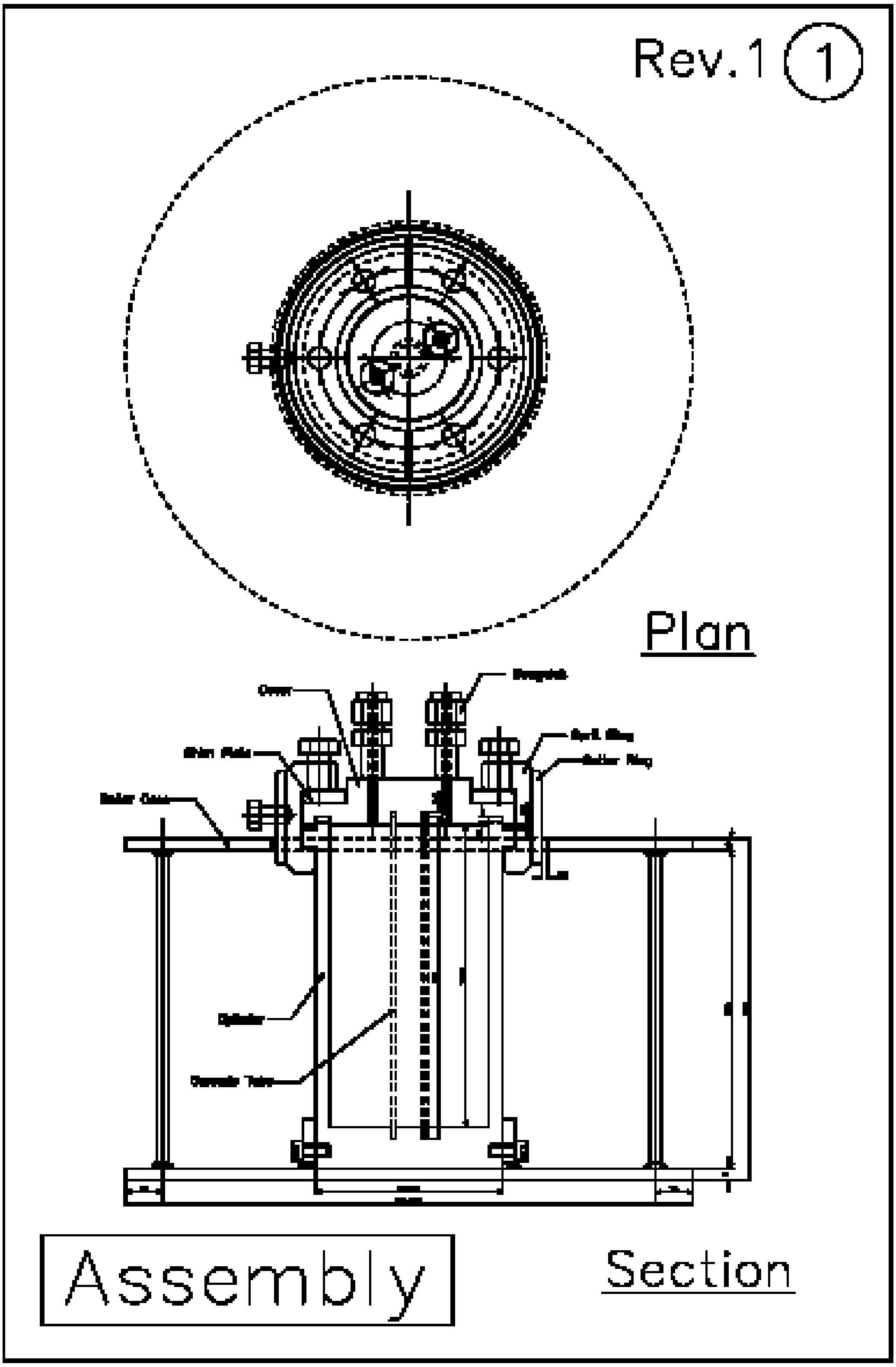
Appendix Table A2 Gel compositions for each experiment on unsuccessful synthesis of SUZ-4 zeolite powder with 300 ml stainless steel autoclave Parr Model 4561.

No.	Gel composition	Crystallization		Stirring	pH	Product
	$a\ K_2O:bAl_2O_3:c\ SiO_2:d\ (TEA)_2O:\ eH_2O$	Temp. (ºC)	Time (day)	(rpm)		
1	$25.73\ K_2O:Al_2O_3:85.51SiO_2:\ 10.97\ TEA_2O:2722.73\ H_2O$	154	4	160	-	Phillipsite
2	$1.21\ K_2O:Al_2O_3:17.31SiO_2:\ 0.93TEA_2O:474.52\ H_2O$	154	4	100	12.7	analcime
3	$3.32\ K_2O:Al_2O_3:20.351SiO_2:\ 1.22\ TEA_2O:587.68\ H_2O$	183	4	80	13.8	orthoclase
4	$13.81K_2O:Al_2O_3:162.70SiO_2:\ 9.80TEA_2O:11849.71\ H_2O$	152	4	300	13.3	Phillipsite
5	$3.40K_2O:Al_2O_3:20.72SiO_2:\ 0.45TEA_2O:583.43\ H_2O$	152	4	80	13.3	amorphous
6	$7.18\ K_2O:Al_2O_3:32.25SiO_2:\ 3.06TEA_2O:946.01\ H_2O$	155	4	80	13.7	unidentified
7	$3.87\ K_2O:Al_2O_3:15.86SiO_2:\ 0.83TEA_2O:704.90\ H_2O$	155	4	80	13.7	unidentified

Note: Experiment No. 1-3: synthesis by using Na^+

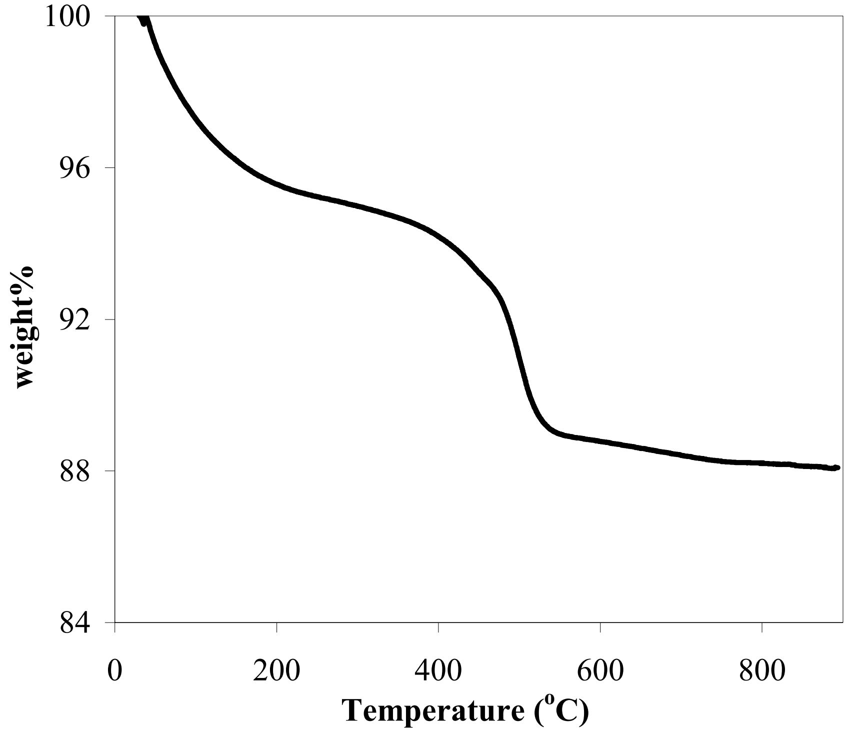
Appendix Figure A1 Stainless steel autoclave- Pressure reactor Parr 300 ml, Model 4561, USA.

Appendix Figure A2 390ml Teflon-lined home-made design stainless steel autoclave with circulating air drying oven (Forced convection BINDER GmbH Model FP240, Germany)



Appendix Figure A3 Detailed design drawing of 390ml Teflon-lined home-made stainless steel autoclave

Thermogravimetric Analysis (TGA) curve shows the thermal decomposition profile for uncalcined SUZ-4. The calcined temperature to burn out TEAOH template is about 550 °C as shown in Figure A4.



Appendix Figure A4 Thermal decomposition profile of TEAOH for uncalcined SUZ-4 zeolite at heating rate 5°C/min in air.

Mullite ceramic properties ($3Al_2O_3.2SiO_2$)

Mullite with both ends open (HB tube, No. 12-402-003, Nikko Corp., Japan) has been used for synthesis SUZ-4 zeolite membrane. The tube size is 15 (OD)*11(ID)*1,000 (L) mm.

Appendix Table A3 Mullite ceramic properties ($3Al_2O_3.2SiO_2$)

Mullite property		unit	
Al_2O_3		%	56
SiO_2		%	41
Density		g/cm^3	2.6
Flexural Strength	Room Temperature	MPa	150
	1200 ^{0}C	MPa	75
Coef.Thermal Expansion		/°C	$4.9*10^{-6}$
Thermal Conductivity		W/m.K	2.9
Service Temperature		Maximum °C	1,600

Source: Specification of mullite tube, Techno Asset Co., Ltd., page Nik.16

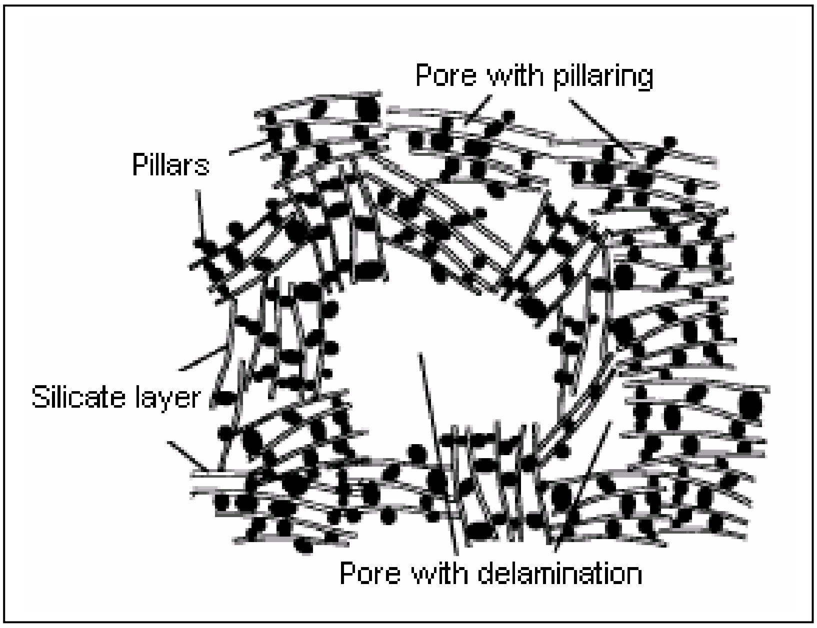
Appendix B

Nanostructures Sorbents for Mercury Capture Experiment

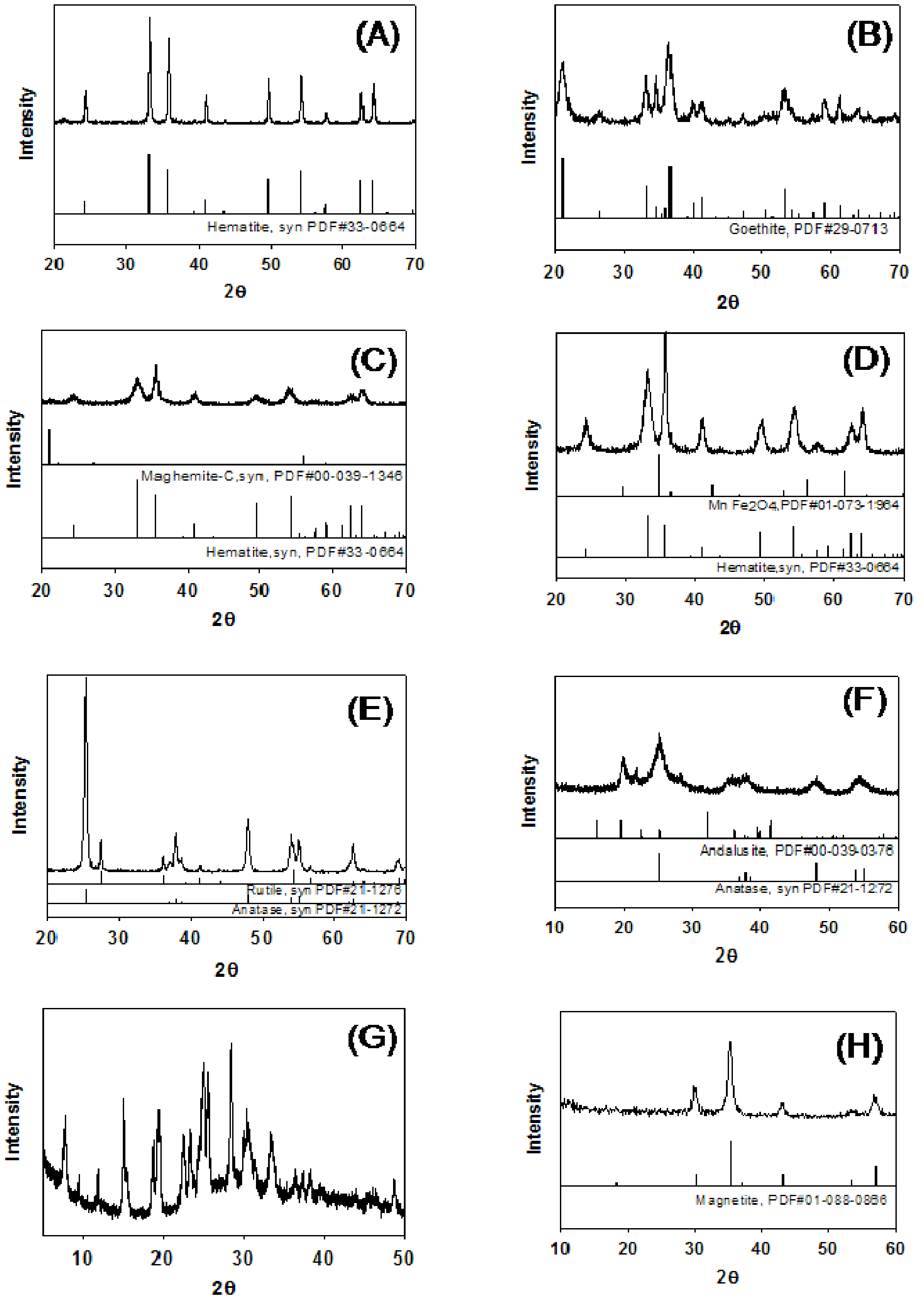
Commercial titania pillared clays

Titania pillared clays (Triton System Inc.) used in this work was prepared by the interaction of the titanium hydroxopolycation $[(TiO)_8(OH)_{12}]^{4+}$ with the clay layers since montmorillonite is naturally occurring layered clay.

Final product in the structure formula was $(TiO_2)_{0.68}$ $(Si_{3.99}$ $Al_{1.92})$ $(Mg_{1.73})$ O_{10} $(OH)_2$ and a schematic structural model of the TiO_2 pillared clay is shown in Figure B1.



Appendix Figure B1 Schematic structure model of the titania pillar intercalated clay.



Appendix Figure B2 X-ray diffraction patterns of various sorbents(a) Iron Oxide Red (b) Trans Oxide Yellow (c) Trans Oxide Red (d) Trans Oxide Brown (e) titanium oxide (f) titanium dioxide pillared clay (g) synthetic SUZ-4 zeolite (h) synthetic magnetite.

Appendix C

Saito-Foley Cylindrical Pore Model

Saito-Foley (SF) Method

Several different approaches to micropore analysis are available on the AUTOSORB. While no single treatment is applicable to all situations, enough flexibility is provided for the user to select the analysis most suitable for a given situation or material. Even though the HK method is adequate for materials with a predominance of slit-like pores (activated carbons, layered clays), certain solids (e.g. zeolites) are better represented assuming cylindrical pore geometry with pore size distribution of micropores. Hence, the SF method was developed as an alternative to the slit-like pore-based HK method. As with the HK method, the SF method enables the calculation of pore size distributions of microporous materials independently form the Kelvin Equation. The computational approach is analogous to that of the HK method, except that cylindrical pore geometry is assumed. The equation is following:

$$RT \ln \frac{P}{P_0} = \frac{3\pi \mathrm{K}}{4} \times \frac{(N_s A_s + N_A A_A)}{(d/2)^4} \times \sum_{k=0}^{\infty} \left(\frac{1}{k+1} \right) G$$

where

$$G = \left[1 - (\frac{d}{D}) \right]^{2k} \left[\left(\frac{21}{32} \right) a_k \left(\frac{d}{D} \right)^{10} - b_k \left(\frac{d}{D} \right)^4 \right]$$

$$a_k = \left(\frac{-4.5 - k}{k} \right)^2$$

$$b_k = \left(\frac{-1.5 - k}{k} \right)^2$$

and $a_0 = b_0 = 1$

$(D - d_s)$ = effective pore diameter

with all other parameters having been defined in the HK method. The numerical solution of the above equations is again analogous to that of the HK method, and yields pore size distributions and cumulative pore volumes for cylindrical pores in the microporous range.

Physical parameters for model

Adsorbent

Width (d, nm)	0.276
Poralizability (α, cm^3/molecule)	$2.5x10^{-24}$
Magnetic susceptibility (χ, cm^3/molecule)	$1.30x10^{-29}$
Density (N, molecule/cm^2)	$13.1x10^{14}$

Adsorbate

Temperature (T, K)	77.35
Diameter (d, nm)	0.3
Poralizability (α, cm^3/molecule)	$1.46x10^{-24}$
Magnetic susceptibility (χ, cm^3/molecule)	$2.00x10^{-29}$
Density (N, molecule/cm^2)	$6.7x10^{14}$
Molecule cross-sectional area for nitrogen	0.162 nm^2
Density conversion factor for nitrogen	$V_{N2,\ gas\ STP} \times 0.0015468 = V_{N2\ ,\ liquid}$

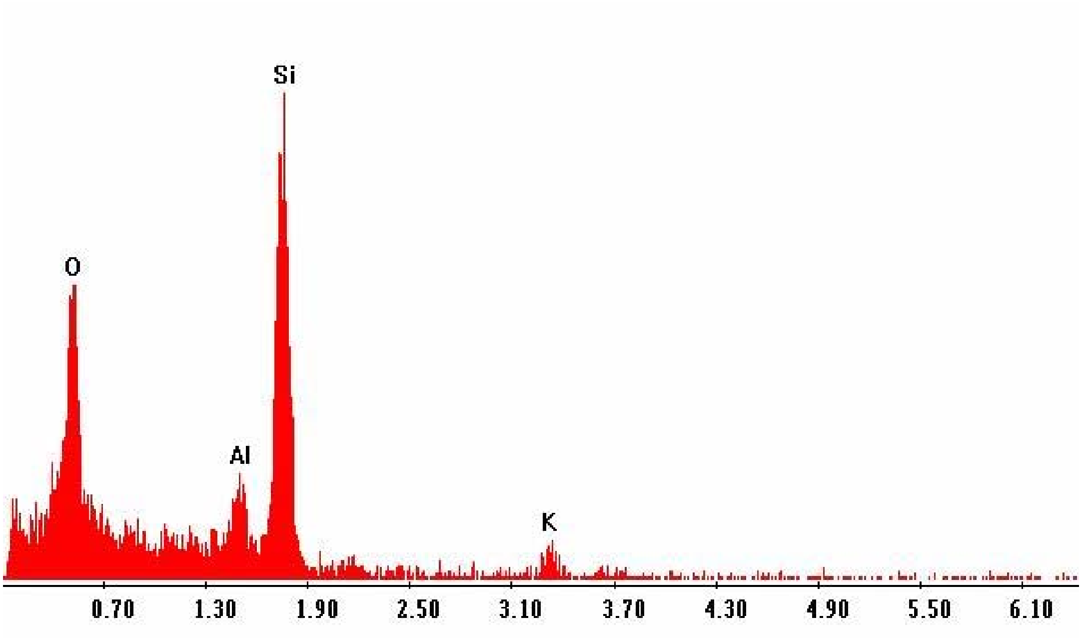
Range of micropore $P/P_0 = 10^{-7}$-0.02

Source: Autosorb 1, Quantachrome Instruments, AS-1-2-Rev B P/N 05061

Appendix D

Elemental Dispersion X-ray Analysis (EDS) Results

SUZ-4 sample

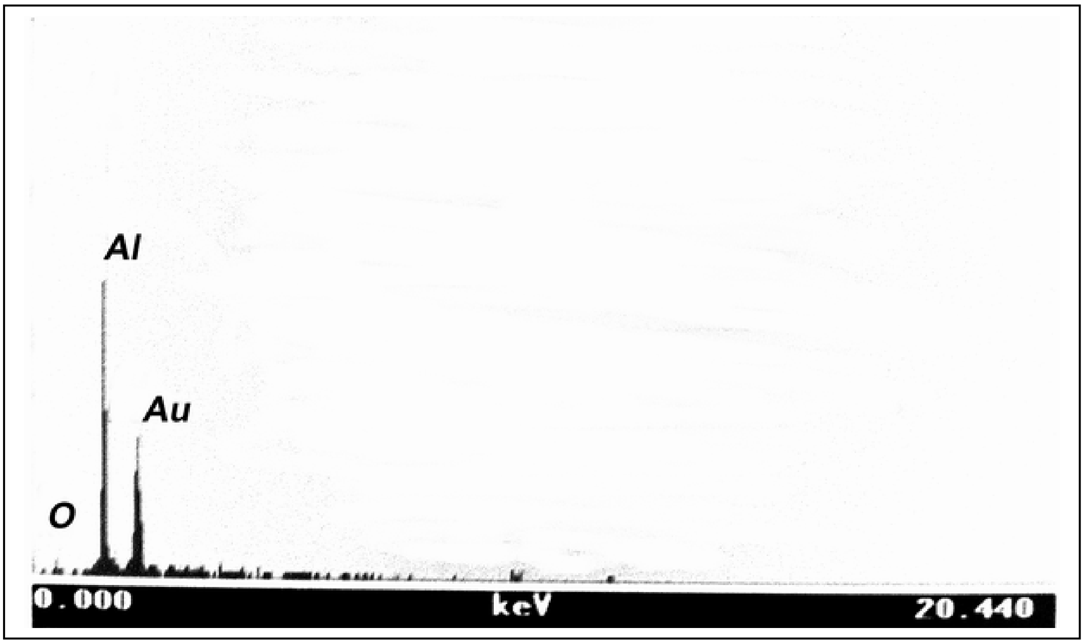


Appendix Figure D1 EDS for 4 days crystallization time at $SiO_2/Al_2O_3 = 21.2$ (SUZ-4 sample No. M2S)

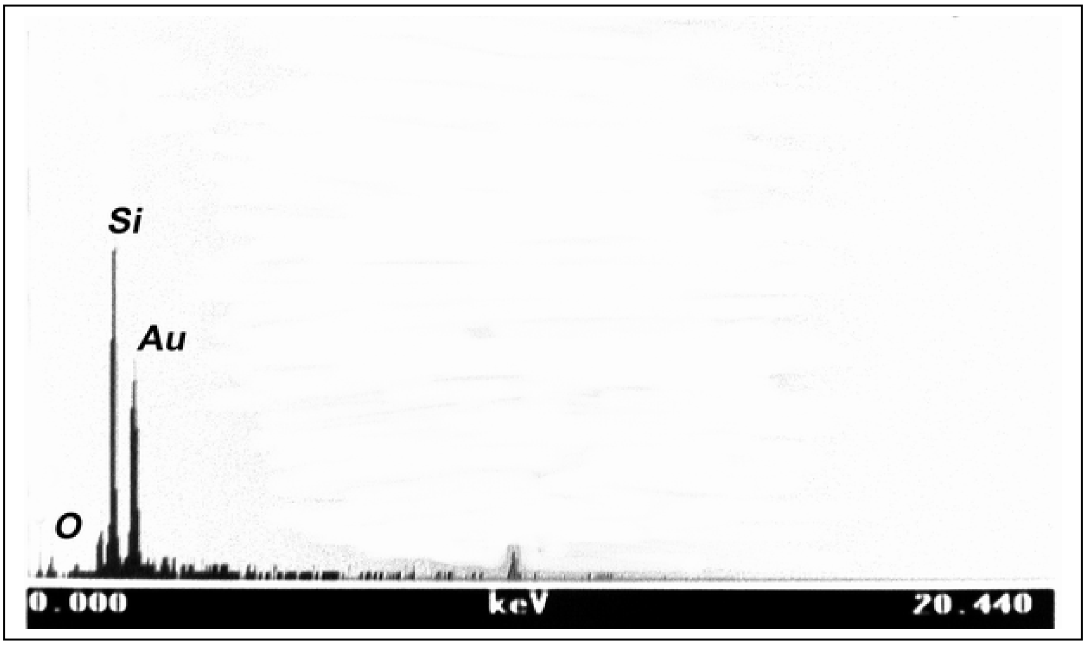
Appendix Table D1 Element normalized in quantification from one spot of sample No. M2S

Element	Weight (%)	Atomic (%)
O	44.59	59.14
Al	6.74	5.30
Si	43.01	32.49
K	5.66	3.07
Total	100	100

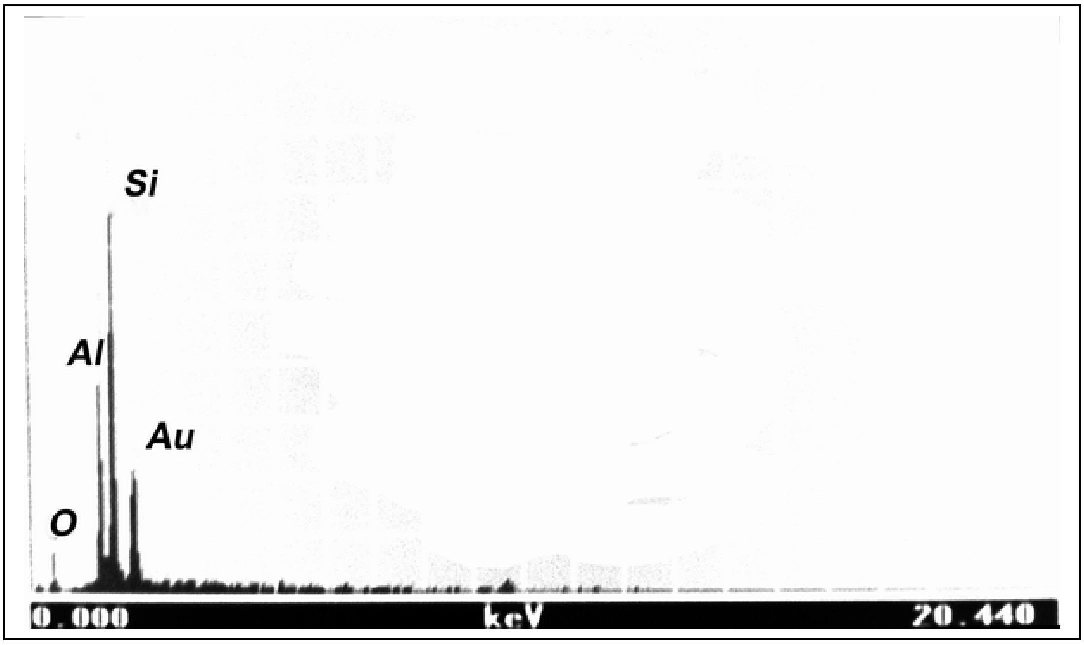
SiO_2-Al_2O_3 system



Appendix Figure D2 EDS for pure Al_2O_3 (Au element from gold sputtering)



Appendix Figure D3 EDS for pure SiO_2 (Au element from gold sputtering)



Appendix Figure D4 EDS for Si:Al = 24 (Au element from gold sputtering)

Appendix E

Concept of Inductively Coupled Plasma Mass Spectrometry Analysis

Concept of Inductively Coupled Plasma Mass Spectrometry Analysis

ICP-MS is an acronym for Inductively Coupled Plasma - Mass Spectrometry: a fast, precise, accurate, and extremely sensitive multielement analytical technique for the determination of trace elements in a variety of liquid and solid sample materials. Chemical analysis with an inductively coupled *plasma* (a state of the matter containing electrons and ionized atoms) is based on the principles of vaporization, dissociation, and ionization of chemical elements when introduced into the hot plasma. These ions can be then separated according to their mass/charge ratios by a high resolution magnetic sector mass analyzer and detected, multiplied, and counted using fast digital electronics.

ICP-MS was first developed in the early 80's and now is increasingly becoming the analytical tool of choice over such techniques as Atomic Absorption Spectrometry (AAS), ICP-Atomic Emission Spectrometry (ICP-AES) and Neutron Activation Analysis (NAA). ICP-MS is a successful, state-of-the-art hybrid of the two classical analytical techniques: ICP and MS. It surpasses most heavy metals detection techniques that are commercially available in terms of:

- sensitivity
- speed of analysis
- versatility
- simplicity of operation

Inductively coupled plasma mass spectrometry (ICP/MS) is a powerful new aid for evaluating the composition of a material that can be homogeneously dissolved (in strong acid, for example) prior to being atomized on entry into a plasma for subsequent ionization and ion selection (into a mass spectrometer). This technique has a linear response of peak intensity for six orders of magnitude of concentration.

ICP/MS with direct injection nebulization (DIN) was used to evaluate impinger solution compositions capable of capturing elemental mercury (Hg^0) in EPA method 5 type sampling. An iodine based impinger solution proved to be very efficient for Hg^0 capture and was amenable to direct analysis by DIN-ICP/MS. Hg^0 capture efficiency using aqueous iodine (I_3^-) can capture 98% of Hg^0 in the first oxidizing impinger.

Percent efficiency of Hg^0 capture is defined as the ratio of the mass of Hg^0 captured in the first oxidizing impinger divided by the total mass of Hg^0 captured in all of the oxidizing impingers multiple by 100 (Hedrick et al, 2001).

ICP/MS is an ideal detector for Hg since ^{202}Hg is a perfectly clean mass with no isobaric or polyatomic interferences: however, long wash-out times and high detection limits made ICP/MS an unattractive technique for Hg analysis for many years. To overcome the problems of memory effects and high detection limits common with conventional liquid nebulization and desolvation using a spray chamber, many researchers have used cold vapor generation methods followed by introduction of Hg^0 to the plasma. ICP/MS detection can be superior to CVAAS since problematic spectral interferences from organics, water vapor, or chlorine gas are not a problem in ICP/MS detection. However, the sample preparation requirements and challenges are the same as for CVAAS since all Hg compounds must be oxidized to Hg^{2+} and in solution so that chemical reduction to Hg^0 is possible. An advance in sample introduction to ICP/MS for high memory elements such as Hg was the direct injection nebulizer (LaFreniere et al., 1987). In this technique the entire liquid sample, versus a fraction of the sample aerosol, is injected directly into the plasma. Using DIN-ICP/MS, Hg can be organically bound or bound to strong ligands. Solutions such as tris+EDTA and hydrogen peroxide are easily analyzed by DIN-ICP.MS with no sample preparation other than the addition of internal standards. The benefits of using DIN-ICP/MS are high sensitively, low required sample volume, speed of analysis, simple sample preparation, and the added benefit of being able to perform multiple metals analyses on the same solutions if desired. Limitations of ICP/MS are low tolerance for high dissolved solids and high salt matrices (Hedrick et al, 2001).

Categories

- ICP (Inductively Coupled Plasma) - this is a high temperature plasma (partly ionised argon) sustained with a radiofrequency electric current, which acts to produce ions. The electric current is transferred to the plasma by an induction coil, wrapped around a configuration of concentric quartz tubes (the plasma torch). The common operating frequencies are 27.12 and 40.68 MHz and operating power is in the range between 800 and 1500 W. The plasma is sustained within a constant flow of argon gas, open to atmosphere and reaches temperatures as high as 10,000 K in the hottest part. To prevent melting of the torch a high flow rate of argon is used in the outermost tubing. The total gas consumption of a typical analytical ICP is in the range of 14 - 18 L/min. In order to reduce capacititive coupling between the coil and plasma, some designs employ an additional metal sheet between the torch body and the induction coil.

- MS (Mass Spectrometry) the ions from the plasma are extracted through a series of cones into a mass spectrometer, usually a quadrupole. The ions are separated on the basis of their mass-to-charge ratio and a detector receives an ion signal proportional to the concentration.

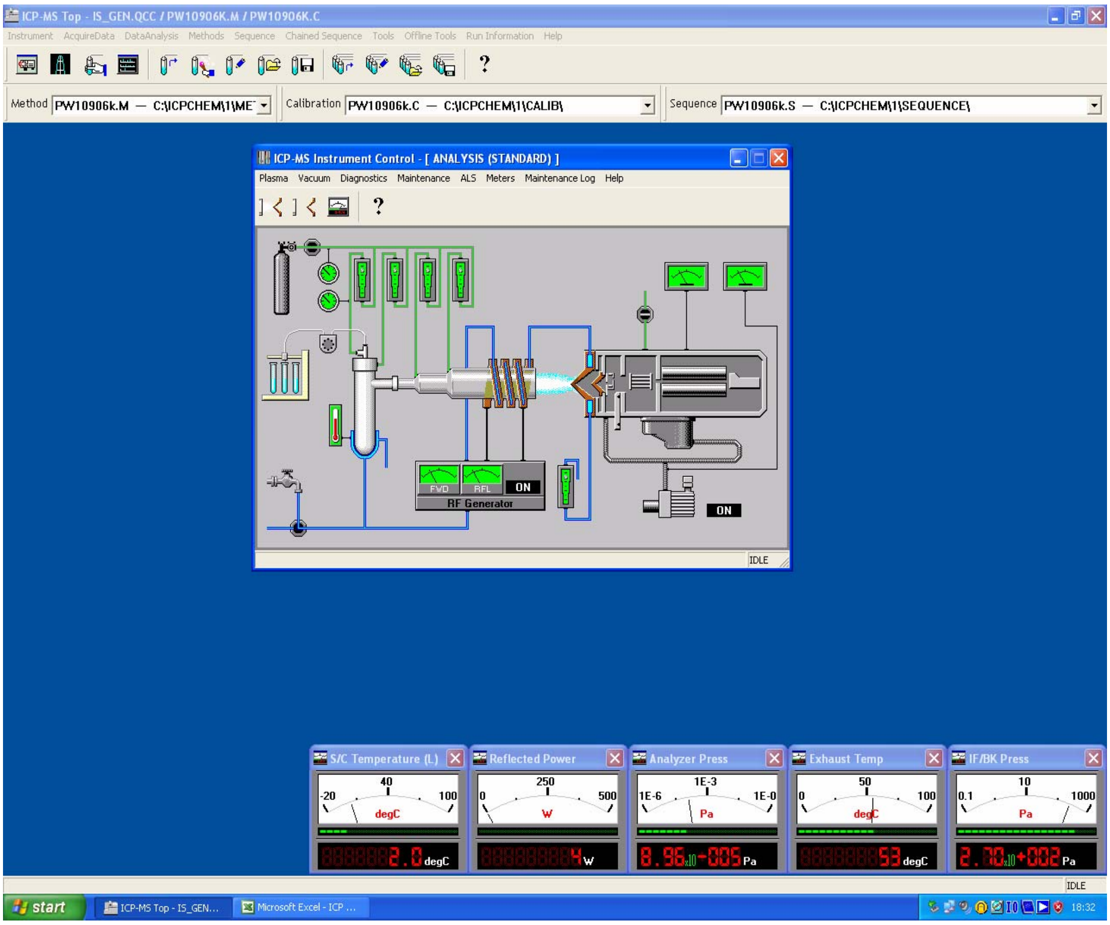
The concentration of a sample can be determined through calibration with elemental standards. ICP-MS also lends itself to quantitative determinations through isotope dilution, a single point method based on an isotopically enriched standard.

Other mass analyzers coupled to ICP systems include double focusing magnetic-electrostatic sector systems with both single and multiple collector, as well as time of flight systems (both with axial and orthogonal accelerators).

Another type of spectrometer using ICP is ICP-AES (Atomic Emission Spectrometer).

There is an increasing trend of using ICP-MS as a tool in Speciation Analysis, which normally involves a front end chromatograph separation and an elemental selective detector, such as AAS and ICP-MS.

Instrument operation



Method PW10906k.M — C:\ICPCHEM\1\ME

Calibration PW10906k.C — C:\ICPCHEM\1\CALIB\

Sequence PW10906k.S — C:\ICPCHEM\1\SEQUENCE\

Appendix Figure E1 ICP-MS Instrument Operation.

A sample is injected into the instrument, normally by an auto sampler. The Sample is atomised and delivered through a glass tube by an argon carrier gas. The sample is then exposed to radio frequency which converts the gas into a plasma. A fraction of the plasma passes through a ~1mm hole and then a ~0.4 mm hole. The purpose of which is to allow a vacuum that is required by the mass spectrophotometer. The sample then passes through charged lenses through the quadrapole and into the detector.

Plasma Generation

As stated above the mode of ionisation is via an argon plasma. Argon has the advantage of being abundant (in the atmosphere, as a result of the radioactive decay of potassium). It is therefore available more cheaply than the other inert gasses. Argon also has the advantage of having a higher first ionisation potential than all other elements except He, F and Ne.

The radio frequency causes the following reaction: $Ar \rightarrow Ar^+ + e^-$. Given the high ionisation potential as cited above reverse reaction will take electrons from any species. This recombination of Ar with an electron $Ar^+ + e^- \rightarrow Ar$ is likely to cause the loss of a electron from a metal $M \rightarrow M^+ + e^-$. Group II metals may become doubly charged species due to their low second ionisation potential.

Elemental Analysis

The ICP-MS allows analysis of elements with mass ranges 7 to 250. This encompasses Li to U. Some masses are prohibited such as 40 due to the abundance of argon in the sample. A typical ICP-MS will be able to detect in the region of ppt to 10 or 100 ppm or around 8 orders of magnitude.

Unlike Atomic Absorption Spectroscopy which can only scan for a single element at a time ICP-MS has the capability to scan for all elements simultaneously. This allows rapid sample processing.

Usage

ICP-MS can be used for analysis of environmental samples such as water and various other non-particulate samples. The instrument can also analyse for metals in urine in the case of mining activities. The instrument is very sensitive to particulate matter and as such solutions like wine will cause the instrument to cease function, requiring cleaning.

Reference:

Thomas, J.M. and W.J.Thomas. 1996. **Principles and Practice of Heterogeneous Catalysi**s, VCH Publishers Inc., New York, p.151.

http://www.gso.uri.edu/icpms/what_is.htm

http://en.wikipedia.org/wiki/ICP-MS

Appendix F

Overview Concept of Zeta Potential

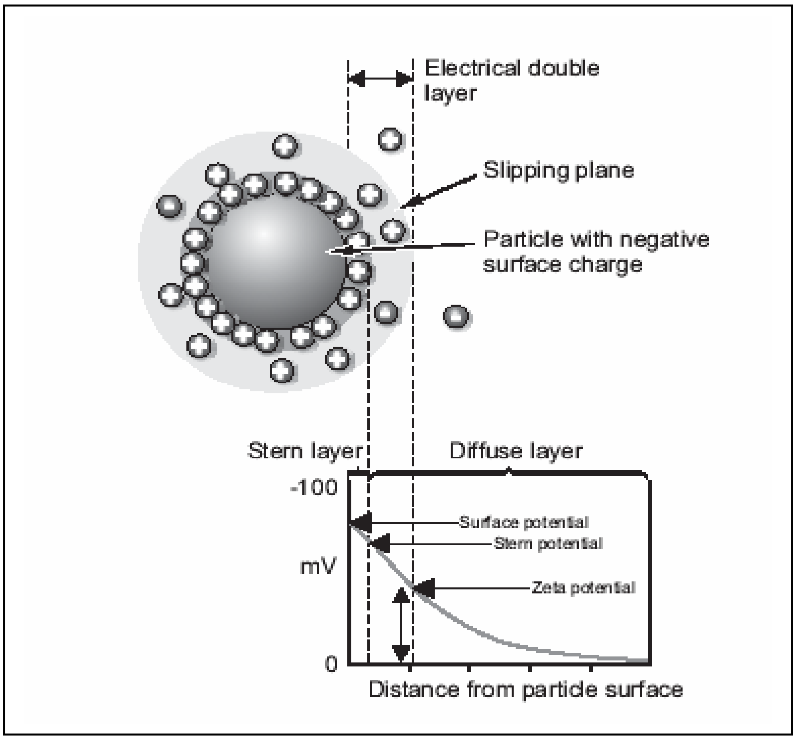
Zetasizer

The Zetasizer Nano series calculates the zeta potential by determining the Electrophoretic Mobility and then applying the Henry equation. The electrophoretic mobility is obtained by performing an electrophoresis experiment on the sample and measuring the velocity of the particles using Laser Doppler Velocimetry (LDV). These techniques are described in the following sections.

Zeta potential and the Electrical double layer

The development of a net charge at the particle surface affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration of counter ions (ions of opposite charge to that of the particle) close to the surface. Thus an electrical double layer exists around each particle. The liquid layer surrounding the particle exists as two parts; an inner region, called the Stern layer, where the ions are strongly bound and an outer, diffuse, region where they are less firmly attached. Within the diffuse layer there is a notional boundary inside which the ions and particles form a stable entity. When a particle moves (e.g. due to gravity), ions within the boundary move with it, but any ions beyond the boundary do not travel with the particle. This boundary is called the surface of hydrodynamic shear or slipping plane. The potential that exists at this boundary is known as the Zeta potential.

The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. A colloidal system is when one of the three states of matter: gas, liquid and solid, are finely dispersed in one of the others. For this technique, we are interested in the two states of: a solid dispersed in a liquid, and a liquid dispersed in a liquid, i.e. an emulsion.



Appendix Figure F1 The development of a net charge at the particle surface.

If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there is no tendency to flocculate. However, if the particles have low zeta potential values then there is no force to prevent the particles coming together and flocculating. The general dividing line between stable and unstable suspensions is generally taken at either +30mV or -30mV. Particles with zeta potentials more positive than +30mV or more negative than -30mV are normally considered stable. The most important factor that affects zeta potential is pH. A zeta potential value on its own without a quoted pH is a virtually meaningless number. Imagine a particle in suspension with a negative zeta potential. If more alkali is added to this suspension then the particles will tend to acquire a more negative charge. If acid is then added to this suspension a point will be reached where the negative charge is neutralised. Any further addition of acid can cause a build up of positive charge. Therefore a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH. The point where the plot passes through zero zeta potential is called the Isoelectric point and is very important from a practical consideration. It is normally the point where the colloidal system is least stable.

Electrokinetic effects

An important consequence of the existence of electrical charges on the surface of particles is that they will exhibit certain effects under the influence of an applied electric field. These effects are collectively defined as electrokinetic effects. There are four distinct effects depending on the way in which the motion is induced. These are: Electrophoresis, Electroosmosis, Streaming potential and Sedimentation potential

Electrophoresis

When an electric field is applied across an electrolyte, charged particles suspended in the electrolyte are attracted towards the electrode of opposite charge. Viscous forces acting on the particles tend to oppose this movement. When equilibrium is reached between these two opposing forces, the particles move with constant velocity. The velocity of the particle is dependent on the following factors:

- Strength of electric field or voltage gradient.
- The Dielectric constant of the medium.
- The Viscosity of the medium.
- The Zeta potential.

The velocity of a particle in an electric field is commonly referred to as its Electrophoretic mobility. With this knowledge we can obtain the zeta potential of the particle by application of the Henry equation. The Henry equation is:

$$U_E = \frac{2\varepsilon z\, f(Ka)}{3\eta}$$

U_E : Electrophoretic mobility.

ε : Dielectric constant.

η : Viscosity.

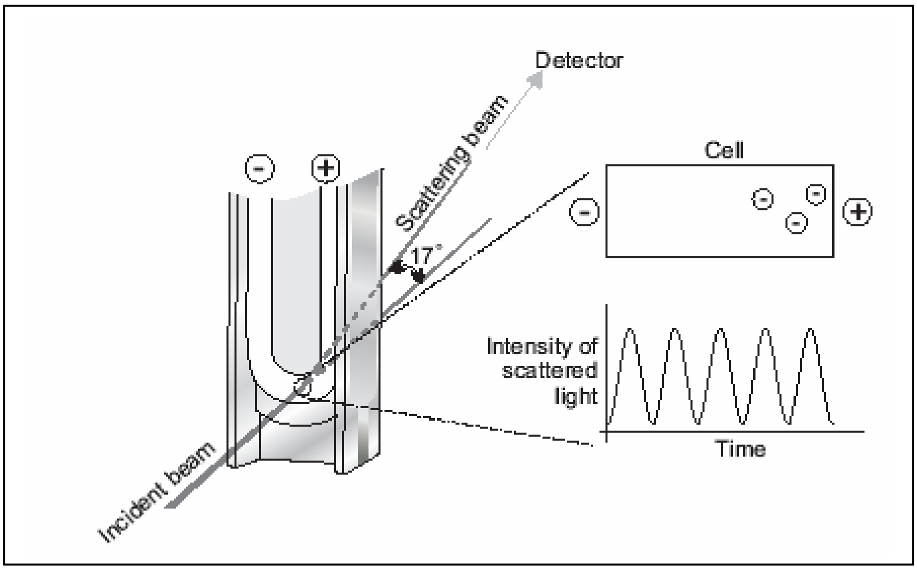
f(Ka) : Henry's function.

Two values are generally used as approximations for the f(Ka) determination (1.5 or 1.0).

Laser Doppler Velocimetry

Laser Doppler Velocimetry (LDV) is a well established technique in engineering for the study of fluid flow in a wide variety of situations, from the supersonic flows around turbine blades in jet engines to the velocity of sap rising in a plant stem. In both these examples, it is actually the velocity of tiny particles within the fluid streams moving at the velocity of the fluid that we are measuring. Therefore, LDV is well placed to measure the velocity of particles moving through a fluid in an electrophoresis experiment. The receiving optics is focused so as to relay the scattering of particles in the cell.

The light scattered at an angle of 17° is combined with the reference beam. This produces a fluctuating intensity signal where the rate of fluctuation is proportional to the speed of the particles. A digital signal processor is used to extract the characteristic frequencies in the scattered light.



Appendix Figure F2 The scattering of particles in the cell from laser droppler velocimetry.

Reference: Manual Zetasizer Nano Series, www.malvern.co.uk