

CHAPTER II

THEORY AND LITERATURE REVIEW

Principle and extraction mechanism of solid phase extraction are described in detail here. Then the focus is shifted to the properties and synthesis of silica. The method for functionalization of silica surface is also described. Then, reviews of several techniques for characterization of materials are delineated. Next, details on doping molecule (1-phenyl-3-methyl-4-stearoyl-5-pyrazolone, HPMSp) and works related to silica modified with HPMSp are summarized.

1. Solid-phase extraction

1.1. Principle

Solid-phase extraction (SPE) is a method of sample preparation that concentrates and purifies analytes from solution by sorption onto sorbent, followed by elution of the analytes with a solvent appropriate for instrumental analysis. The SPE provides a number of advantages over liquid-liquid extraction technique include high recoveries of analytes, purified extraction, ease of automation and reduction in the consumption of organic solvents. A further advantage is that the solid phase can be repeatedly used [1-3].

As a result of the flexibility that SPE offers, it has found application in the preparation of environmental, clinical and pharmaceutical sample [3]. In addition, the SPE technique provides low detection limits and helps to avoid matrix interferences in the analysis of real sample [12].

In solid phase extraction, analytes are extracted from a liquid phase into a solid phase. The extraction mechanism is shown below.



Where M is the analytes in the liquid phase

S is the sorbent

l is the liquid phase

s is the solid phase

In the case of metal extraction, the amount of metal ion on the sorbent and the distribution ratios of the metal were calculated according to the following equation [13].

$$q = (C_i - C_e) \times L/W$$

$$D = q/C_e$$

Where q is the amount of metal on the adsorbents (mol/kg)

D is the distribution ratio of the metal (L/kg)

C_i is the initial metal concentration in the liquid phase (mol/L)

C_e is the metal concentration in the liquid phase at equilibrium (mol/L)

L is the volume of the liquid phase (L)

W is the weight of the adsorbents (kg)

The solid phase typically consists of sorbents that are derived from immobilization of organic compounds onto the surface of solid support. Generally, the solid support is either polymeric as polystyrene-divinylbenzene resins, or inorganic as silica. The extraction can take place in a batch mode in which the solid sorbent is intimately mixed with the liquid sample solution. In chemical analysis, it is more common to pack the solid sorbent into a small tube and pass the liquid sample through the tube.

1.2. Adsorption mechanisms

There are three mechanisms of separation in solid phase extraction i.e. reversed phase, normal phase and ion exchange. Reversed phase mechanism involves the partitioning of organic solutes from a polar mobile phase, such as water, into a nonpolar phase, such as the C-18 sorbent. The mechanism of separation is a nonpolar interaction, called van der Waals, dispersion forces or partitioning. Normal phase mechanism refers to the sorption of an analyte by a polar surface. The mechanism of separation is a polar interaction, such as hydrogen bonding, dipole-dipole interaction, π - π interaction and induced dipole-dipole interaction. The mechanism involves the sorption of the functional groups of the analyte to the polar sites of sorbents. The types of sorbent used for normal phase SPE are non-bonded phase of silica, alumina and magnesium silicate (Florisol). Several bonded phases may also be used for normal

phase SPE, including aminopropyl, cyanopropyl and propyl diol. Ion-exchange mechanism is used to extract ionic analytes or analytes that can be converted to ionic form by adjusting the sample pH. This mechanism of separation is ionic interaction. The extracted ions may be removed from the ion-exchange sites by elution with a solvent containing a relatively high concentration of a displacing ion. Sorbent used for ion-exchange contains cation-exchange groups or anion-exchange groups [3].

2. Silica

2.1. Generality

Silica is an inorganic polymer with the general structure formula of $\text{SiO}_2 \cdot x\text{H}_2\text{O}$. Silica is a porous structure and can be classified in three types depending on its pore size.

1. Microporous silica with pore diameter smaller than 2 nm
2. Mesoporous silica with pore diameter between 2 and 50 nm
3. Macroporous silica with pore diameter larger than 50 nm

The silica used in most chromatographic applications and in typical SPE procedures is an amorphous porous solid with a surface area of 200 to 600 m^2/g . Generally, the particles are irregular in size with an average particle diameter of 40 μm have an average pore size of 60 nm [3]. The primary advantages of silica are its availability in a wide range of well-defined surface area and pore size as well as its relative low cost. Furthermore, the silica is the most widely used solid support due to its high thermal, chemical and mechanical stability properties compared to other organic and inorganic supports.

Amorphous silica with a porous structure consists of three kinds of silanol (Si-OH) on the surface: isolated, germinal, and vicinal. The surface also contains siloxane bonds (Si-O-Si). The silanols are hydrophilic while siloxanes are hydrophobic [1,14]. The surface of amorphous silica is depicted in Figure 2.1.

Most chemical properties of silica are due to surface silanols. The silanol groups form strong hydrogen bonding with water molecules. These adsorbed water molecules can be removed by heating at 150 °C under vacuum for several hours [14-15]. The hydroxyl groups on the porous silica surface have also an acidic character.

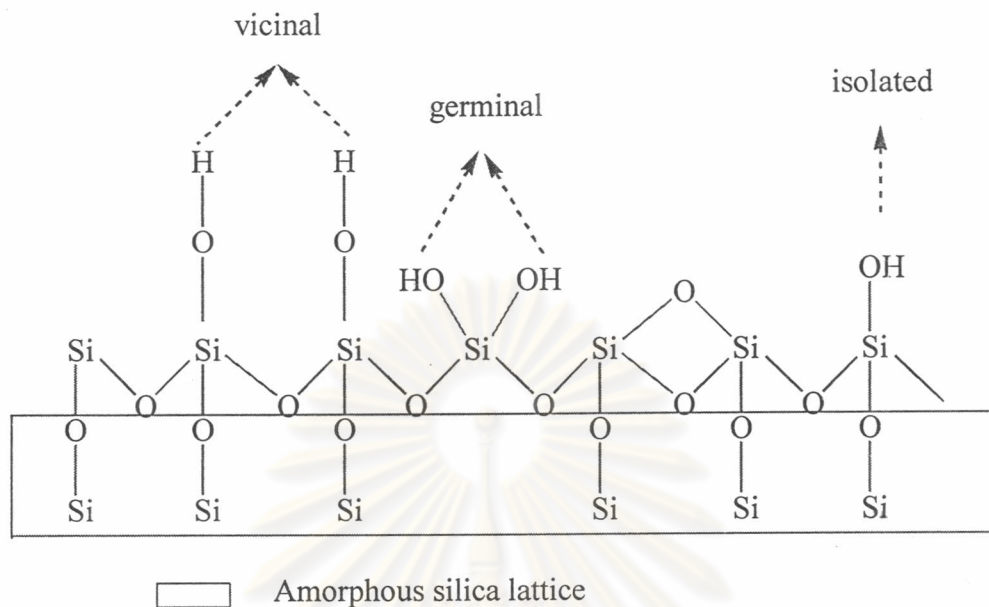
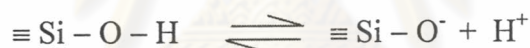


Figure 2.1 Three types of hydroxyl groups on the amorphous silica surface.

The pK_a value of the ionization reaction

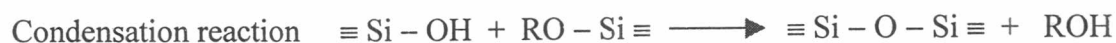


is about 6.8 (± 0.5). The acidic character of surface silanols confirms some ion-exchange properties on porous silica. At $\text{pH} = 7$, silica consists of negative charge in solution [15]. For this reason, the silica is known to act as inorganic ion exchanger, but its application to the extraction of ionic species is not so popular because the interaction between many metal ions and the silica surface is weak and non-selective. Therefore, it is essential to increase the selectivity of extraction of silica by functionalization process [14-15].

2.2. Synthesis

Synthetic silica was prepared by sol-gel process, which is a method to produce solid from gel. The preparation method starts with a silicon alkoxide in an organic medium is first hydrolyzed by addition of water, followed by polymerization of the hydrolyzed alkoxide through condensation of the hydroxyl groups. When the polymerization and cross-linking of polymeric molecules become extensive, the entire solution becomes rigid and a solid gel is formed [7, 16]. With a silicon alkoxide

(Si(OR)₄ as a precursor, sol-gel chemistry can be described in terms of two separated reactions as shown below :



The hydrolysis reaction occurs when an amount of water is added to the silicon alkoxide. Intermediates obtained as a result of this reaction include alcohol, which corresponds to the alkoxide used. In the condensation or polymerization reactions, alkoxide groups (-SiOR) react with hydroxyl groups (-SiOH), which were formed during the hydrolysis step, to yield siloxane bonds (-Si-O-Si-). Both hydrolysis and condensation reactions of the alkoxide precursor is occurred by acid or base catalyzed bimolecule displacement reactions [16-17]

Any factors that affect the hydrolysis and the condensation steps are likely to impact properties of the solid. Parameters that affect the structure of obtained silica are type of solvent, water content, acid or base content, precursor concentration and temperature [16-17]. Silica prepared by the sol-gel process has several promising advantages over other methods. In general, sol-gel synthesis offers better control over surface area, pore size distribution. Moreover, sol-gel method allows the formulation of a number of gels with high uniformity and stability.

The most widely used precursors in silica synthesis are low molecular mass tetraalkoxysilanes, tetramethoxysilane (TMOS), or tetraethoxysilanes (TEOS). Since alkoxysilane is not miscible in aqueous solution, methanol or ethanol is used for homogenization. This route of synthesis provides microporous silica. In addition, the incorporation of surfactant at a low concentration in precursor solution prevents fractures of silica during drying process. The addition of surfactant molecules at a level well above their critical micelle concentration (CMC) provides mesoporous silica.

2.3. Mesoporous silica

Mesoporous silica is expected to provide superior extraction ability of metal ions from solution because of its high surface area [10]. This mesoporous material typically has surface areas above 700 m²/g [11]. The mesoporous silica is much more

readily accessible to reacting chemical species than microporous silica [1]. The preparation of mesoporous silica can be achieved by the sol-gel process of alkoxy silane in the presence of surfactant with concentration greater than the CMC. The most surfactant used in synthesis is cetyltrimethylammonium bromide ($\text{CH}_3(\text{CH}_2)_{11}\text{NBr}(\text{CH}_3)_3$, CTAB). The CMC value of CTAB is 8.5×10^{-4} M [18]. A liquid crystal templating mechanism (LCT) in which surfactant liquid crystal structures serve as organic templates has been proposed for the formation of the mesoporous silica [19]. The mesoporous silica prepared by a micelle-templated sol-gel polymerization method possesses pore diameters adjustable between 20 and 300 Å, with narrow pore-size distribution, and high surface area [10]. The final size and characteristics of mesoporous silica depend on the type and initial concentration of catalysts, type of surfactants, type of silicon alkoxides (methyl, ethyl, pentyl, etc.), type of solvent and synthesis temperature [19-21].

A.C. Voegtlin and co-workers reported that the synthesis pH is an essential parameter in the preparation of mesoporous silica at room temperature. The degree of polycondensation of the silicate species increases as the synthesis pH decreases [22]. J.C. Vartuli and co-workers demonstrated that the structure of mesoporous silica depends on surfactant-to-silica molar ratio in the synthesis [23]. K.J. Elder and co-workers described that the synthesis of mesoporous silica is highly dependent on a number of factors, e.g. heating time, concentrations of acid catalyst and surfactant [24].

2.4. Functionalization of silica

Chemical derivatization, impregnation and doping are technologies currently used to functionalization of the organic compounds on the surface of silica [7]. Chemical derivatization is based on chemical bond formation between the silica gel surface groups and organic modifier molecules. The ligand-bond silica gel adsorbents have the advantages of stability, but their preparation is complicated and time-consuming. Moreover, the chelating agents that can bond to silica gel are limited. Impregnation technique is carried out by exposing the porous silica to a concentrated solution of the reagent in the organic solvent, which after drying gives a support coated in reagent. This technique is highly versatile and a large variety of reagents have already been loaded on silica. However, the binding force is quite low

in this case and leaching is currently observed. Consequently, the lifetime of the support is short. Doping technique is the direct encapsulation of organic molecules by using sol-gel process. In this technique, the synthesis of silica is carried out in solution and at low temperature, which allows the introduction of the organic molecules in a mixture of sol-gel precursors. The derivatization of chemical reagent is not required prior to the encapsulation step and thus reactivity and specificity of the dopant are generally maintained [7, 25-26].

3. Characterization of materials

3.1. Characterization of porous structure

3.1.1. Generality

Adsorbents of high surface area are generally porous. There are many different kinds of pores. A classification is usually done by measuring the accessibility of adsorbent to an external fluid (Figure 2.2.). From this viewpoint, pores totally isolated from their neighbors are called closed pores (a). They influence the macroscopic properties of the solid, but they are inactive in term of chemical reactions. On the other hand, pores that are open to the external surface of the solid, called open pores such as (b), (c), (d), (e), and (f) in Figure 2.2.

To describe qualitatively and quantitatively a porous solid, more information is necessary, such as the specific surface area, or the pore size and the pore size distribution of the porous solid. The definition of surface area is the accessible (or detectable) area of solid surface per unit mass of material. The pore size also called pore diameter is the distance of two opposite walls of the pore.



Figure 2.2 Different types of pores.

3.1.2. Adsorption Isotherm

Gas adsorption measurements are widely used for determining the surface area and pore size distribution of a variety of solid materials. The measurement of adsorption at the gas/solid interface also forms an essential part of many fundamental and applied investigations of the nature and behavior of solid surfaces.

The adsorption isotherm is a plot of amount-adsorbed nitrogen against the equilibrium relative pressure (p/p_0), where p_0 is the saturation pressure of the pure adsorptive (adsorbable gas) at the temperature of the measurement. Isotherm shape depends on the solid porous texture. The majority of adsorption isotherms may be grouped into six types according to IUPAC as illustrated in Figure 2.3 [27-29].

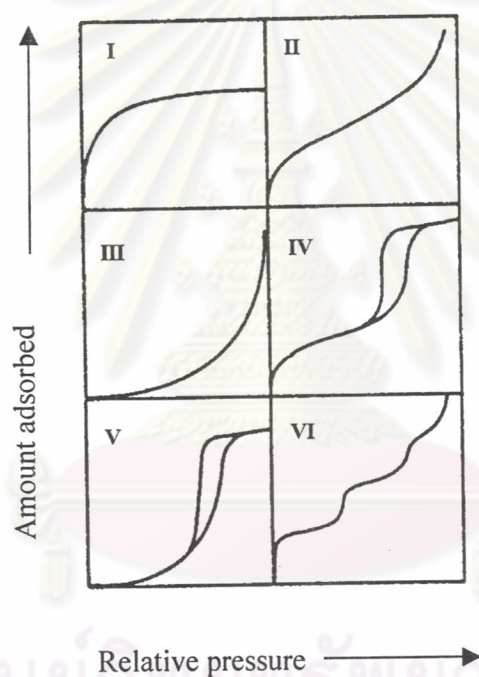


Figure 2.3 Six types of adsorption isotherm.

Type I isotherm is given by a microporous solid having relatively small external surfaces (e.g. activated carbons, molecular sieve zeolites and certain porous oxides). Type II isotherm is the normal form of isotherm obtained from a non-porous or macroporous adsorbent. Characteristics of the type IV isotherm are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and limiting uptake over a range of high p/p_0 ratio. The initial part of the type IV isotherm

is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of a type II isotherm obtained from the adsorbent in a non-porous form with the same surface area. Type IV isotherm is given by many mesoporous adsorbents. The remaining isotherms are less common: type VI represents stepwise multilayer adsorption on a uniform non-porous surface, whereas type III and V are associated with weak adsorbent-adsorbate interactions [27-28].

3.1.3. Application of BET (Brunauer-Emmett-Teller) equation for specific surface area measurement

The Brunauer-Emmett-Teller (BET) gas adsorption method is still the most widely used procedure for the determination of the surface area of porous materials [26-27]. This method is based on an oversimplified extension of the Langmuir mechanism to multilayer adsorption.

The BET equation is usually expressed in the linear form

$$\frac{p}{n(p_0 - p)} = \frac{1}{n_m C} + \frac{(C - 1) p}{n_m C p_0}$$

Where n is the amount of gas adsorbed at the relative pressure p/p_0 and n_m is the monolayer capacity. According to the theory, C is a constant which is related exponentially to the heat of first layer adsorption. The linear relation between $p/n(p_0 - p)$ and p/p_0 provides the C and n_m values. The application of the BET method is the calculation of the surface area (often called the BET area) from the n_m value. The equation for calculation the BET surface area is

$$A(\text{BET}) = n_m \cdot L \cdot a_m$$

Where $A(\text{BET})$ is the surface area of the adsorbent, L is the Avogadro constant and a_m is the average area occupied by the adsorbate molecules in the complete monolayer. The value of a_m of nitrogen at 77 K is usually taken as 0.162 nm^2 .

3.1.4. Mesoporosity

3.1.4.1. Adsorption hysteresis

Gas adsorption in mesopores takes place in two more or less distinct stages (monolayer-multilayer adsorption and capillary condensation). In monolayer adsorption, all the adsorbed molecules are in contact with the surface layer of the adsorbent. In multilayer adsorption, the adsorption space accommodates more than one layer of the adsorbent. In capillary condensation, the residual pore space which remains after multilayer adsorption is filled with condensate separated from the gas phase by menisci.

Capillary condensation usually gives rise to hysteresis in the multilayer region of the physisorption isotherm. Four characteristic types of hysteresis loop are shown in Figure 2.4. Type H1 loops are given by porous materials having narrow distributions of mesopore size. Many porous oxides tend to give type H2 loop, but in these systems the distribution of pore size and shape is not well defined and the broadness of the loop appears to be associated with pore blockage effects. The type H3 loop, which does not exhibit any limiting adsorption at high p/p_0 , is observed with aggregates of plate-like particles giving rise to slit-shaped pores. Similarly, the type H4 loop is often associated with narrow slit-like pores [27-28].

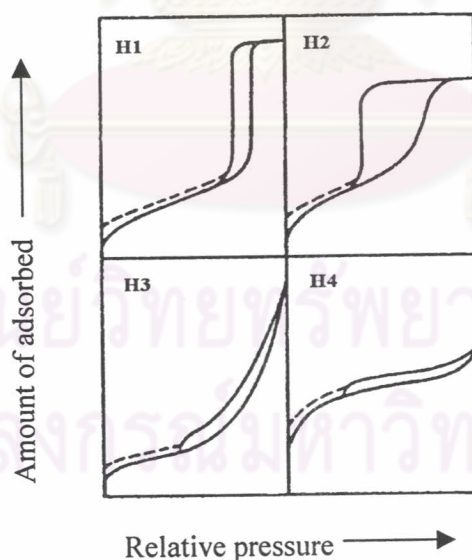


Figure 2.4 Four types of hysteresis loops.

3.1.4.2. Computation of mesopore size

The mesopore size is usually calculated with the aid of the Kelvin equation in the form:

$$r_k = \frac{2\gamma V_L}{RT \ln(p_0/p)}$$

Where p/p_0 is the relative pressure at which condensation occurs, r_k is the radius of a hemispherical meniscus. γ and V_L are respectively the surface tension and molar volume of the liquid condensate.

If the radius of a cylindrical pore is r_p and a correction is made for the thickness, t , of the layer already adsorbed on the pore walls, then

$$r_p = r_k + t$$

Alternatively, for a parallel-sided slit, the pore width, d_p , is given by

$$d_p = r_k + 2t$$

Values of t are best obtained from experimental data determined on non-porous reference materials, i.e. standard multilayer data [27-28].

3.1.5. Method for determination of adsorption isotherm

Many different procedures have been employed for determining the amount of gas adsorbed. Volumetric methods are generally used for measuring nitrogen adsorption at temperature 77 K. The adsorption isotherm is usually constructed point-by-point by the admission of successive charges of gas, with sufficient time allowed for equilibration at each point. Recently, various automated techniques have been developed. In some cases these involve the continuous admission of the adsorptive and thus provide a measure of the adsorption under quasi-equilibrium conditions. Alternatively a carrier gas technique, which makes use of conventional gas chromatographic equipment, may be employed-provided that the adsorption of the carrier gas (e.g. He) is negligible under the conditions used.

Prior to the determination of the adsorption isotherm it is usually considered necessary to remove all physisorbed materials. However, the exact conditions (temperature, time of pumping, and residual pressure) required to attain a clean surface depend on the nature of the adsorption system and the purpose of the investigation. For the determination of the surface area and pore size distribution by

nitrogen adsorption, outgassing to a residual pressure of 10^{-4} Torr is generally acceptable. The rate of desorption is strongly temperature-dependent and at elevated temperature is therefore desirable, but obvious changes in the adsorbent structure or surface composition must be avoided [27-28].

3.2. X-ray diffraction analysis

3.2.1. Principle

The simplest basic structural unit in the structure is repeated regularly in three dimensions. When an X-ray beam strikes a crystal surface at some angle θ . A surface of crystalline material will act as diffraction grating for X-rays. In Figure 2.5, the beam of X-ray striking the crystal surface is partly scattered by the atoms in the first layer. Another portion is scattered by the second layer, and so on. The cumulative effect of this scattering from the regularly spaced centers of the crystal is a diffraction of the beam in much the same way as a visible radiation is diffracted by a reflection grating. The requirements for diffraction: (1) the spacing between layers of atoms must be roughly the same as the wavelength of the radiation and (2) the scattering centers must be distributed in a highly regular way [30, 32].

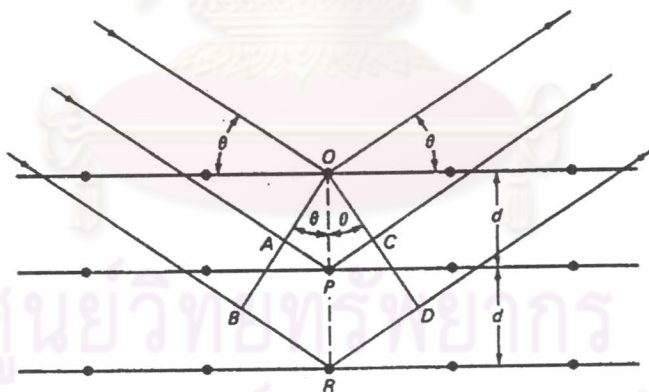


Figure 2.5 Diffraction of X-rays by a crystal.

W.L. Bragg treated the diffraction of X-rays by crystal as shown in Figure 2.5. Here, the Bragg equation obtained from this treatment.

$$n\lambda = 2d\sin\theta$$

where n is the order of diffraction

λ is the wavelength of beam

θ is the diffraction angle

d is the interplanar distance of the crystal

3.2.2. Apparatus and measurement

Diffraction patterns are usually recorded with a Debye-Scherrer powder camera, shown schematically in Figure 2.6. The sample is held in a thin glass tube or spread with a binder on a plastic film. X-rays from a Coolidge tube are filtered to produce a nearly monochromatic beam. The undiffracted portion of the beam is trapped and adsorbed, while the diffracted rays take a conical shape emanating from the sample. Since both λ and θ are known, values of d are calculated from Bragg equation. For most routine work, the identification of crystals is based on a comparison of d -spacings and relative intensities of the sample with those of the known compounds. Most modern instruments plot the intensity of the diffracted beam against the scattering angle (2θ), or the d -spacing [30-32].

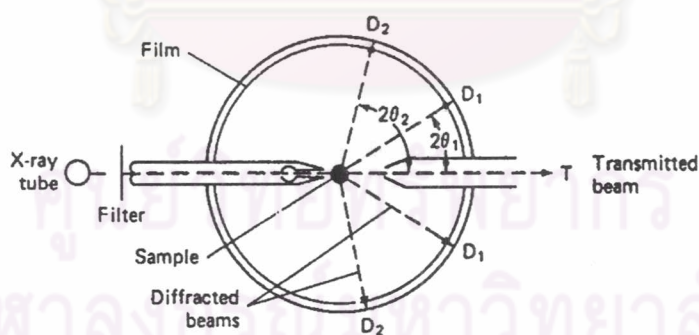


Figure 2.6 Schematic diagram of Debye-Scherrer powder camera.

3.3. Thermogravimetry

3.3.1. Principle

Thermogravimetry (TG) or thermogravimetric analysis (TGA) is an analytical technique in which the mass of a substance is monitored as a function of temperature. TG curve is a plot of either the actual mass or the percentage of the original mass against temperature and provides information about drying processes, loss of solvent of crystallization (and hence the amount of solvent present in the sample), thermal decomposition reactions and oxidation reactions [30-32].

3.3.2. Apparatus and measurement

The apparatus required for a thermogravimetric analysis includes: (1) a sensitive analytical balance that measures the mass changes during heating; (2) a furnace; (3) a furnace temperature controller and programmer; (4) a recorder that provides a plot of sample mass as a function of temperature.

Figure 2.7 is a schematic diagram of the Mettler thermobalance. The sample holder is housed in a furnace that is thermally isolated from the remainder of the balance. A change in the sample mass causes a deflection of the beam, which interposes a light shutter between a lamp and one of two photodiodes. The resulting imbalance in the photodiode current is amplified and fed into coil E, which is situated between the poles of the permanent magnet F. The magnetic field generated by the current also determines the position of the pen of recorder. The Mettler instrument has several weight ranges (1,10,100 and 1000 mg) and has a reproducibility of $\pm 10 \mu\text{g}$. The furnace of a thermogravimetric apparatus is generally programmed to increase the temperature linearly at predetermined rates (typically, from 0.5 to 25 °C/min). The temperature range for most instruments is from ambient to 1200 °C. Temperatures are determined by a thermocouple located as close as possible to the sample. Insulation and cooling of the exterior of the furnace is required to avoid heat transfer to the balance [30-32].

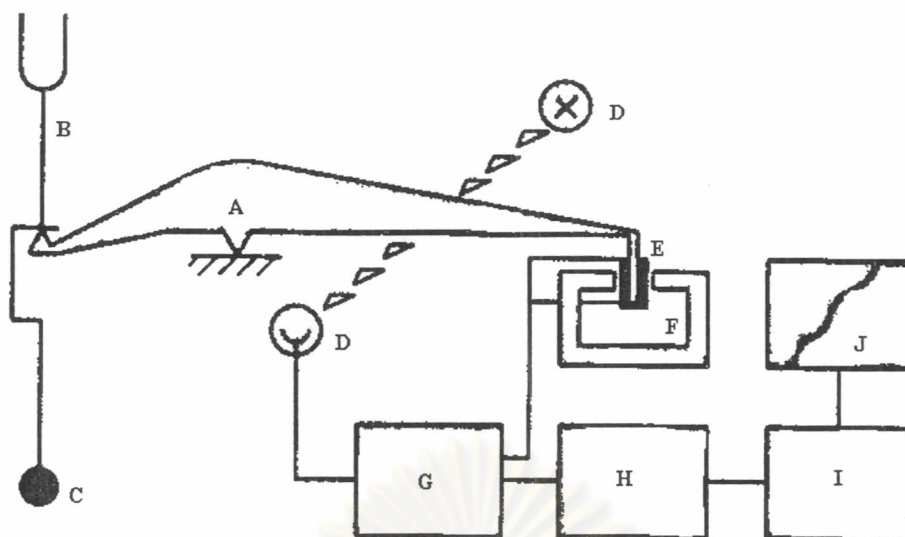


Figure 2.7 Components of a thermal balance. A, Beam; B, sample cup and holder; C, counterweight; D, lamp and photodiodes; E, coil; F, magnet; G, control amplifier; H, tare calculator; I, amplifier; and J, recorder. (Courtesy Mettler Instrument Corp., Hightstown, New Jersey).

3.4. Particle size measurement

3.4.1. Principle

In this research, the particle size was measured by the Malvern laser diffraction technique. This technique is based upon measurements of the forward diffracted light from a disperse suspension. The angle of diffraction is inversely proportional to particle size and the intensity of the diffracted beam at any angle is a measure of the mean projected areas of particles of a specific size [33].

3.4.2. Apparatus and measurement

This apparatus consist of a small He-Ne laser fitted with a spatial filter and a collimating lens which provides a parallel, monochromatic, coherent incident beam. The particles are placed in this beam and the diffracted light is collected by a lens and brought to a focus on a special detector placed in the focal plane of the lens. This detector consists of 30 concentric, semicircular, photosensitive rings. The signal is transmitted to a computer and the whole system is controlled by a teletype [33].

4. Doping molecules

In this research, 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP) (Figure 2.8) is chosen as a doping molecule incorporated into mesoporous silica. This compound is widely used in analytical chemistry as reagent with potential complexation properties. Silica modified with HPMSP has been the subject of intensive interest [34-36]. A. Tong described the preparation of HPMSP supported on microporous silica by impregnation technique [34-35]. The proposed adsorbent showed an excellent extraction capacity for copper, cobalt and nickel. Each metal was completely retained on the adsorbent at the pH values higher than 4. Copper was adsorbed quantitatively from pH 2 onwards. However, cobalt and nickel quantitative extraction began at pH 4. The extraction capacity of HPMSP for copper, cobalt, and nickel was 0.043, 0.045, and 0.049 mol/kg, respectively [34].

A. Intasiri described the encapsulation of HPMSP in microporous and mesoporous silica by doping technique [36]. The results showed that the doped silica has no loss of HPMSP during the synthesis and extraction process. The extraction capacity of HPMSP doped microporous silica for copper, cobalt, and nickel was about 0.04, 0.03, and 0.04 mol/kg, respectively, whereas that of HPMSP doped mesoporous silica for copper was about 0.2 mol/kg. Interestingly, the sol-gel HPMSP doped mesoporous silica provides a high copper extraction capacity. The HPMSP doped mesoporous silica was prepared from a solution of compositions (in mole ratio) 1 TEOS : 140 H₂O : 13 CH₃OH : 0.18 CTAB : 0.06 HPMSP, where H₂O is the 0.1 M NaOH solution which is used as catalyst for the synthesis. However, the parameters affecting the synthesis of doped mesoporous silica and the extraction behaviors of the doped mesoporous silica with cobalt and nickel have not been elucidated.

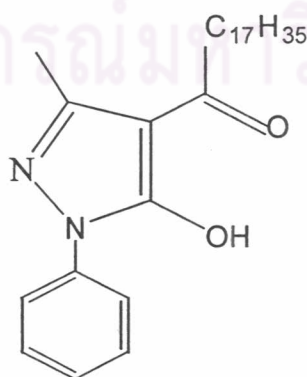


Figure 2.8 The chemical structure of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone.

5. Research objectives

1. To study the synthesis of HPMSP doped mesoporous silica for using as a sorbent in solid-phase extraction of metal from aqueous solution.
2. To study metal extraction behaviors of HPMSP doped mesoporous silica.



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