



CHAPTER III

RESEARCH METHODOLOGY

Specifying of Contaminants

Virgin resins may have several sources of contaminants as shown in Figure 3.1

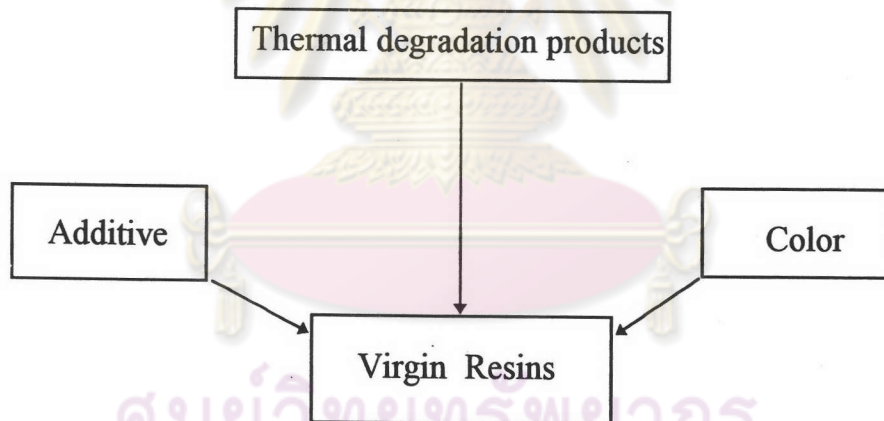


Figure 3.1 Typical contaminant sources in virgin plastics.

Recycled resins generally have greater types of contaminants than virgin resins. By the group of impurity divided as illustrated in Figure 3.2.

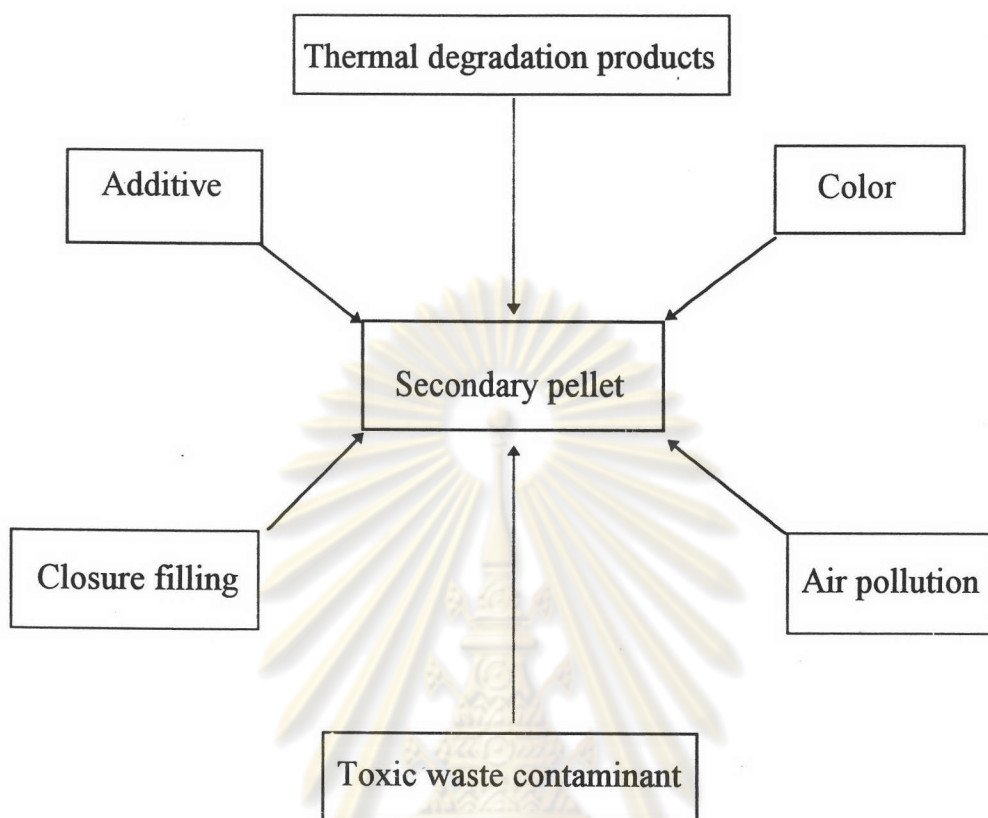


Figure 3.2 Typical sources of contaminants in secondary pellets.

1. Additives

The role of the "additive" can, in general terms, be described as a property modifier for the base polymer or resin in relation to its processability or fitness for purpose. The main categories comprise fillers and/or reinforcements, stabilizers (both heat and light), plasticizers, fire retardants, antistatic agents, lubricants and blowing agents.

Without additives, plastics would be wholly unsuitable for a large number of current applications. Additives have upgraded plastics to the extent that they have become "engineering or structural materials" in their own right

compared with the early plastics which are regarded essentially as decorative materials, at least in so far as the thermoplastics were concerned.[8,9]

2. Colorants

There are essentially two methods for the colouring of plastics : surface colouration (painting , printing, dyeing) and mass colouration. The major proportion of plastics, can be subdivided into organic and inorganic types. The organics, both dyes and pigments, are based upon carbon chemistry whereas the inorganic pigments are mainly metal compounds. Compounding still remains the most accurate colouring technique and is particularly valid for small lots. One of the advantages of compounding is that the density of colour is higher than with other techniques, and in some instances it will produce a better dispersion of the colour than is possible using the so-called masterbatch technique. The major share of the colouring business today based upon what is termed a universal carrier system. The bulk of the masterbatch business is in black and white formulations and a high proportion of this goes into the film market.

Factors that affect the choice of a colourant include:(1) heat fastness and sublimation fastness, (2) light and weathering fastness, (3) non-migratory, non-bloom or plate-out, (4) dispersion, (5) toxicity factors, (6) special requirements, such as fluorescence, alkali fastness, etc., and, (7) cost/performance

Among recent developments in the colour field is the introduction of hyperdispersants. Originally for non-aqueous systems in the printing ink field. Their use extended into the plastics field and they are now well established colour/solid concentrations.

The two most important factors influencing the development of pigments and dyes for plastics are (1) environmental aspects, with attention exterior durability, e.g. improved light and weather fastness, and (2) resistance to stress cracking, etc. The newer polymers (including the engineering plastics) are placing a demand on pigment and dye manufacturers in view of the high processing and end use temperature associated with some of these plastics. The market for polycyclic polymer dyes has grown dramatically in the past five years, and this growth is likely to continue. Organic yellows, oranges and reds will continue to make inroads into cadmium, lead and chrome markets. The lead-based and chrome-based pigments are hardly used today and accepted in applications where they are unlikely to come into regular contact with the public. Despite the frequently aired discussions on cadmium-based pigments, colouring companies see no replacement in sight for these products, particularly the reds. These cadmium pigments are bright, strong and very stable and when incorporated into the plastic material, they present no danger to the consumer. They do, however, need careful handling.

3. Thermal Degradation Products

Polymer degradation is the collective name given to various processes which are harmful and avoid or ruin their outward appearance. Sometimes, although not very often, polymer degradation may be useful. Depolymerization leading to high purity monomers may be exploited for practical production of such material. Degradation may happen during every phase of a polymer's life, i.e., during its synthesis, processing, and use.

During polymer synthesis, depolymerization (polymer degradation) may be taken place. Depolymerization is the inverse of polymerization, namely, a stepwise separation of monomers from the growing chain end.

Polymerization is possible only below the equilibrium temperature of the system, the so-called ceiling temperature. From a practical point of view, it is important that the eventual fate of a polymeric material is often decided during its synthesis. Depending on the polymerization technology, varying amount of "weak sites" may be built into the polymer which will later occasion its deterioration.

During processing, the material is subjected to a very high thermal and mechanical stress. These drastic stresses may initiate a variety of polymer degradation processes leading to a deterioration of properties even during processing. On the other hand, the damaging of the material may result in the introduction of various defects in the polymer which will work as degradation sources during its subsequent service life.

During use, the polymers are in contact with the soil and the same types of bacteria probably attack them, the biodegradability of the polymer employed should thus be very different, On the other hand, if polymers are applied in the outdoor the built stiffening and discoloration of those polymers. [10]

There are various schemes to classify polymer degradation. Because of its complexity, with regard to both the causes and response of the polymer, classification is usually performed on the basis of the dominating features. One of the most frequent classifications has been based on the main factors responsible for degradation.[11]

4. Closure Filling

Plastic bottles and containers are generally to contain consumer products such as detergent, cosmetics shampoo, vegetable oil, medicine, chemicals, etc.[12] These products may adhere to the containers.

5. Air Pollution

Normal air contains about 78% nitrogen and 21% oxygen, the remaining 1% being made up of carbon dioxide. Oxygen is the most immediately important part of the nonliving environment. Human beings can live for weeks without food, for several days without water, but for only minutes without oxygen.

Air is a resource, and air quality is something that must be preserved. Air pollution is thus the transfer of harmful amounts of natural and synthetic material into the atmosphere as a direct or indirect consequence of human activity. Air pollution is the dust, gas and droplets that stir up. Air pollution is a complex pollution because a pollutant can be any of a number of chemical substances existing in gaseous, liquid (aerosol), or solid form (roughly 90% of the weight of all pollutants in the air is gas).

Air pollutants have many different kinds of effects on humans and other parts of the natural world. Air pollution can give a psychological impact; it can make the environment unpleasant. Air pollutants can erode statues and painted surfaces, cause things to become soiled, and damage property in other ways. Air pollution can impair human health and the health of other organisms.

[13]

In Thailand, the agency who detect air quality is Office of the National Environment Board (ONEB). It built eight stations for measure composition of air in Bangkok including big provinces such as Chiangmai, Udornthani, etc. These stations started to detect air quality in 1983. The objective of detection as followed

1. To follow and study air pollution.

2. To analyze and study of hazardous of air pollution and bring to lay down measures for reduce air pollutants.

3. To evaluate the result of regulation of air quality by using standard value of air pollutant.

Those stations are placed in a commercial zone, industrial zone, and household zone. A major air pollutants are given in Table 3.3.[14]

Table 3.1. Average National Ambient Air Quality of Bangkok in 1983

Pollutants	1-hr average value mg/m ³	8-hrs average value mg/m ³	24-hrs average value mg/m ³	1-year average value mg/m ³
Carbon monoxide (CO)	50	20	-	-
Nitrogen dioxide (NO ₂)	0.32	-	-	-
Sulfur dioxide (SO ₂)	-	-	0.30	0.10
Suspended Particulate	-	-	0.33	0.10
Ozone(O ₃)	0.20	-	-	-
Lead(Pb)	-	-	0.01	-

5.1. Carbon Monoxide (CO)

Carbon monoxide(CO) is produced when organic material, such as gasoline, coal, wood, and trash are incompletely burned. The automobile is responsible for most of the CO produced in cities. The number of

automobiles is a great part of this problem. Although the use of catalytic converters has reduced CO emissions, it still remains a problem because the number of automobiles has increased.

Exposure to air containing 0.001 percent of CO for several hours can cause death. Because CO remains attached to hemoglobin for a long time, even small amounts of CO tend to accumulate and reduce the oxygen-carrying capacity of the blood. The amount of CO produced in heavy traffic can cause headache, drowsiness, and blurred vision.

Fortunately, CO is not a persistent pollutant. Natural processes convert CO to other compounds that are not harmful. Therefore, the air can be cleared of CO if no new CO is introduced into the atmosphere.

5.2. Nitrogen Dioxide (NO₂)

When combustion takes place in air, the nitrogen and oxygen molecules from the air may react with each other and oxides of nitrogen result:



A mixture is usually produced, and the mixture is called No_x. These nitrogen compounds produce a reddish-brown color in the atmosphere and react with other compounds to produce photochemical smog. The primary source of nitrogen oxide is the automobile engine but catalytic converters reduce the amount of nitrogen oxides released from the internal combustion engine.

5.3. Sulfur Dioxide

Sulfur dioxide (SO₂) is a compound containing sulfur and oxygen that is produced when sulfur-containing fossil fuels are burned. Coal

and oil were produced from organisms that had sulfur as one of the component parts of their living structure. When the coal or oil was formed, some of the sulfur was incorporated into the fossil fuel and it is released as sulfur dioxide when the fuel is burned. SO_2 has a sharp odor and irritates respiratory tissue. It also reacts with water, oxygen, and other materials in the air to form sulfur-containing acids. The acids can become attached to particles. When inhaled, such particles are very corrosive to lung tissue.

5.4. Particulates

Particulates constitute the third largest category of air pollutants. These are small pieces of solid materials that are dispersed into the atmosphere. Small particles from fires, bits of asbestos from brake linings and insulation, dust particles, and ash from industrial plants contribute to the particulate load. Particulates cause problems ranging from the annoyance of soot settling on your backyard picnic table to the carcinogenic effects of asbestos. Particulates frequently get a lot of attention because they are so readily detected by the general public. The heavy black smoke from a factory can be seen by anyone without any expensive monitoring equipment.

5.5. Lead

Lead is fairly well known as an environmental problem related to its use in paint. This has been a serious problem in rundown old housing where very young children eat leaded paint chips, apparently because they taste sweet, and suffer lead poisoning. The general problem of atmospheric lead contamination comes largely from the automobile and the high-compression engine.

Tetraethyl lead was introduced as a motor fuel additive in the 1920s, as a means to slow gasoline combustion to reduce engine knock and engine wear. Nearly all of that lead gets back into the environment through the air. The

leaded gasoline is the main source of atmospheric lead was made clear by the impact of unleaded gasoline.

Because the automobile has been and still is a major source of lead pollution (almost half the gas used today still contains lead), urban air gas concentrations of lead 5-10 times those of sparsely populated areas and several thousand times more than would be found in the air over mid-ocean.[15]

6 Toxic Waste Contaminants

6.1. Municipal Waste

Municipal refuse is composed of a vast array of products which have lost their usefulness and have been discarded. These wastes include home wastes, commercial wastes and city wastes while home and commercial wastes are usually collect elsewhere and require special handling and disposal.

Home wastes include such diverse products as glass bottles, cans, plastics toys, paper, cellophane, cardboard, nails, small appliances, tools, light bulbs, clothes, rubber products, wood and food items. If these products are not seperated into classes such as metal, glass, paper, and etc, in the home, this waste becomes very heterogeneous.

Commercial wastes are generated by retail business and in stitutions such as hospitals, banks and schools. Although these wastes are also heterogeneous, they contain high percentages of office wastes and packaging materials. City wastes include automobile bodies, large appliances, tires, dead animals, demolition wastes, street sweepings, crankcase oil and sewage sludge.

The typical of municipal refuse is given in Table 3.2[16]. The composition of municipal waste from different state will also varied because of geographical location. The composition of municipal refuse in Bangkok is showed in Table 3.3[17].

Organic wastes, sewage sludges, animal wastes, crop wastes and food wastes and high-nutrient mineral wastes must be returned to the soil, implying the displacement of synthetic soil nutrients. Metals must be returned to the soil, implying the displacement of synthetic soil nutrients. Metals must be returned to industries that generate them, implying the displacement of ores and associated raw materials.

Material made of natural fibers, wood paper, paperboard, and some textiles can be returned to their originating industries implying the displacement of pulp wood, sheep's wool, cotton and so forth. These synthetic materials like synthetic textiles, plastics, and rubber can be converted directly into energy or into fuels, displacing fossil fuels.

Glass, ceramics, ashes, mine wastes, and similar minerals must move into construction materials, they must complete in and industry traditional in its structure and practices.

Table 3.2 Typical municipal refuse.

Paper
-corrugated paper boxes
-newspaper
-magazine paper
-brown paper
-mail
-paper food cartons
-tissue paper
-wax cartons
-plastic coated paper

Table 3.2 continued.

Moisture
Garbage
-vegetable food wastes
-cirtus rinds and seeds
-metal scraps
-fried fats
Glass, ceramics, ash
Vegetation
-ripe tree leaves
-flower garden plants
-grass
-evergreen
Metals
Miscellaneous
-wood
-plastics
-rags
-leather goods
-rubber composition
-paint and oils
-vacuum cleaner catch
-dirt

Table 3.3 Composition of municipal refuse in Bangkok.

Category	weight percent
1. Combustible	59.30
-paper	15.40
-cloth and textile	4.50
-plastic and foam	16.02
-wood and tree leaf	4.24
-fruit and vegetable garbage	15.36
-bone and shell	1.21
-leather and rubber	2.17
2. Non combustible	7.78
-metal	2.52
-glass	4.65
-stone, soil, ash and ceramics	0.61
3. Miscellaneous	
-size less than 6 mm	7.92
-size more than 5 mm	25.00

จุฬาลงกรณ์มหาวิทยาลัย

Experimental

The following are lists of chemicals, glasswares and apparatus used in this work.

Chemicals

- | | |
|----------------------------------------------------------------|---------------------------|
| 1. Chloroform (CHCl_3), AR grade | : Fluka |
| 2. Methanol (CH_3OH), AR grade | : Fluka |
| 3. n-Butyl benzene ($\text{C}_{10}\text{H}_{14}$), AR grade | : Fluka |
| 4. Styrene monomer, distilled and stored at 20°C | : TPI |
| 5. Nitric acid (HNO_3), AR grade | : Carlo Erba |
| 6. Sulfuric acid (H_2SO_4), AR grade | : Carlo Erba |
| 7. Vanadium pentoxide (V_2O_5), Ar grade | : Fluka |
| 8. Hydrogen peroxide | : Fluka |
| 9. Dry ice | : Air product Co.
Ltd. |

Glasswares

1. Volumetric flask 50, 100, 250, 500 cm^3
2. Beaker 25, 50, 100, 250 cm^3
3. Condenser
4. Crucible
5. Stirring rod
6. Micro-syringe 1 to 50 μl
7. Conical flask with serum cap closure



Apparatus

1. Centrifuger : IEC model CL centrifuger
2. Carbolite furnace : Erotherm 808
3. Atomic Absorption Spectrophotometer (AA) : Varian model spectra AA300
4. Gas chromatography : Shimadzu GC-7AC
5. Simultaneous Thermal Analyzer (TG/DTA) : Netzsch STA 409
6. X-ray diffractrometer : JDX-8030

Procedure

1. Determination of Lead in Packaging Plastics

Lead in plastics, both resin form and product form can be determined by quantitative flame absorption technique.[18]

1.1 Preparation of lead solution

Plastic was weighed exactly 2.00 grams and transferred to 75 ml crucible. Plastic was digested with 1 ml of concentrated sulfuric acid. It was subsequently burned directly with lightly fire until loss of smoke. The crucible was put into carbolite furnace at 500°C for 3 hours. The temperature of furnace was raised slowly to prevent ignition of the sample. The obtained product was ash. This ash was dissolved with 20% volume of nitric acid after filtered with

filter paper. The received solution was kept in 50 ml volumetric flask and added with distilled water until the volume of solution equals 50 ml.

The blank was determined by using all reagents without sample.

1.2. Atomic absorption operation condition

Instrument mode	: Absorbance
Calibration mode	: Concentration (Rational fit)
Measurement mode	: Integration
Lamp position	: 4
Lamp current (mA)	: 5
Slit width(nm)	: 1.0
Slit height	: Normal
Wavelength (nm)	: 217.0
Flame	: Air-Acetylene
Sample introduction	: Manual
Delay time (sec)	: 6
Time constant	: 0.05
Measurement time (sec)	: 20
Replicates	: 3
Background correction	: on
Air flow (L/min)	: 13.5
Acetylene flow (L/min)	: 2.00
Rinse rate	: 1
Rinse time (sec)	: 5.0
Recalibration rate	: 0
Reslope rate	: 0

1.3. Atomic absorption of sample and calibration

1.3.1. Calibration curve

The lead standard solution 5, 10, 15, 20 ppm, respectively, was prepared from lead standard solution 1000 ppm. A series of these standard solutions were measured by atomic absorption at 217.0 nm. The obtained data was the absorbance and the amount of lead. The plotted curve was shown in Appendix A

1.3.2. Sample analysis

Sample solution which was prepared from 1.1 was measured the absorbance and compared to obtained calibration curve. The result of data was given as the concentration of lead in ppm. The detailed methods of the calculation was described in Appendix A

2. Determination of Cadmium in Packaging Plastics

Cadmium in plastics can be determined by flame absorption technique.[18]

2.2. Preparation of cadmium solution

Plastic was weighed exactly 1.00 gram and transferred to 75 ml crucible. This plastic was added from a dropper of 1 ml of concentrated sulfuric acid. It was subsequently burned directly with lightly fire until the almost sulfuric acid was volatilized. This crucible was heated subsequently by the carbolite furnace at 450°C about 2 hours. The sample form was changed into ash. This ash was wetted by concentrated sulfuric acid and heated by the carbolite furnace at 450 °C again. The ash was made at the same condition until the obtained ash as almost white. The almost white ash was dissolved in

0.1 mol/l of nitric acid and added with 0.1 mol/l nitric acid until the volume of solution equals 100 ml. The solution was stirred as homogeneous mixture.

The blank was prepared by using all reagents without sample, through the entire procedure.

2.2. Atomic absorption operation condition

Instrument mode	: Absorbance
Calibration mode	: Concentration (Ratio fit)
Measurement mode	: Integration
Lamp position	: 1
Lamp current (mA)	: 4
Slit width(nm)	: 0.5
Slit height	: Normal
Wavelength (nm)	: 228.8
Flame	: Air-acetylene
Sample introduction	: Manual
Delay time (sec)	: 6
Time constant	: 0.05
Measurement time(sec)	: 2.0
Replicates	: 3.
Background correction	: on
Air flow (L/min)	: 13.5
Acetylene flow (L/min)	: 2.00
Rinse rate	: 1
Rinse time (sec)	: 5.0
Recalibration rate	: 0
Reslope rate	: 0

2.3. Atomic absorption of sample and calibration

2.3.1. Calibration curve

The cadmium standard solution 0.125, 0.25, 0.5, 1.0 ppm, respectively, was prepared from cadmium standard solution 1000 ppm. A series of these standard solution were measured by atomic absorption of 228.8 nm. The obtained data was the absorbance value. The curve was plotted linearity between absorbance and the number of cadmium. The plotted curve was shown in Appendix B

2.3.2. Sample analysis

Sample solution which prepared from 2.1 was measured the absorbance and compared the obtained calibration curve. The result of data was given as the concentration of cadmium in ppm. The detailed methods of the calculation was described in Appendix B

3. Determination of Mercury in Packaging Plastics [19,20]

The mercury content was determined by a cold vapour atomic absorption technique.

3.1. Preparation of mercury solution

The equipment setup is shown in Figure 3.3. It carried out digestion in heavy draft fume hood.

The vanadium pentoxide, grounded plastic were weighed 0.25 g, 5.00 g, respectively, into 200 ml-2 necked Erlenmeyer flask. The resin was added to soak with 6 ml concentrated HNO_3 while the cold finger was filled with dry ice. The flask was heated on hot plate at 95°C for 2 hours to initiate oxidation. (during digestion, the cold finger was sufficient filled with dry ice all times.) When vigorous setted in, the heater was turned off to abate frothing and

cautiously 2 ml concentrated H_2SO_4 added to the flask, 2-3 drops at a time, to control condition. After completely addition of H_2SO_4 , resumed gentle heating followed by dropwise addition of 12 ml concentrated $\text{HNO}_3\text{-H}_2\text{SO}_4$ (1+1) mixture 5-10 drops at a time. After addition of acid mixture, continued gentle heating for 30 mins and solution was cooled. When digestate had attained room temperature, 30% H_2O_2 added with gentle swirling. Dry ice was lost from cold finger (to avoid dropping ice sticking to its outer surface)

The outer portion of cold finger, tip of dropping funnel, water cooled condensor, and inner surface of outer jacket were rinsed with minimum volume of 3% H_2SO_4 and added the rinse to digestion flask (total volume should not exceed 70-80 ml). Subsequently, this solution was filtered through conical flask with filter paper (prewashed with H_2SO_4) into a 100 ml volumetric flask. The content of digestion flask was transferred quantitatively with several rinsings and diluted to volume with 3% H_2SO_4 .

The blank was prepared by using all reagents without sample, through the entire procedure.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

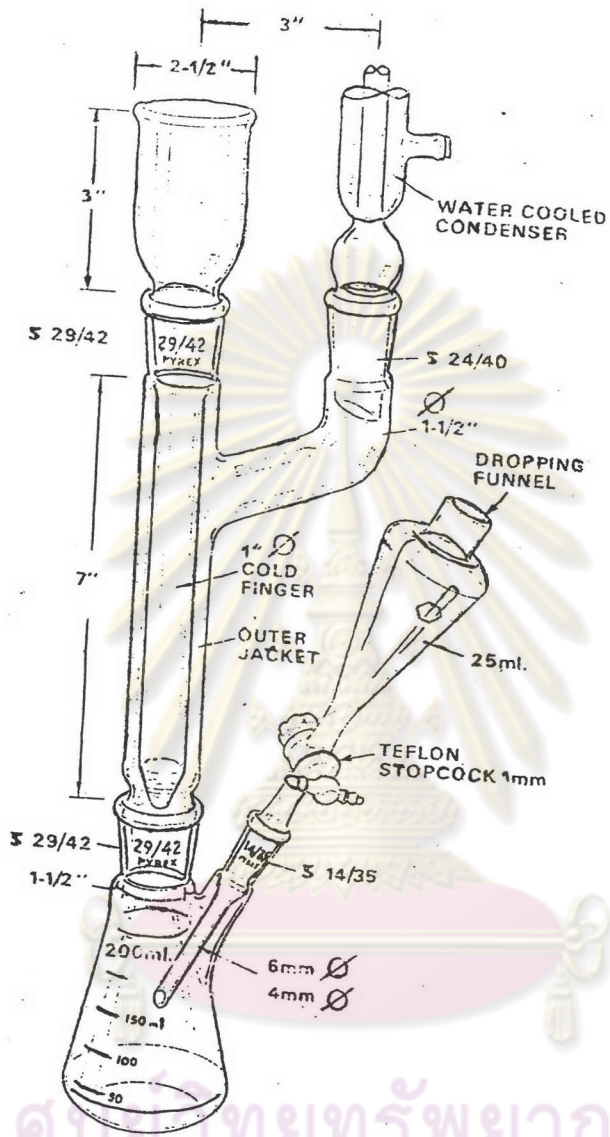


Figure 3.3 Digestion equipment.

ศูนย์วิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

3.2 Atomic absorption operating condition

Instrument mode	: Absorbance
Calibration mode	: Concentration
Lamp position	: 1
Lamp current (mA)	: 4
Slit width (nm)	: 0.5
Slit height	: Normal
Wavelength(nm)	: 253.7
Flame	: Air only
Sample introduction	: Manual
Delay time(sec)	: 60
Time constant	: 0.05
Measurement time (sec)	: 1.0
Replicates	: 3
Background correction	: on
Air flow (L/min)	: 0.00

3.3. Atomic absorption of sample and calibration

3.3.1. Calibration curve

The mercury standard solution; 20, 40, 60, 80 ppb was prepared from mercuric chloride standard solution 1000 ppb. A series of these standard solutions were measured by atomic absorption at 253.7 nm. The obtained data was the absorbance and the amount of mercury. The plotted curve was shown in Appendix C.

3.3.2. Sample analysis

A sample (5 grams) of polyethylene, polypropylene, polystyrene were digested by using this procedure. After analysis of calibration

standards, analyze digestate as described above and checked performance of instrument by interposing standard solution after many samples. The detailed methods of the calculation was described in Appendix C.

4. Determination of Residual Styrene Monomer in Polystyrene

[21]

The International Standard specifies a method for the determination of residual styrene monomer in polystyrene by gas chromatography, it may be used also for the simultaneous determination of other volatile aromatic hydrocarbon in polystyrene. It is applicable both to styrene homopolymer and to butadiene modified polystyrene.

4.1. Preparation of solvent for the styrene monomer

n-Butylbenzene was weighed 900 ± 1 mg into a 25 ml flask, transferred quantitatively into a 1000 volumetric flask, and diluted to 1000 ml with chloroform. During the dilution process, the liquid was maintained at a temperature of $20 \pm 0.5^\circ\text{C}$.

4.2. Preparation of the styrene monomer

The polymer sample was weighed 1.500 ± 0.001 g. and transferred to a 100 ml conical flask, preferably with a serum cap closure. The sample was added from a pipette exactly 100 ml of the solvent which prepared according to 4.1 and kept at $20 \pm 0.5^\circ\text{C}$. After the flask was dissolved, with shaking if necessary. After complete dissolution, the solution was added exactly with 5 ml of methanol and kept at $20 \pm 0.5^\circ\text{C}$ either by syringe or from a pipette. After vigorous shaking, the precipitate was allowed settle. For injection into gas

chromatograph, the required amount with the syringe from the supernatant solution.

4.3. Preparation of calibration solution

Preparation of solution for calibration was weighed 600 ± 0.5 mg of n-butylbenzene together with an appropriate amount of styrene to be determined, and diluted in a volumetric flask to 1000 ml with a mixture of chloroform and methanol in volume ratio 2:1. Appropriate amounts of styrene monomer were

50, 100, 150, 200, 300, and 400 mg

Styrene monomer was weighed to the nearest 0.5 mg. The temperature of liquid should be $20 \pm 0.5^\circ\text{C}$. A separated calibration solution, or a series of calibration solutions, was prepared for each single hydrocarbon to be determined. The solutions were kept for injection into the gas chromatograph.

4.4. Gas Chromatographic Operating condition

4.4.1. Gas chromatographic operation condition

Column	: SP 1200
Column temperature	: 120°C (isothermal)
Temperature of injection port	: 200°C
Temperature of detector compartment	: 200°C , FID
Carrier gas	: Nitrogen
Fuel gas	: Hydrogen , air
Flow rate of carrier gas	: 40 ml/min
Recorder speed	: 0.3 mm/min

4.4.2. Gas Chromatographic recording of sample and calibration solution

According to the sensitivity of the gas chromatograph used 1 μ l of the styrene solution injected and prepared according to 4.2 or calibration solution (prepared according to 4.3). The injection volume was not critical for the calculation of results, but should be identical for corresponding sample and calibration solution.

Gas chromatograph was developed until the n-butylbenzene was completely eluted. The calibration curve and the calculation were shown in Appendix D.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย