Chapter 8
Food Waste and Manure

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Abstract Investigation of composition of biomass is an important pre-requisite for determining its suitability for various downstream applications. In recent times, food waste has emerged as a valuable biomass feedstock which could be valorized for production of fuels, chemicals and materials. Prior to use as a feedstock, it is pertinent to perform a detailed composition analysis and gather critical information about nutrient content including carbon, nitrogen and lipid. Additionally, analysis of minor constituents in food waste is significant to understand the possibility of their toxic or inhibitory effects during biotechnological conversions. Another abundant biomass source is manure which primarily arises from animal feeding operations. The major application of manure is land-applied fertilizer besides the recent investigations for fuel and energy. These intended applications demand complete characterization of nutrient content and quality. Thus, this chapter is focused on characterization and analysis of food waste and manure. Methods for sampling, handling and pretreatment of food waste and manure are discussed. Furthermore, a detailed nutrient analysis and equipment used for analysis is

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described. We further discuss the application of food waste processing techniques which could facilitate the characterization, treatment and product recovery.

8.1 Generation of Food Waste and Manure and Need for Characterization

Food waste is defined as the food which is still able for human consumption has been removed from food supply chain and it is commonly but not completely occurring at both retail and consumer levels [1, 2]. Every year approximately 1.3 billion tonnes of food produced for human consumption in the world is wasted. According to the Food and Agricultural Organisation (FAO), approximately 40–50% of fruits, vegetables and root crops, 35% of fish, 30% of cereals and 20% of meats, dairy and oil seeds are wasted globally every year [3]. Conventionally, this type of food waste undergoes the first generation waste treatment including disposal in landfills and incineration. Both options are undesirable since landfilling may cause severe health and sustainability issues, whereas incineration of high moisture content of food waste results in release of dioxins that lead to environmental problems [4].

Food waste is a valuable resource for biofuels, biochemicals and biomaterials production [5]. Food waste mainly contains carbohydrates, proteins, lipids and trace minerals. It also contains minor constituents such as food and colour additives. Nutrients in food waste can be used by microorganism to produce value added products. Food wastes can have various compositions, for example, food waste consisting of rice is rich in carbohydrate, and food waste consisting of meat is rich in proteins and lipids [4]. Proper procedures for food waste handling and storage is needed because food waste contains high content of moisture. It is easy to spoil and release bad odour. Besides that, accurate knowledge of physical, chemical and composition of food waste is important information for food waste valorization application. Food waste characterization can be done in several methods. Its nature, composition and nutritional value are the properties to determine the methods of food waste collection, storage, handling and utilization. Determination of chemical composition such as carbohydrate and amino acids of food waste is important because it affects hydrolysis and fermentation application [6]. The presence of preservatives and colorants in food waste also can cause inhibition of enzymatic hydrolysis and fermentation. Hence, knowledge of methods and standard procedures for proper handling and characterization of food waste is important. Such methods are introduced in this chapter, which include sampling and preconditioning of food waste, physico-chemical characterization and composition analysis, extraction techniques for recovery of useful components and equipment used for characterization.

Manure is a valuable source of nutrients for crops and it can improve soil productivity. It is an organic matter which is mostly composed of animal faeces and urine, and may contain livestock bedding, additional water and wasted feed.

It contains a wide range of nutrients such as nitrogen, phosphorous and potassium as well as secondary or micro-nutrients such as copper, manganese, zinc and sodium [7, 8]. The additional bedding in manures makes them an excellent source of organic matter which helps to improve soil quality when applied to land. However, the properties of manure depend on a broad array of factors including animal species, age, diet, digestibility, housing, environment and stage of production [9]. Furthermore, the handling and storage of manure before land application also influence the final quality of manure nutrients [10]. This makes manure management more difficult than synthetic fertilizers. Accurate knowledge of physical and chemical properties of manure is important to derive its full benefits as a fertilizer and ensures its efficient land application. An additional concern is the possible environmental contamination in the case of excessive manure application and/or leaching [11]. Manure characterization can be done in several ways. Its solid content, size and composition are the properties which determine manure collection, storage, handling and utilization. Determination of important nutrients such as nitrogen, phosphorous and potassium is essential since it affects land application rates and treatment techniques [12]. A detailed account of presence of secondary elements, trace (heavy) elements and other contaminants such as pesticides is also important to avoid environmental risks to surface and groundwater, as well as threats to human and livestock health through the food chain [13]. Therefore, there is a pressing need for efficient manure management through proper characterization to enable sustainable use of nutrients and mitigate environmental impacts.

8.2 Introduction of Sampling and Preconditioning of Food Waste

The main sources of food waste include manufacturers, retailers, catering business and consumers. Food waste from manufacturers, retailers and catering business is also known as ‘industrial food waste’, and another type of food waste is known as ‘household food waste’ [14], which includes meat and fish, dairy and eggs, bakery, cakes and desserts, fresh fruit, drinks, fresh vegetables and salads, meals and others [15]. Industrial food waste includes molasses and bagasse from sugar refining, fruit and vegetable residues, residues from wineries, breweries and dairy wastes [14]. Besides that, grocery retail store food waste is also categorized as industrial food waste.

8.2.1 Sampling Method

Sampling of food waste is an important and useful procedure because a quality estimate of food waste can be obtained quickly and accurately without the need for analysis of total population of food waste [16]. Probability sampling technique is

used to ensure valid and reliable inferences from a sample. There are four types of methods which are commonly used in sampling. These include simple random sampling, stratified sampling, systematic sampling and cluster sampling. Every subject has an equal chance to be selected for the study in a simple random sampling method. In stratified sampling method, the sample is divided into subgroups and then sample is withdrawn from each subgroup using simple random sample method. In the systematic sampling method, the sample is selected with a fixed periodic interval. Sampling interval is calculated according the population size and divided by the desired sample size. Cluster sampling involves the random selection of the sample from a subset of the clusters wherein the population of food waste is divided into clusters. These clusters are normally based on geographic area and district [17]. Simple random sampling normally applies on homogenous food waste [18]. Stratified sampling should be applied when certain factors of the area was studied (e.g. seasonal, geographical and socio-economic factors), those factors affect the composition of food waste [19]. Systematic sampling is suitable for not stratified homogenous food waste [18]. Cluster sampling should be applied when all elements for sample frame is not suitable [20].

8.2.2 Sampling Conditioning Before Analysis

Food waste is rich in nutrients such as carbon, nitrogen and lipid sources. In addition, the moisture content of food waste is high. Therefore, it has to be treated immediately after collection as microbial growth will rapidly cause food waste spoilage and release of bad odour.

Different methods can be used for food waste treatment. According to our former study, food waste was blended after collection and kept at 4 °C until further processing [21]. Subsequently, the blended food waste was processed using a food waste treatment machine to produce food waste powder. The two processes involved in food waste treatment include shredding and dehydration at 100–150 °C. On the other hand, Yu et al. [22] used a freeze drying process to treat the food waste after collection [22]. The freeze-dried food waste was then ground and sieved through 0.2 mm mesh. Finally, the food waste powder was stored in cold room at 4 °C under dark conditions. Li et al. [23] collected fruits and vegetables waste from street market (Sham Shui Po, Hong Kong) [23]. After that, they were washed with deionized water and blended into pastes using a blender. The resultant pastes were kept at −20 °C until further use. Pagliaccia et al. [24] collected food waste, chopped and screened it. A knife was applied to shred the food waste [24]. Storage occurred at −20 °C. Different methods of pre-treatment have different impact of shelf life of storage. Freeze drying method enables longer shelf life for food waste storage as compared to dehydration and wet storage. Since the moisture content of food waste using freeze drying method is lower than dehydration and wet storage [25].

8.3 Physico-Chemical Characterization and Composition Analysis of Food Waste

In a sustainable waste management strategy, determination of nature, composition and nutritional value of food waste is an important step. Identification and quantification of food waste provides knowledge of food waste composition. This information is useful for selection of further processing methods. The food waste composition plays an important role in producing valuable products and waste treatment [26]. For example, high carbohydrate content is suitable for alcohol production. However, carbohydrate content could be too high thereby causing inhibitory effect on microbial growth and alcohol production. Hence, suitable sugar concentration is needed for fermentation and this critical information can be obtained through composition analysis [27].

Physical characterization of food waste includes determination of weight, moisture, total solid, ash and volume. The moisture content of a sample is important because it affects the food waste composition. Total solid content provides information of the age, origin or pretreatment. Chemical characterization of food waste includes proximate analysis i.e. total carbohydrates, proteins, lipids and pH. The pH of food waste represents freshness of the waste, pH changes upon hydrolysis, fermentation or storage [26].

8.3.1 Moisture Content

Determination of moisture content is necessary in order to calculate food constituents on a dry weight basis. Different types of equipment can be used to determine moisture content. This includes forced draft oven, vacuum oven, microwave drying, rapid moisture analyzer, toluene distillation, Karl Fisher and near infrared spectroscopy.

In the forced draft oven method, the moisture content of a sample is calculated on the basis of weight loss after heating at specified conditions (AOAC 2005, Method 930.29) [28]. Moisture content determination using the vacuum oven method is similar to forced draft oven method, except that it involves heating of sample at reduced pressure conditions for water removal (AOAC 2005, Method 926.12) [28]. In the microwave drying method, the moisture content of a sample is calculated based on weight loss after heating using microwave energy (AOAC 2005, Method 985.26) [28]. Rapid moisture analyzer method measures the percentage of moisture in a sample based on weight loss upon heating at controlled high heating condition [29]. Principle of toluene distillation method is the moisture content which is measured through volume of water removed from distillation, where moisture in sample is co-distilled with toluene (AOAC 2005, Method 925.04) [28]. Karl Fisher method is a titration-based method which is based on the principle that the amount of water in a sample is directly proportional to the volume

of Karl Fisher reagent (KF) needed to achieve the endpoint of titration (AOAC 2005, Method 991.01, 984.20) [28]. Iodine is reduced by sulphur dioxide from KF reagent when it reacts with water. Principle of near infrared analyzer method is based on the determination of moisture content of a sample by measuring the energy that is transmitted by the sample, which is inversely proportional to the energy absorbed [29].

8.3.2 *Carbohydrate Content (Total Carbohydrate, Starch, Free Sugar)*

Carbohydrate content of food waste is important because it indicates the amount of total carbohydrate, starch and free sugar that can be recovered and reused as nutrient sources in microbial fermentation for production of value-added products.

In 1956, Dubois et al. developed a colorimetric method to determine the carbohydrate content. Free reducing groups from polysaccharides, oligosaccharides, simple sugars and derivatives react with phenol and concentrated sulfuric acid to form orange-yellow colour solution. This method could be used for measuring small quantities of sugars in samples which could be extracted with volatile solvent [30]. In 1972, Lever developed another colorimetric method for determination of carbohydrates. Reducing carbohydrates react with acid hydrazides in alkaline solution to give yellow anions. It can be used to detect glucose or monosaccharides with concentration less than 1 μg [31]. Phenol-Sulfuric method and UV-Vis spectrophotometer have been applied in determination of total carbohydrate in food waste by WRAP [32].

In 1969, Gur et al. used colorimetric method for starch determination based on the Nielsen method which includes colorimetric determination of starch with iodine, and the Morell method which includes precipitation of starch with iodine and its subsequent hydrolysis to release reducing sugar [33]. In a new analytical method, starch content was measured through glucose produced from enzymatic hydrolysis of starch. Starch was hydrolyzed by thermostable α-amylase into soluble maltodextrins. Then, it underwent hydrolysis to produce glucose using amyloglucosidase [34]. Megazyme's total starch kit was applied for starch content determination in food waste by Pleissner et al. and Ma et al. [35, 36].

Free sugar determination was performed by cold water extraction. Approximately 5 g of dried food waste powder was added with 50 mL deionized water and shaken for half an hour. After that, 2 mL of zinc sulphate solution (30%, w/w) and potassium ferrocyanide (15%, w/w) were added sequentially. After shaking, the filtrate was analyzed by HPLC [37]. Another free sugar determination was carried out by water extraction in which 1 g of dried food waste powder sample was mixed with 10 mL deionized water. Extraction of free sugar from food waste was then performed by sonication for 30 min. After that, centrifugation of food waste mixture was carried out at 10,000 g for 10 min. Supernatant was filtered and analyzed with HPLC [38].

8.3.3 Protein and Free Amino Nitrogen Content

Nitrogen is present in all organisms in the form of proteins, amino acids, nucleotides as well as heteroatom in molecules. Due to the ubiquitous occurrence of nitrogen, the investigation of quantification methods has a long history. For instance, the determination of proteins in blood was carried out using the so-called 'van Slyke method' just over a hundred years ago. The van Slyke method is based on the reaction of aliphatic amino groups with nitrous acid and quantification of released gaseous nitrogen [39]. This method was a highly recommended method among others for quantitative analyses of nitrogen-containing compounds. Examples include (i) the relative digestibility of proteins, (ii) proteolytic enzymes, (iii) amino acids and (iv) amino nitrogen in urine. Pleissner et al. and Ulusoy et al. built upon this method and used the reaction of aliphatic amino groups with nitrous acid in order to convert amino acids into their corresponding α-hydroxy acids [40, 41]. Their motivations were to develop a chromatographic method to analyze amino acids in fermentation broth using an Aminex HPX-87H column (Bio-Rad, CA, USA). This column was packed with a polymer-based matrix which contains 8% cross-linked resin in ionic hydrogen form. Therefore, it would exclude ionic molecules. Since sulfuric acid was used as an eluent, amino acids were in ionic form and therefore it was not separated. By converting amino acids into their corresponding α-hydroxy acids and determination of the latter, single amino acids could be analyzed indirectly even in complex solutions such as fermentation broths [40, 41]. Therefore, the application of this chromatographic method for the quantification and identification of amino acids in food waste hydrolysates can be considered as an alternative option.

In 1973, Lie published a method for determination of free α-amino nitrogen in malt and wort using ninhydrin [42]. Ninhydrin causes an oxidative decarboxylation of α-amino acids and production of CO_2, NH_3 and an aldehyde with one carbon atom less than the parent amino acid. Reduced ninhydrin reacts with unreduced ninhydrin and forms a blue complex. The intensity of the blue complex corresponds with the concentration of free α-amino nitrogen and it can be measured photometrically at a wavelength of 570 nm [42]. In the past, this method has not only been applied for the analysis of malt and wort, but also for food waste hydrolysates [36], wheat flour hydrolysate [43] and hydrolyzed rapeseed meal [44].

The van Slyke method, the modified methods by Pleissner et al. and Ulusoy et al. as well as the ninhydrin method of Lie work when amino acids are presented as monomers with a free amino nitrogen group [39–42]. However, proteins and peptides need to be hydrolyzed first. The simplest method for analyzing the content of proteins is by UV-spectroscopy. Aromatic amino acids such as tryptophan and tyrosine absorb at 280 nm. Nevertheless, the composition of aromatic amino acids can be different between proteins, and thus this method is only reliable for quantification of the same protein. Another option is the Bradford assay based on the binding of Coomassie Blue dye to proteins. Binding of the dye is non-covalent, which includes interaction with basic and hydrophobic surfaces. Higher quantity of

proteins would lead to more bindings of dyes. The fraction of Coomassie dye interacting with protein can be quantified photometrically at 595 nm [45]. However, the interaction of Coomassie dye with protein might be disturbed when proteins are modified, for instance, by glycosylation.

Complex materials such as food waste and manure may contain compounds either interacting with dyes or also absorbing at 280 nm. Furthermore, the complexity and recalcitrance of solid biomass may hinder the quantification of nitrogen-containing compounds. Therefore, a tough pretreatment is needed in order to release all nitrogen-containing compounds for the analysis of nitrogen in complex substrates with a certain solid fraction. One of the approaches is the digestion of the compact structure using strong acids under heat, and the nitrogen measurement would be conducted using a total nitrogen analyzer [36]. However, the chemical standard method is the determination of total nitrogen according to Kjeldahl. Johan Kjeldahl developed this method in 1883 and even more than 130 years later, it is still one of the most widely used standard in many laboratories worldwide. Total nitrogen is in the forms of dissolved inorganic and organic nitrogen, as well as of particulate inorganic and organic nitrogen. An advantage of the Kjeldahl method is that it can be used for analyses of both liquid and solid environmental samples.

The Kjeldahl method is based on a complete breakdown of materials using hot sulfuric acid. Furthermore, the addition of salts, oxidative agents and catalysts such as mercury used in early days can improve the digestion [46]. Over the years, several improvements of the Kjeldahl method have been reported. One of the improved methods is the microscale Kjeldahl nitrogen determination [47]. Campins-Falco et al. aimed at reducing the scale of the conventional Kjeldahl method from 800 mL to 25 mL [47]. This reduction in scale results in the reduction of volumes of reactants, which is in line with effort associated to the recent development of green and sustainable chemistry approaches. For 20 mL of sample, 0.75 mL of concentrated sulfuric acid was added and heated at 370 °C for 25 min. After dilution of the digestion residue, 12.5 M NaOH was added and ammonium was distilled. Distilled ammonia was neutralized using 0.02 M sulfuric acid. Sodium hydroxide (10 M) was added to the distillation solution and the Kjeldahl nitrogen was measured using an ammonia selective electrode. According to Campins-Falco et al., almost 100% recoveries and good precision have been achieved, and the cost of analysis was significantly reduced in comparison to the conventional Kjeldahl method by a factor of 10 [47].

In addition, conversion factors have been established for estimation of protein content in biomass and food waste based on free amino nitrogen or Kjeldahl nitrogen determination. For instance, Mariotti et al. reviewed a couple of conversion factors related to food [48]. They proposed an average conversion of 5.6, which was more appropriate than the commonly used factor of 6.25. Since food waste consists of food, a factor of 5.6 can be applied to estimate its protein content. Based on the quantification of free amino nitrogen by Lie [42] and Pleissner et al. [49], a conversion factor of 5.7 can be used to estimate the protein content. This is similar to the value suggested by Merrill and Watt [50].

8.3.4 Lipid Content

Lipid content determination is important because lipids influence aerobic and anaerobic fermentation in various ways, including growth stimulation, improving the tolerance and as antifoam agents [26]. Free fatty acids in lipids have been responsible for controlling ethanol tolerance of yeast [51]. Furthermore, when molasses were used as substrate for fermentation, a low lipid content stimulated high production of ethanol, high lipid content of molasses reduced ethanol production [26]. There are many methods to determine the lipids content of food waste. Hexane/isopropanol (3:2) method was applied in determination of lipid content of food waste by Ma et al. [35]. Lipid content of food waste was determined using the chloroform methanol extraction method by WRAP [32].

Lipid content of food waste was determined by a method of Bligh and Dyer [52]. Principle of the lipid content determination is based on the fact that when a mixture of chloroform and methanol is homogenized with the tissue of food waste, it forms a monophasic solution. When the homogenate is diluted with water, it forms a biphasic solution system. The methanol-water layer contains non-lipids substance and the chloroforms layer contains the lipids. Then, the chloroform layer is isolated to obtain the lipid extract. Oven-dried food waste (100 mg) is re-suspended in 5 mL of CH_3Cl:CH_3OH (1:2 v/v) and shaken for 24 h at room temperature. After that, pellets and supernatant are separated by centrifugation at 5,000 g for 5 min. Pellets are re-suspended in CH_3Cl:CH_3OH (1:1 v/v), and shaken for 12 h at room temperature. Then, supernatant is collected by centrifugation at 5,000 g for 5 min. Supernatants from both extractions are combined. Distilled water in the ratio of 1:5 is added and shaken for 15 min to remove non-lipid components. The organic phase is collected and evaporated at 60 °C. Then, the mass of the lipid extract is measured [52].

8.3.5 Minor Constituent Analysis of Food Waste

The addition of food and colour ingredients into food is to improve food safety and maintain its freshness. For instance, preservatives slow down the rate of product spoilage by microbial growth in order to maintain the food quality. In addition, food and colour ingredients also improve and maintain the nutritional values. For example, fortification of food with fibre, vitamins and minerals is done to reduce malnutrition. Food and colour ingredients also improve taste, texture and appearance of foods. Food colorant is usually added to improve the appearance, while emulsifiers and thickeners are added to provide food texture [53].

Colour additive is any dye, pigment or any substance which is applied to food for the purpose of imparting colour. Colour additives are usually added to beverages, candies, snack foods and processed meat. Typical colour additives includes tartrazine, sunset yellow, ponceau-4R and indigo carmine [53]. The type of food

ingredients includes preservatives, colour additives and food additives. Preservatives are normally applied to baked goods, beverages, cured meat, cereals etc. The most common preservatives include sodium benzoate, potassium sorbate and calcium propionate. Since many food preservatives and colour additives are added to food, determination of preservatives and colorants is needed for identification and quantification. Preservatives and colorants might have significant effects towards enzymatic hydrolysis and fermentation using food waste as substrate.

8.3.5.1 Determination of Preservatives

Preservatives are food additives that are added in different food products for prevention from microbial spoilage and extension of their shelf life [54]. Preservatives in food waste might have inhibition effects on enzymatic hydrolysis. Hence, determination of preservatives content is needed for identification and quantification. Janovitz-Klapp et al. [55] conducted inhibition studies to prove that apple polyphenol oxidase was inhibited by aromatic carboxylic acids including benzoic acid [55]. Further evidence of inhibition was provided through raw starch hydrolysis in which *Chalara paradoxa* glucoamylase was strongly inhibited by potassium metabisulfite [56].

Several methods can be used for determination of preservatives in food waste. Flow injection analysis has been used to detect preservatives in meat product by Ruiz-Capillas and Jimenez-Colmenero [57]. Determination of calcium propionate in breads has been carried out using colour complex formation method by Phechkrajang and Yooyong [58]. Preservatives determination in food waste was carried out according to Aubin [59]. Sample was prepared first by mixing 1 g of oven dried food waste with 10 mL of 30% acetonitrile. The mixture was sonicated and filtered for HPLC analysis. The HPLC analysis for preservatives and caffeine involves the use of two types of mobile phases in isocratic elution, which include 10 mmol sodium phosphate buffer at pH 6.0 (mobile phase A), and acetonitrile (mobile phase B). The flow rate was 0.9 mL/min with a solvent ratio of 98% mobile phase A and 2% mobile phase B. Preservatives were separated using ACQUITY UPLC BEH column C18 at 40 °C. The absorbance was detected at a wavelength of 214 nm using the photodiode array (PDA) detector.

8.3.5.2 Colorants Determination

Many analytical methods have been developed for synthetic colorant determination in food and beverages. The methods include Raman spectroscopic [60], capillary electrophoresis [61], voltammetry, HPLC with diode array detection [62–64], ultra-performance liquid chromatography (UPLC) with PDA detection [65] and spectrophotometry [66]. Colorant was extracted by adding 5 mL of 80:1:19 ethanol: ammonia: water solution to a food waste sample and sonication for 30 min and analyzed using UV/Vis spectrophotometer at different wavelengths corresponding

to each colorant (tartrazine, sunset yellow, ponceau-4R, indigo carmine). Standard curve was obtained by measuring the absorbance of different concentrations of colorant standards [66]. Colorant of sample was further analyzed with Acquity UPLC BEH C18 column using UPLC equipped with PDA conditions. Three mobile phases were applied, which contained ammonium acetate, methanol and acetonitrile, respectively, and the flow rate was set at 0.45 mL/min [65]. Capillary electrophoresis with photodiode array detection (CE-PDA) was used for separation of synthetic dyes by López-Montes et al. [61]. Separations was carried out using a fused-silica capillary. Peak identification was done using UV spectrum and migration times.

8.4 Storage and Handling of Manure

Manures are cheap sources of valuable nutrients required for plant growth and contribute significantly to long term fertility of soil. These are important aspects of any farming system which does not rely on expensive fertilizers. However, much of the nutrient values contained in manures can be lost due to improper handling and storage of materials. Primarily, the system and length of storage affect the nitrogen content of manure. Long term storages often result in reduced organic nitrogen and increased ammonium nitrogen with the increased possibility of the latter being released into the atmosphere along with risk of nitrous oxide emissions, thus causing environmental damage [11]. Furthermore, poorly managed manure can harbour intestinal parasites and enter to the water cycle via surface runoff or leach into groundwater, and thereby cause environmental concerns. Efficient removal of manure from livestock production facility is essential for optimal livestock productivity [10]. Thus, correct storage and handling is necessary to preserve the quality of manure and maintain their utility for crop growth and soil improvement. Such manure management practices are discussed in this section.

The components of manure management system include collection, transfer, storage, treatment and utilization. Laws, regulations, guidelines and procedures for design and construction of manure handling and storage are provided by district, provincial or national regulatory authorities to meet the desired objectives. Some of these regulations are provided by for e.g. the United States Department of Agriculture (USDA) [67], Ministry of Agriculture in British Columbia, Agricultural Operations Act, Ministry of Agriculture and Forestry, Alberta in Canada, and Joint Food and Agricultural Organization and International Atomic Energy Agency (FAO/IAEA) [68] in Asian countries.

Prior to storage, the handling of manure, equipment selection and maintenance is governed by the manure type. The latter is classified as either a liquid, semi-solid (slurry) or solid, based on its solid content. Liquid manure contains less than 5% solids while semi-solid manure has 5–25% solids. Solid manure contains greater than 25% solids by addition of bedding or removal of liquid by draining or drying.

The type of storage structure and its operation affect the nutrient uniformity and losses upon recovery of manure from storage and thus it should be carefully designed [69].

8.4.1 Manure Handling Equipment

When handling manure, it is important to ensure that handling equipment is designed for that purpose and it is used according to manufacturer's instructions. The equipment must be capable of functioning reliably in a corrosive environment. It also requires proper maintenance if it is expected to have a long service life. Liquid manure systems are generally handled using pumps. The presence of solid clumps in liquid manure can clog the pumps. Problems occur when ear tags, hair, teeth, tails, and other objects enter the pump. Therefore, it is essential to adopt some method of screening or cutting solid material. For proper storage of liquid manures, agitation of solids is sometimes required to bring them back into suspension. In such circumstances, the use of chopper pumps is appropriate since these do not become easily clogged with solids and it can be operated at high speeds. Solid and semi-solid manures are transferred by conveyers, augers, piston pumps or front-end loaders to storage area [67].

8.4.2 Manure Storage Structure

Manures are usually stored in confinement, either in open lots or enclosed, roofed structures. Manure storage facilities are designed based on the type and consistency of manure to be handled in the system, location, size required and the methods of filling and emptying. In general, a good storage structure should fulfil the following purposes [70]:

(i) be sufficiently impervious to prevent leakages;
(ii) provide an appropriate level of odour control; and
(iii) provide appropriate flexibility for timing application operations.

The location of storage structure should be close to barns to allow convenient filling without limiting the expansion of facilities. It is also important that it is located sufficiently close to fields for application purposes and/or can easily be connected by long distance pipelines. Due to odour and unsightly nature of manure, the location of storage should be out of sight of roads and dwellings. Storages must not be constructed on banks of river or drainage channels to avoid collecting surface runoff and surface/groundwater should be protected from potential spills from storage structure.

The size of storage is determined by volume of manure produced and length of time the manure will be contained in it. The volume in turn depends on the size of operation, management practices and facilities design. Furthermore, the volume of manure can increase due to water spillage and washing. Overall, it is important to determine the manure production rates as accurately as possible, particularly for expensive concrete storage structures. Additional consideration should be paid to storage of solids manure which contains large amount of bedding and are often stored as stockpiles for subsequent spreading operations. In such cases, it should be ensured that storage has reserved capacity to accommodate precipitation and runoff.

The storage structures should be constructed to accommodate equipment for pumping and agitating the storage in sufficient locations to ensure that stored manure can be completely removed. Wet manure or liquid runoff is usually stored in three types of storages. These include earthen dykes, concrete tanks below ground and concrete or steel tanks above the ground. Variations of these storage structures are used in specific countries in accordance with the regulations to develop efficient manure management practices. While earthen storage ponds, concrete storage structures, large roofed buildings are usually used in the US, covered dumpsters, covered free-standing manure piles, enclosed truck bed, 3-walled structures roof or tarp cover are used in the Canadian region [67, 70]. The situation in Asian countries is, however, different and diverse methods are used for manure storage. Manual separation of excreta into liquid and solid fractions with storage on floor is quite common in small-sized farms. In some other small farms, the fattening pens are divided into two parts, including a living area with concrete floor and a lower lying channel area where excreta are collected by scraping the solid floor area, which is followed by mixing with straw. In some big farms, the solids are not separated from liquid manure and a slurry is produced which is stored on solid or slatted floors [68].

Earthen storage structures offer low capital cost relative to volume stored. However, the major disadvantage of this structure is that due to its anaerobic conditions and large exposed surface area, large quantities of odorous gases are released in the air. Additionally, high permeability of earthen dykes results in undesirable nutrient losses during storage. In contrast, concrete tanks below ground are more expensive than earthen dykes, however, their impermeable nature makes them suitable for maintaining valuable manure nutrients, especially in areas having sandy soils. The problem of odour release is also avoided in concrete tanks except during the agitation of manure for emptying the storage. The design and operation of concrete tanks needs additional consideration. Due to its closed design, sufficient access ports should be provided for the pump and compartmentalization may be necessitated for more effective agitation. Appropriate safety precautions should be taken against noxious and explosive gas (e.g. methane) hazards while inspecting or working in the storage tank [71]. Concrete tanks above the ground could be more expensive than tanks below the ground, depending on their sizes. These are either circular silo type with an open or closed-top or rectangular structure. Concrete staves, reinforced cast-in place concrete, glass lined steel panels or spiral wound coated steel may be considered for construction of these storage tanks [72]. The

possibility of creation of a crust on top in such tank structures allows considerable odour reduction. However, due to their high construction costs, these structures might only be used in situations where space is limited or where soil conditions do not permit use of an in-ground storage.

Storage of manure as solids offers certain advantages. These include less volume, less odour due to less bacterial action at lower moisture content, less runoff potential and relatively high nutrient retention [73]. Conditions for storing solid manure differ for low-rainfall (arid) and humid areas. For arid areas, solid manure is usually stacked or stockpiled, with appropriate provisions for runoff collection and treatment. In more humid areas, concrete structures with walls are used to confine solids. These facilities may be provided with roofs to eliminate the effects of rainfall. Another widely operation in used solid manure storage system is composting. Composting manures further improves the biological, chemical and physical properties of soil by promoting the growth of beneficial microorganisms. Due to its high pH, composting results in a more favourable soil environment for plant growth as compared to fresh manure. Depending on the temperature used for composting, the process can also reduce or kill weed seeds, plant and animal pathogens present in manure to promote a safer plant growth.

8.5 Physico-Chemical Characterization and Composition Analysis of Manure

The properties and quality of manure is affected by several factors including animal species, diet, digestibility and storage conditions. To allow efficient land application of manure, a detailed and accurate knowledge of its physical and chemical properties is important. Moisture content, total solids/volatile solids ratio, macro-nutrient content in terms of nitrogen, phosphorous, potassium, and minor constituents such as sulphur, calcium, magnesium and trace metals are some of the nutritional components of manure which are required to be analyzed. Methods for determination of these physico-chemical properties are discussed in Sect. 8.5.1–8.5.6.

8.5.1 Dry Matter (DM) or Moisture Content

Manure is a valuable source of nutrients for crops and it can improve soil productivity. It is characterized in several ways. Important properties for manure collection, storage, handling and utilization include the solids content (the percentage of solids per unit of liquid), size and makeup of manure solids (fixed and volatile solids, suspended solids and dissolved solids) [74]. In general, manure can be classified based on how manure must be handled. However, the most suitable

way to classify manure depends primarily on its dry matter content, as the manure handling characteristics vary as consistency changes from liquid to solid.

On one end of the spectrum is lagoon liquid with very low solids content (less than 1%) that can be used for irrigation by either big guns or center pivot irrigation systems with small nozzles. On the other end of the spectrum is solid manure, which normally has more than 25% solids. In between of these two conditions are the ones containing 5–25% solids. Sand is another challenging solid that is sometimes used as dairy bedding. Alternatively, the most typical manures, such as dairy, beef, and swine manure, may be either solid or liquid (with inclusion of urine or barn floor and milking parl or wash water), while horse and poultry manures are solid. Solid manures often include bedding materials [75]. In general, the nutrient values are related to solids concentration: the higher the solids concentration, the higher the nutrient concentration.

Nitrogen, phosphorus, and potassium are the major nutrients of manure. Nutrients are divided between soluble and insoluble states. While the major soluble nutrients are found in the liquid (urine) that are more readily available for crop usage, the remaining soluble and insoluble nutrients are found in the solids (faeces) of excreted manure. For example, 80% of the phosphorus is insoluble and exists in settled solids, but 80% of the potassium is highly soluble.

Normally, the moisture content of the manure is determined by dry weight method. After the collection of manure, samples will be homogenized in a blender to pass a 3 mm screen [76], and then put into an oven at 105 °C for 24 h [77].

8.5.2 Total Solids/Volatile Solid Ratio

As one of the major components in manure, total solids (TS) is the solids left after the water is excluded [78]. Generally, TS is comprised of total dissolved solids (TDS), total suspended solids (TSS), and settleable solids. TDS is composed of the substance in solution or suspension liquid that with the size smaller than 1.5 μm [79]. TSS is the solids in the liquid stream that exceed 2 μm and remains suspended in the solution indefinitely [80]. Settleable solids are the matters, with any size, which do not remain in suspension or dissolved form. These solids can impact the characteristics of manure, including the particle size, nutrient and salt concentrations. Normally, manure contains various nutrients such as nitrogen (N), phosphorous (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), manganese (Mn), copper (Cu), zinc (Zn), chlorine (Cl), boron (B), iron (Fe) and molybdenum (Mo) [81], but their contents vary depending on the species, manure handling practices and storage time. Table 8.1 shows the values of the major nutrients in 1 ton (or 241 gallons) of fresh manure and 1 ton of dry manure (solids) at 15% moisture for each animal type [82]. According to Table 8.1, N, P and K with relatively high concentrations are found in the manure. However, as phosphorus tends to form a precipitate or adhere to particles (solids) in manure, the concentration of phosphorus in the TS stream is often thought to be higher than in the

Table 8.1 Nutrient content for different sources of manures

Animal type	Animal size	Nutrient content						
		Ratio	Water	TS	VS	N	P	K
	lb.	*Wm/Wa*	*% wb*	*% db*	*% db*	*% db*	*% db*	*% db*
Dairy cattle								
Calf	150	–	88	12	85.7	3.2	0.6	2.6
Heifer	750	0.09	88	12	85.3	3	0.9	2.8
Dry cow	1000	0.08	88	12	85.3	3.7	0.6	2.4
Lactating cow	1400	0.09	88	12	85	5.5	0.7	2.5
Veal	250	0.04	96	4	43.8	11.1	8.3	16.7
Beef cattle								
Calf	450	0.06	92	8	84.7	6.7	4.8	5.3
High forage	1100	0.08	92	8	89.4	8.3	2.9	4.9
High energy	1100	0.07	92	8	91.9	8.4	3.3	5
Cow	1000	0.06	88	12	77.9	4.1	2.5	3.4
Swine								
Nursey	25	0.11	89	11	81.5	6.7	3.4	3.4
Grow-finish	150	0.06	89	11	80	7.7	4.8	3.8
Gestating	275	0.03	91	9	85.5	7.4	5.9	5.9
Lactating sow	375	0.06	90	10	90.2	8	5.8	6.2
Boar	350	0.02	91	9	89.4	7.7	6.2	6.2
Sheep								
Ewes	100	0.04	75	25	82.7	4	2	4
Poultry								
Layer	4	0.07	75	25	75.4	5.4	4.2	2.5
Broiler	2	0.09	74	26	72.3	4.9	3	2.4
Turkey	20	0.05	75	25	76	5.6	4.8	2.4
Duck	6	0.06	73	27	59.6	5.2	4.3	3.1
Equine								
Horse	1100	0.05	85	15	85	2.3	0.3	0.7

Reference Adapted from Bulletin 604 [82]. *Wm*: daily weight of manure, *Wa*: average weight of animal during this stage of production, *% wb*: percent wet basis, *% db*: percent dry basis

un-separated manure. Moller et al. indicated that dry matter (DM) fractions >0.5 mm will contain 5–7% of the total phosphorus [83].

Nevertheless, with the diminishing of the natural nutrients and fertilizer prices trending higher, the importance to retain and effectively apply manure nutrients in agriculture has been recognized. According to the prediction, world supply of phosphate fertilizer will reach a peak in 2033 and then decline [84]. In the meanwhile, another nutrient that receives special attention due to its decline from atmospheric concentrations is sulphur [85, 86].

On the other hand, TS can also be subdivided as volatile solids (VS) and fixed solids or ash. The VS is always determined by the ignition of dry solids at 550 °C

and gives an approximation of the organic matter present in the waste [87, 88]. Normally, the VS is composed of bio-degradable volatile solids (BVS) including saccharine, starch, organic acids, cellulose, lipids and proteins that can be easily decomposed by microorganisms in most storages and lagoons [81], and the refractory volatile solids (RVS) which resists bacterial digestion.

During the degradation process, VS in manure is broken down by anaerobic bacteria. Normally, the organic nitrogen is converted to ammonium nitrogen, but sometimes this ammonium nitrogen would be lost to the atmosphere as ammonia. Thanks to this process, the unavailable organic nitrogen in plant can be converted to ammonium-N that is useful for plant. On the other hand, owing to the complicate reactions including anaerobic digestion, mineralization and volatilization during the production, collection and storage of manure, the VS of manure vary with the digestibility of the ration, animal age, the amount of feed wasted, manure handling methods and storage time [81]. Therefore, the determination of volatile solids is indispensable in the design and operation of manure digestion, vacuum filter and incineration plants.

8.5.3 Total Kjeldahl Nitrogen and Total Ammonium Content

All types of manure contain nitrogen source. Normally nitrogen found in manure is made up by organic nitrogen and ammonium nitrogen. The amount and form of nitrogen source in manure determine the quality of manure fertilizer. Nitrogen is an essential element of nucleic acids and proteins. However, crops required large amounts of nitrogen, which is always deficient in agricultural soils [89].

Measurement of total nitrogen in manure is to determine all type of nitrogen present. This includes organic nitrogen, ammonium nitrogen and any type of nitrate. The concentration of nitrogen in manure is variable and not all types of nitrogen are presented in manures. Quantification of ammonium content in manure is to determine the main inorganic form of nitrogen. Ammonium is obtained from the breakdown of organic nitrogen in faeces, and conversion of uric acid and urea in urine.

Liquid manures contain more ammonium nitrogen than solid manure. Ammonium nitrogen is very useful for plants because it can be readily used by plants [89].

Pan et al. [90] analyzed nitrogen in manure using Kjeldahl nitrogen method [90]. Test portions were digested with sulfuric acid, potassium sulphate and copper catalyst in an aluminum block at 420 °C. Subsequently, the digestate was neutralized by concentrated sodium hydroxide. Steam distillation was applied to liberate ammonia and trapped in weak boric acid. Colorimetric titration using hydrochloric acid was performed to obtain nitrogen content. Powell et al. [91] determined nitrogen content in manure using Elementar VarioMax CN analyzer

(Elementar, Germany) [91]. Liu et al. [23] determined ammonia nitrogen content using formaldehyde method in China National or Industrial Standards (GB/T3600-2000) [92]. Ammonium cation was detected by flow analysis and spectrometric detection [93].

8.5.4 Phosphorous Content

Similar to nitrogen, phosphorous is present in all organic materials. Among the nitrogen-containing base and five-carbon sugar, phosphorous forms the backbone of DNA and it is a part of the energy carrier adenosine triphosphate. Therefore, production of biomass would not be possible without phosphorous. Phosphorous is one of the essential elements for life, which cannot get lost and its recovery is absolutely necessary in order to cover the demand of phosphorous-containing fertilizers in agriculture. Phosphorous in biomass appears either as phosphate or polyphosphate. First developments regarding the determination of phosphate were made in medicine. In 1925, Fiske and Subbarow developed a method for determination of phosphate in blood and urine [94]. Methods of choice were colorimetric ones based on the reaction of phosphate and molybdic acid to form phosphomolybdic acid, and its subsequent reduction by hydroquinone resulting in formation of a blue colour. The intensity of colour was directly proportional to the concentration of phosphate. The determination was relatively simple where phosphate and molybdic acid could react. However, the application of such method would be challenging for solid or complex materials, or when phosphate is present in the form of polyphosphate, such as phytic acid, or when inorganic and organic phosphorous are present. Nevertheless, materials can be digested and free phosphate released by acidic treatment. Commonly used acids are sulfuric acid, nitric acid and hydrogen peroxide. However, when the quantity of sulfuric acid is too high, then the reduction of phosphomolybdic acid is disturbed. When the quantity is too low, then portion of phosphate is not released, and thus it was neither quantified.

The colorimetric phosphate determination method has been used for several biological feedstocks. Jakubus used this method for determination of total phosphorous in compost and its waste residues [95]. They incinerated 1 g sample at 550 °C for 3 h. Afterwards, 5 mL concentrated HCl was added to the ash and heated for 30 min at 180 °C. The concentration range was in g per kg. Lugo-Ospina et al. evaluated quick tests for determinations in dairy manure. Tests were based on the molybdic acid assay, but pretreatments were different [96]. For instance, potassium persulfate and 12 mL 5.5 M H_2SO_4 were added to 2 mL manure suspensions in one of the approaches. The mixture was heated for 30 min at 180 °C and digested at 350 °C for 30 min to reduce the overall volume to 4–5 mL. Afterwards, the solution was diluted with demineralized water to 35 mL and used in total phosphorous determination. Jastrzebska further determined phosphorous in meat samples [97]. Concentration of phosphorous was determined using colorimetric method after mineralization of meat using a Kjeldahl apparatus with nitric acid and hydrogen peroxide.

8.5.5 Potassium Content

Potassium from manure is good for plant growth. Potassium content in manure is variable and it is present in a water soluble and inorganic form [89]. Potassium is an essential macronutrient for plants growth and development. It controls enzyme activity, concentration of metabolites and transcription level of a number of genes in plants. It is important for crop yield as well as human nutrition [98]. Spectrochemical methods have been applied for long time to determine elemental concentrations in manures. Colorimetry, atomic absorption spectroscopy (AAS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) are some methods which have been used to determine elemental concentrations in manure. Advantage of AAS is its high specificity for individual elements. ICP-AES is generally free from interferences [99]. Colorimetry method is a rapid and reliable method which is applicable to large number of samples [100].

In 1950, Whittles and Little [100] invented a colorimetric method to determine small amount of potassium [100]. The method involves sample extraction with Bray's extracting reagent and precipitation of potassium as cobalt nitrite. Nitrite group in cobalt nitrite precipitate undergoes diazotization of sulphanilic acid and subsequent coupling with dimethylaniline to give methyl orange whose colour is measured with a Spekker absorptiometer. Recently, Montégut et al. [93] measured mineral composition in manure including potassium oxide (K_2O) using inductively coupled plasma optical emission spectrometry (ICP-OES) [93]. Potassium ion (K) concentration was determined by a Varian A.A 240 FS atomic absorption spectrometer. Hollow cathode lamps of K was used as a radiation source. The wavelength and applied electric current were 766.5 nm and 5.0 mA, respectively. Potassium analyses used 13.5 of air-acetylene flame with flow rates of 2.0 L/min, respectively. According to Roa-Espinosa et al. [101], X-ray fluorescence (XRF) spectrometry is a rapid and precise method that can be used to determine quantitative elemental analysis of macro- and micro-nutrients in dairy manure [101]. It can be used to determine elements includes N, P, K, Ca, Mg and others. Sample was pelletized under 4 tons of pressure for 2 min using hydraulic press. After that, sample underwent elemental analysis using a PHILIPS MagiX apparatus to perform wavelength dispersive XRF.

8.5.6 Secondary Elements, Heavy Metals and Trace Contaminants Content

Due to the use of feed additives, manure from factory farms contains high considerable amount of heavy metals, especially the heavy metals such as copper and zinc. Their potential accumulation on land raises concerns regarding the environmental risks to surface and groundwater, in addition to threatening the food chain and agriculture. In addition to heavy metal contamination, manures might also

contain trace amounts of pesticides, especially herbicides [102]. Pyridine carboxylic acid-based herbicides such as aminopyralid, fluroxypyr, picloram, clopyralid, and triclopyr are usually applied to hay fields or pastures which are considered to be safe for livestock consumption. Upon passage through animals' digestive tract, these are excreted in urine and manure, and it can actually remain active in manure for an unusually long period of time. The use of such contaminated manures in fields can cause devastating damage to crops. Therefore, it is essential to perform complete assessment of contaminants such as heavy metals, pesticides and mycotoxins in manure to ensure their safe application in agro-ecosystem.

The method for determination of dissolved anions and cations concentration (secondary elements) in manure is based on UNE-EN ISO 10304-1 and Standard Methods 21st ED [103, 104]. The latter is a joint publication of the American Public Health Association (APHA), the American Water Works Association (AWWA) and the Water Environment Federation (WEF). The analysis is carried out by HPLC using anion or cation-selective columns. The method is simple which involves sample filtration by 0.2 μm followed by *in situ* analysis. Position of the maximum in the obtained chromatographs indicates the presence of a specific ion, while area indicates the concentration of ion.

Trace metals in manures exist in different forms. These include water-soluble, exchangeable, linked to organic substances, co-precipitated with oxides, carbonates and phosphates and ions in crystalline lattices of primary minerals. The metals present in the first three forms are the most readily available for plant uptake [105]. Several methods have been developed for heavy metal assessment in manure. Phytoavailability of metals has been largely applied as a one-step soil extracting procedure to predict the size of pool that may be depleted by plant during the growth period. Although a simple method, phytoavailability does not indicate the total heavy metal content of sample. Another method is called the sequential extraction procedure which allows the determination of different chemical forms in which the element appears to be associated in a sample [106]. As opposed to phytoavailability, this method provides key information about the extent of retention of elements in sample and their ability to be released in soil. These sequential extraction methods are usually used to evaluate the actual and potential mobility of metals in the environment. This helps to understand the uptake of metals by plants in comparison with chemical pool available in soil. Heavy metal specification is a more sophisticated method for heavy metal assessment since it determines the availability of metals for plant uptake and potential for contamination of groundwater following the application of manure to agricultural lands. Sequential fractionation method categorizes metals which are associated with chemically homogenous fractions, which ultimately decide its availability for uptake. Therefore, the method can determine the amount and proportions of metals in different forms such as water-soluble, exchangeable or linked to organic substances in manure samples [107, 108]. Since the specific chemical form of metals in manures affects its mobility and bioavailability, evaluations based on chemical associations are considered to be important while analyzing manure samples.

For the determination of heavy metals, the manure samples are air-dried, crushed and sieved to ensure homogeneity. This is followed by digestion of samples in a mixture of acids such as HNO_3 and $HClO_4$. Specifically, 0.25 g sample is digested with 5 mL concentrated $HClO_4$ over a hot plate for 1 h after which it is dried. Subsequently, 20% HNO_3 is added to the sample with heating for an additional hour. The resulting solution is then diluted to 50 mL with water and passed through a 0.2 μm filter. Total elemental analysis for quantification of common metals such as nickel, iron, zinc, mercury, cadmium is performed using an atomic absorption spectrophotometer. Modified versions of sequential extraction method have also been employed to fractionate the solid-phase chemical forms of the metals. Sequential extraction has been performed using 0.01 M CH_3COOH for 16 h, 0.1 M $NH_2OH{\cdot}HCl$ for 16 h, H_2O_2 for 1 h, followed by heating at 85 °C for 1 h and final extraction with 1 M ammonium acetate for 16 h [109]. In another method, trace elements are fractionated into exchangeable, adsorbed, organically bound, carbonate precipitated and residual forms by sequential extractions with 25 mL of following reagents: 0.5 M KNO_3 for 16 h, 3 times extraction with de-ionized water for 2 h, 0.5 M NaOH for 16 h, 0.05 M Na_2EDTA for 6 h, and 4 M HNO_3 for 16 h at 80 °C [106]. After each extraction, the sample is centrifuged at 5,000 rpm for 15 min and the resultant supernatant is decanted, filtered and then analysed.

An European standard EN 15662: Determination of pesticide residues using gas chromatography-mass spectrometry GC-MS (Agilent 7890) and/or liquid chromatography-mass spectrometry/mass spectrometry LC-MS/MS (Agilent 6400), following acetonitrile extraction/partitioning and clean-up by dispersive SPE-QuEChERS-method (Solid Phase Extraction Quick-easy-Cheap-Effective-Robust-Safe) are used for determination of pesticides in manure [110]. Manure samples are extracted with 10 mL acetonitrile. Solid manure samples with low water content (<80%) are diluted with water to obtain approximately 10 g water sample. Magnesium sulphate, sodium chloride and buffering citrate salts are added to sample which is then shaken intensively for 1 min and centrifuged for 5 min at >3,000 g for phase separation. Organic phase is then cleaned up by dispersive solid phase extraction (DSPE) to remove the residual water. Formic acid (50 μL, 5%, w/v) is added to 5 mL extract to acidify and improve the storage solubility of base-sensitive pesticides. The final extract is then analysed by LC or GC-based determination analysis.

8.6 Advanced Analytical Methods for Food Waste and Manure Characterization

The section describes the advanced analytical methods which have been used for characterization of food waste and manure.

8.6.1 High Performance Liquid Chromatography (HPLC)

According to IUPAC definition, chromatography is a physical separation method in which the components to be separated are distributed between stationary and mobile phases [111]. HPLC is a fast technique, which separates mixtures into individual components with high precision and specificity. HPLC instruments include pumps, solvent reservoirs, injector, detector and a data acquisition system [112]. HPLC can be used in diverse research areas including environmental, food and flavour, pharmaceutical and forensics.

There are several kinds of HPLC, such as normal phase chromatography, reverse phase chromatography, ion exchange chromatography, size exclusion chromatography and their applications depending on the nature of compounds to be separated. For normal phase chromatography, the stationary phase is polar and mobile phase is nonpolar. Polar samples are retained for longer periods on polar surface of the column than less polar molecules. For reverse phase chromatography, the stationary phase is nonpolar compounds and mobile phase is a polar solvent. Here, nonpolar samples are retained for longer time in column than polar molecules. In the case of ion exchange chromatography, the stationary phase is an opposite ionically charged surface to the sample ions and mobile phase is an aqueous buffer. Strongly charged samples are retained for longer time on ionic surface. Size exclusion chromatography separates the samples on the basis of molecular size. The column is packed with materials with controlled pore size. Large molecules are washed out from the column first, then followed by small molecules [112].

Carbohydrates in food waste can be analysed by HPLC. Type of carbohydrates in food waste includes *monosaccharides,* such as glucose, fructose, galactose and sorbitol; *disaccharides,* such as sucrose, lactose and maltose; *trisaccharides* such as raffinose; and *polysaccharides,* such as starch [112]. Aminex HPX-87H column (Bio-Rad, USA) is commonly used for analysis of carbohydrates presented in biological fluids. Properties of this column include 8% of cross-linked resin, hydrogen ionic form, pH range from 1 to 3 and 300 × 7.8 mm column size. Recent research conducted by our groups applied HPX-87H column to analyze sugar and organic acids, with the use of H_2SO_4 as mobile phase [21, 113]. A C_{18} column can be used to separate organic acids in food waste including preservatives such a ssodium benzoate and potassium sorbate, caffeine. Kuprovskytė et al. [54] performed separation of preservatives includes benzoate sorbate, methyl, ethyl and propyl esters of p-hydroxybenzoic acid in beverages using the Separon SGX C_{18} column (TESSEK Ltd., Prague) [54]. Mobile phase contained 5 mmol/L aqueous acetate buffer (pH 5) with 40% (v/v) acetonitrile at a flow rate of 0.2 mL/min and UV detection at 254 nm. Similarly, Aubin [59] performed separation of preservatives and caffeine from soft drinks using ACQUITY UPLC BEH C_{18} Column [59]. Column temperature was set to 40 °C, mobile phase (Solvent A: 10 mmol sodium phosphate buffer, pH 6 and Solvent B: acetonitrile) with 0.9 mL/min of flow rate, and the wavelength of UV detector was set to 214 nm.

HPLC can be used to determine the concentrations of constituents of food waste, such as sugars, amino acids, preservatives and colourants concentration, and manure including secondary elements, heavy metals and trace contaminants concentration. The constituents of food waste and manure obtained from HPLC would provide useful information for further processing. The advantage of HPLC is that the compounds being analysed do not need to be volatile, unlike gas chromatography. However, the compounds have to solubilize in the mobile phase [114].

8.6.2 *Gas Chromatography and Mass Spectrometry (GC-MS)*

Gas chromatography (GC) is a common type of chromatography used for separation and analyses of compounds that can be vaporized without decomposition. GC is commonly used for determination of the purity of a particular substance, or for identification and quantification of compounds in a mixture via separations using a gas as the mobile phase [115]. The system is mainly composed of a carrier gas as the mobile phase, an inlet to deliver sample to a column, the column where separations occur, an oven as a thermostat for the column, a detector to register the presence of a chemical in the column, and a data system to record and display the chromatogram. These components of a gas chromatograph have been unchanged in function or purpose during the last 40 years although technology has been improved in design, materials, and methodology [116].

The carrier gas or mobile phase in GC is an essential, but limiting, facet in separations. Carrier gas is needed to carry constituents of a sample through the column and yet the choice of possible gases is restricted [116]. The inert gas of helium remains the most commonly used carrier gas in about 90% of instruments although nitrogen or hydrogen is preferred for improved separations [117]. The chromatographic process begins when sample is introduced into the column, ideally without disrupting flows in the column. In order to keep the results to be reproducible, suitable sample inlet methods are preferable for the least change in pressure or flow of the carrier gas or mobile phase. Currently, syringe injection is the commonly used method for placing samples to a GC column, since it is convenient and generally effective although the thermoplastic septum develops leaks after repeated injections. Other options such as pyrolysis GC and purge-and-trap methods are also popular in certain specific applications [116]. Samples either in liquids or solids form, must be converted to gaseous state before passing through the GC column. Therefore, most gas chromatographs are equipped with ovens to keep the column at temperatures from 40 to 350 °C. Conventional ovens consisted of a resistive wire coil that spread heat into the inner volume of the oven. Alternatives to conventional ovens were designed later and may be helpful for short columns or conditions where the space is limited [117, 118]. Effluent from the column enters a detector where the composition of the carrier gas stream is characterized.

The mainstays in GC have been the flame ionization detector (FID), the thermal conductivity detector (TCD) and the electron capture detector (ECD). Other commercially available detectors include the photoionization detector (PID), the nitrogen–phosphorus detector and the atomic emission detector, though these have been less prevalent historically than the FID, TCD, and ECD [119].

Currently, with the increasing complexity of analytes and consequent increase in the demand for analytical accuracy, GC becomes a technique with obvious limitation. Even though GC equipped with a traditional detector such as flame ionization detector can separate volatile and semi-volatile compounds with great resolution, it cannot identify them. In contrast, the specific detector of mass spectrum (MS) can provide detailed structural information on most compounds so that they can be exactly identified and quantified. However, it cannot readily separate them [120]. In this case, combining the two techniques, namely Gas Chromatography-Mass Spectrometry (GC-MS), can take the advantages of GC and MS to identify different substances within a test sample with high resolution [121]. During the GC-MS process, different molecules in a mixture are retained by the column of GC due to their chemical properties and then eluted from the column at different times, which allows the downstream MS to capture, ionize, accelerate, deflect and detect the ionized molecules separately. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass-to-charge ratio [121].

Since GC-MS is highly effective and versatile, it is widely used for research purposes in diverse fields, such as monitoring and tracking organic pollutants in the environment, analysis of nutrients, harmful materials or aromatic compounds in food, beverage, flavour and fragrance, bio-analysis of blood and urine for biological and pesticides detections, and it is also emerging as an important technique in the field of food waste and manure characterization [120–124].

Food wastes are usually composed of highly complex nutrients and organic materials such as fats, sugars, proteins and vitamins, and inorganic material, such as water and minerals. Apart from natural constituents, xenobiotic compounds derived from a variety of sources could also be introduced to the waste. Similarly, manures contain various materials including carbohydrates, lipids, proteins, volatile compounds and minerals that can be determined by the GC-MS regardless of the species of the manures and their handling practices or storage time.

The analysis of food can vary in a scope. For example, a GC–MS method can be used for the qualitative/quantitative analyses of untargeted volatiles (for example, aroma) or targeted ones such as pesticides. Furthermore, a GC–MS method can also be exploited for the generation of a chromatography profile (fingerprinting), with the aim of distinguishing between food samples of the same type, for example, to determine geographical origin of samples. However, for any purpose, the extent to which one or more of the aforementioned features prevails is dependent on the initial analytical objective. The methods and equipment conditions for the composition determination of food waste [120, 125] and manure [123, 124] can be found from the related studies [44, 122].

8.6.3 Ultraviolet-Visible Spectrophotometer

Spectrophotometry is the equipment for the measurement of the refection or absorption properties of a material. A broad range of wavelength can be dealt by spectrophotometry, including near-ultraviolet, visible light and near-infrared. Ultraviolet and visible regions of the spectrum are most commonly used in spectrophotometers, in which the wavelength ranges from 190 to 1100 nm. Spectrophotometry is made up of two parts, a spectrometer and a photometer. The spectrometer is used for providing any wavelength of light (near-ultraviolet, visible light and near-infrared), while the function of photometer is to measure the intensity of light. The sample is placed between spectrometer and photometer. The intensity of light passing through the sample (I) is measured and compared to the intensity of light before passing through the sample (I_0). The ratio of light intensity after and before passing through sample (I/I_0) is called transmittance ($\%T$). The output result (absorbance) is calculated by the transmittance (Eq. 8.1):

$$\mathrm{A} = -\log\left(\frac{\%T}{100\%}\right) \tag{8.1}$$

A basic spectrophotometer includes the following parts: a light source, a holder for the sample, a monochromator and a detector [126]. A Tungsten filament is used for visible light region, and a deuterium arc lamp for ultraviolet region (190–400 nm). The typical parts of a detector consist of a photomultiplier tube, a photodiode, a photodiode array or a charge-coupled device (CCD) [127]. Single photodiode detectors and photomultiplier tubes are used with scanning monochromators, which can filter the light so that only a single wavelength reaches the detector at a time [128].

Samples for UV-V is spectrophotometry are most often in the form of liquids, although the gas and solid forms are also acceptable for measurement. In general, liquid samples are placed in a transparent cell, known as a cuvette. The shape of cuvettes is typically rectangular, commonly with a width of 1 cm. Glass test tubes can also be used as cuvettes in some instruments. The criterion of sample container is that radiation can pass over the spectral region of interest. The most widely used cuvettes are made of silica or quartz glass because they can allow the UV wavelength to pass without any absorption. Glass and plastic cuvettes are also common, but they can be only used for visible wavelengths since the glass and most of plastics can absorb UV wavelengths. UV-V is spectrophotometer can be used in various research fields, like materials, chemistry, biochemistry and biology. They are widely used in laboratories for various studies, for example, enzyme activity assay, determinations of nitrogen and protein concentration, measurements of phosphate component. Information about colorant impurities in food waste hydrolysate can also be obtained from the ultraviolet and visible regions of the spectrum. Any hydrolysate containing large amounts of organic matter may have absorption peaks in the UV-V is region of the spectrum. Most of the colour in the sample appears in the wavelength of 250–700 nm [129].

8.6.4 Total Nitrogen Unit

There are four methods to determine total nitrogen including Total Kjeldahl Nitrogen (TKN), Ammonia (NH_3^+), Nitrite (NO_2^-) and Nitrate (NO_3^{2-}). TKN is an analysis method for bound nitrogen. All these methods suffer from certain disadvantages, the most common one being time-consuming and laborious sample preparation technique. TKN method and method of ammonia determination also use hazardous chemicals such as mercuric oxide, sulfuric acid, boric acid and phenol which are harmful to both life and land. Nitrate analysis requires a separate sampling for acidification of the sample before analysis, while nitrite analysis is time consuming [130, 131].

With the aim to provide simple and non-hazardous sample preparation for nitrogen analysis, the Total Nitrogen Module (TNM-1) was introduced by Shimadzu Company. The advantage of TNM-1 is that it allows analysis of sample in less than 4 min, requires no chemicals for sample preparation and/or analysis and produces no hazardous wastes. In TNM-1, samples containing nitrogen are introduced into an oxygen-rich combustion tube with platinum catalyst at 720 °C. Bound nitrogen is converted to nitrogen monoxide (NO), further oxidized to nitrite (NO_2) in the presence of ozone, and then it is detected by the chemiluminescence detector [131]. The CN analyzer (Vario Max CN, Elementar, Hanau, Germany) was introduced in 1988, it was the first combustion type nitrogen analyzer. It applied Dumas combustion method for determination of nitrogen in different fields such as food and agricultural products. It is fast, safe and environmental friendly compared to wet chemical Kjeldahl method [132].

Nitrogen content in food waste and manure can be determined using the Total Nitrogen Module. Pleissner et al. [49] performed total nitrogen content using a TOC-V CSH total organic carbon analyzer (Shimadzu, Japan) equipped with a TNM-1 total nitrogen measuring unit (Shimadzu, Japan) [49]. Nitrogen compounds from food waste were extracted through acid hydrolysis, then samples were diluted and filtered prior to total nitrogen content determination. Xu et al. [133] measured total nitrogen concentration in manures using combustion oxidation on a CN analyzer (Vario Max CN, Elementar, Hanau, Germany) [133].

8.6.5 ^{31}P-NMR Spectroscopy

The assessment of phosphorous composition in animal manures is of great interest for their long-term application to land. This is because the manure phosphorous holding capacity of soil depends mainly on the forms and bioavailability of phosphorous in manure. The latter must be considered for manure application to land to avoid soil phosphorous accumulation and an acceleration of eutrophication [134]. Traditionally, four solution-based techniques have been used to analyze the phosphorous composition of animal manure. These include sequential fractionation,

ion-pair chromatography, enzymatic hydrolysis, and solution ^{31}-P nuclear magnetic resonance (^{31}P-NMR) spectroscopy [12, 134–136]. While fractionation procedure has been successfully used to evaluate manure phosphorous composition particularly in terms of phytic acid, (myo-inositol hexakisphosphate), the most dominant organic phosphorous compound in a wide range of manures, the analysis by chromatographic techniques becomes complicated and erroneous since phosphates exist in complexes with mineral and organic compounds in manures [137]. Several researchers have used ^{31}P-NMR to identify organic phosphorous in foods, animal feeds, digestate and manures. ^{31}P-NMR offers an advantage that an entire range of phosphorous compounds including both organic and inorganic can be identified with one simple extraction procedure to provide better characterization of phosphorous in the samples. Solution ^{31}P-NMR has been used for quantification of phytic acid in food, animal feed and sewage sludge. Orthophosphate monoesters and diesters in NaOH extracts of swine slurry were identified by ^{31}P-NMR method [138]. Crouse et al. [139] characterized functional phosphorous groups in NaOH-EDTA extracts of turkey litter using ^{31}P-NMR [139]. The value of solid-state ^{31}P-NMR had been limited due to poor spectral resolution. However, improvements in extraction procedure, signal identification and understanding of compound degradation during extraction and analyses have advanced this technique. Information on the forms of phosphorous in manure has been pivotal to determine its environmental fate.

For solution ^{31}P-NMR, 2 g manure is extracted with 40 mL NaOH-EDTA for 4 h at 20 °C. The inclusion of EDTA in alkaline extraction solution markedly improves phosphorous recovery [140]. The mixtures are shaken horizontally and then centrifuged at 10,000 g for 30 min. The aliquots are analysed for total phosphorous by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Reactive phosphorous, which amounts to inorganic orthophosphate is determined by molybdate colorimetry. Unreactive phosphorous (organic phosphorous plus inorganic polyphosphates) is calculated as the difference between total and reactive phosphorous [141]. Remaining extract after centrifugation is frozen rapidly at −80 °C, lyophilized and ground to a fine powder. Immediately before ^{31}P-NMR, ∼100 mg freeze dried extract is redissolved in 0.9 mL 1 M NaOH and 0.1 mL D_2O (for signal lock) and transferred to 5 mm NMR tube. Spectra are obtained using spectrometer operating at 200 MHz for ^{31}P and 500.134 MHz for ^{1}H. Individual phosphorous compounds or functional groups from ^{31}P-NMR spectra are identified by their chemical shifts of signals (ppm) relative to 85% H_3PO_4, and comparison with literature reports. Signal areas are calculated by integration and phosphorous concentrations are calculated by multiplying the proportion of total spectral area assigned to a specific signal by the total phosphorous concentration in the original extract [136]. In well-resolved spectra, sum of areas of four signals at approximately 5.95, 5.06, 4.70 and 4.54 ppm in the ratio 1:2:2:1 is used to quantify phytic acid concentrations. In the case of overlapping of phytic acid signal with those from other monoesters, the signal from the phosphate at C-2 position on the inositol ring (at ∼5.95 ppm) is multiplied by 6 to calculate phytic acid concentration. This is considered suitable since the signal at this position is often well

resolved compared to that from other orthophosphate and monoester signals. Usually for manure samples, analytical errors are estimated to be approximately 5% for larger signals and 10% for smaller signals [137, 138]. Statistical analysis is performed using Statistical Analysis System [142] and regression analysis is performed using the generalized linear models function in SAS.

8.6.6 X-Ray Absorption Near Edge Structure (XANES) Spectroscopy

Identification of the chemical phosphorous species which exist in manures is important for our understanding of the long-term potential of P loss to water when manure is land applied [7]. Forty to fifty percent of phosphorous in manures such as those from poultry waste is in the organic form and mainly consists of organic phosphorous compounds such as inositol phosphates, sugar phosphates, nucleic acids and phospholipids. Phosphates sorbed on the surfaces of clay minerals and iron or aluminum hydroxides are important inorganic phosphorous forms which are less bioavailable in water. Additionally, manures such as poultry litters also contain phosphorous in mineral-phase litters e.g. potassium phosphate, pyrophosphate and aluminum phosphate. Thus, it is important to characterize phosphorous into organic and inorganic forms during phosphorous speciation for correct prediction of their environmental mobility. Several fractionation techniques have been applied, where phosphorous is partitioned into operationally defined fractions based on its solubility in a series of extractants and provide information about organic and inorganic phosphorous species in manure [143]. While these techniques can assist in predicting the effects of land application of organic phosphorous sources on soil phosphorous, these cannot provide specific information about the exact chemical species of phosphorous in manure [144]. This does not allow prediction of long term effects of manure phosphorous on water quality due to non-availability of information on actual phases of phosphorous present in these materials. Sequential extraction procedures can be complemented with X-Ray absorption near edge structure (XANES) spectroscopy to characterize the different forms of phosphorous in soils and manures [145, 146].

XANES spectroscopy offers a means of analyzing solids at in situ moisture contents, ambient pressures and temperatures without extensive alteration of samples [147]. It is used to specify phosphorous in a series of manure with a proper detection of organic and inorganic phosphorous species. Analysis by XANES spectroscopy starts with sample characterization for P, Al and Ca using inductively coupled plasma atomic emission spectroscopy (ICP-AES). This is followed by phosphorous sequential extraction which determines the molybdate-reactive P (inorganic P), as the percentage of amount of phosphorous removal in each extraction is measured using the ascorbic acidphosphomolybednum blue method. The resulting data is compared with the total phosphorous estimated by ICP-AES to

determine the relative distribution of phosphorous in organic and inorganic phases. For XANES spectroscopic analysis, the residue after each step of sequential fractionation is used. Several steps are followed for sample preparation. The samples are shock-frozen with liquid nitrogen and freeze-dried for 24 h before analysis. Dried manure samples are ground into a fine powder using an agate mortar and pestle, following which a thin layer is mounted on a Plexiglas sample holder using phosphorus-free cellophane tape. XANES spectroscopy is conducted at beamlines X-19 A and X-15 B. These two beamlines tender X-ray lines designed for light element X-ray analysis. Data is collected for both samples and standards on beamline X-19 A using a monochromator with Si (111) crystals and a specific flux. A helium-purged sample chamber with a fluorescence detector is used for data collection at this line. Standard spectra are also collected at beamline X-15 B using a monochromator at specific flux. The monochromator is calibrated to the maximum peak energy of the first derivative (E_0 2149 eV) using a standard at the start of every run and after every beam dump, usually every 12 h [146]. In some other protocols, the monochromator can also be calibrated using NaH_2PO_4 powder and maximum of the standard spectra is assigned an energy value of 2,158.5 eV. The energy scale is normalized by subtracting the calibration energy from all obtained spectra. P XANES-spectra from manure samples are compared with spectra collected for organic phosphorous standard using a linear combination fitting method, a tool available with XANES spectroscopy equipment. Linear combination fitting is conducted across the energy range of 2,142–2,179 eV. Linear relationships between the XANES linear combination data and chemical fractionation data are analysed using statistical analysis methods such as PROC REG [148].

8.6.7 Fourier Transform Infrared Reflectance Photoacoustic (FTIRPAS) Spectroscopy

Infrared techniques such as transmittance spectroscopy and reflectance spectroscopy in combination with multivariate analysis can be used in characterization of manure, particularly for rapid quantification of mineralizable or labile fraction of carbon in manure [8, 149]. Since near infrared region consists of highly overlapping overtones and combination bands, it possesses some limits in qualitative analysis about chemical components. Additionally, optical opaque samples such as manure make the quantitative analysis even more difficult. Diffuse reflectance mid-infrared Fourier transform spectroscopy (DRIFT) and attenuated total reflectance mid-infrared Fourier transform spectroscopy (ATR-FTIR) have been used in the past for characterization of soil particles, and other organic waste products [150, 151]. The existence of abundant literature for interpretation of spectra generated by FTIR techniques provides an advantage over NIRS. However, DRIFT strongly depends upon material particle size and therefore it requires time to prepare samples of appropriate size suitable for analysis. ATR-FTIR requires little sample

preparation but the sample should be close to water saturation to ensure a good contact between the sample and ATR crystal. It also typically results in low resolution with very dark and opaque samples such as manures [152]. Sample dilution with potassium bromide powder is often used to increase reflectance and avoid spectral distortion and non-linearities.

Recently, Fourier transform mid-infrared photoacoustic spectroscopy (FTIR-PAS) has been applied to soil samples and shown to overcome the above limitations. It is considered to be very suitable for characterization of manure. FTIR-PAS is a combination of FTIR and a photoacoustic detector (PAS) and the analysis is based on the absorption of electromagnetic radiation by analyte molecules [153]. Development of highly sensitive microphones in the last decade has increased the sensitivity of PAS and facilitated to achieve better results than the traditional FTIR. FTIR-PAS generates a signal by interaction of infrared beam with the surface of sample. This leads to production of a heat wave that can be detected by a sensitive microphone and transformed into a regular absorption spectrum. The resulting spectrum differs from both the equivalent transmittance and reflectance spectra since the technique detects non-radiative transitions in the sample. The detected wave amplitude in PAS is proportional to sample concentration and therefore this technique allows measurement of infrared absorption of relatively dark samples, such as manure without any pre-treatment [154]. When coupled with multivariate statistical analysis such as partial least squares (PLS), FTIR-PAS can be used for quickly and effortlessly to obtain important information such as chemical composition and carbon mineralization of samples. This provides critical information to develop application strategies, such as time of application and application amounts of manure in the fields. The manure samples are air-dried at room temperature and passed through a 2 mm sieve for analysis. Photoacoustic spectra are recorded for samples using an infrared spectrophotometer which is equipped with a photoacoustic cell. Around 200 mg sample is placed in the cell holding cup and purged with dry helium at 10 mL/min for 10 s. Subsequently, the scans are conducted in the wavelength range of 500–4,000 cm^{-1} with a resolution of 4 cm^{-1} [155]. For data processing, data reduction is achieved by the principal component analysis (PCA), which is commonly used to reduce the dimensionality of infrared spectra by generating a small number of coefficients called PCA scores that retain most of the variability (information) present in the original data. Probabilistic neural networks (PNN) are used to make manure identification [156]. Number of PCA scores retained from PCA decomposition and number of training samples are used to determine the number of input and hidden nodes, respectively. PAS spectra are coupled to PLS model consisting of for example 75% samples randomly chosen as calibration set, and 25% samples used as validation set. This information is used for quantitative analysis of organic matter content in manure samples. Distinctive bands for different animal manure spectra are generated by FTIR-PAS which establish its application for fast characterization of animal manures.

8.6.8 Near Infrared (NIR) Spectroscopy

Presently, several methods are used to determine the constituents of interest such as nitrogen fractions, mineral and dry matter content. There are two main methods to obtain these analyses which include (i) book values based on average of manure samples from a particular region, and (ii) analyses in commercial testing laboratory. Manure nutrient contents can vary substantially depending on age, species, nutrition of animal, amount of bedding and storage practices [9]. In such a case, using book values to determine the nutrient content can be inaccurate. The lab-based methods are accurate but time consuming, expensive and inconvenient for most producers. Furthermore, in order to combine manure analyses with precision agriculture, a rapid and accurate method is needed to use the correct amount of manure to the correct field location. Spectroscopic methods such as near-infrared diffuse reflectance spectroscopy (NIRS) offers the possibility of rapid, non-destructive analyses of manure without generating chemical wastes as those obtained from traditional digestion based methods. NIRS requires little or no sample preparation and allows simultaneous measurement of several analytes, thus making it more suitable for real-time analysis during spreading of manure in the field [157].

NIRS was firstly developed in the early 1970s for rapid analysis of moisture content of cereal grains. However, over the past few decades, it has rapidly developed to be a fast and robust analytical tool for characterization of agricultural, pharmaceutical and food products. The technique is particularly useful for determination of moisture and organic (carbon, nitrogen) content of soils and other organic waste products [158]. NIRS combines applied spectroscopy and statistics. Its principle is based on the absorbance of covalent chemical bonds formed between light atoms such as carbon, nitrogen, oxygen and hydrogen. These bonds have primary absorbances in the infrared region (IR) and combination bands that absorb light in the NIR region i.e. 780–2500 nm. This region of the electromagnetic spectrum is particularly useful since a linear relationship between absorbance and concentration is exhibited by many biological and agricultural samples, in contrast to the case in the IR region [149]. Thus, light reflected by or transmitted from samples in the NIR region is amplified, digitized and recorded as absorbance. For samples under analysis, spectral data is collected statistically and converted to calibration equations. This is then used with results of conventional chemical analyses on the same samples to predict the concentrations of constituents in further samples of a similar type [159]. The NIRS technique utilizes samples in dry or ground or 'as it is' form. Samples are scanned using a transport module with the sample placed in a polyethylene bag, thus allowing a sample path $\sim$12 cm to be scanned. Though exact protocols can vary, usually the data is collected every 2 nm at a nominal bandwidth of 10 nm. A ceramic standard is used for background spectra and spectra are computed as log (1/R), where R is reflectance [160].

Several researchers have reported the use of NIRS to analyze nutrient concentrations in manure samples. Total nitrogen, total carbon and crude ash in cattle manure was analysed [161]. NIRS was used to predict the total solids (TS), total

nitrogen (TN), ammonia-nitrogen and potassium in swine lagoon effluent and solid beef manure samples using spectral data [162]. It was also reported that NIRS could measure organic nitrogen, TN, and moisture but not the mineral content in poultry manure [9]. The use of NIRS for total dissolved nitrogen, suspended nitrogen, soluble reactive phosphorous, magnesium, potassium, and suspended phosphorous in hog manure was demonstrated [163]. In general, the application of NIRS for mineral content analysis of manures has been limited.

In addition to manure, NIRS also finds applications in food products to determine its constituents such as fat, moisture, proteins, acid and neutral detergent fibres [164]. In dairy industry, NIRS has been used for analyzing major components of milk, skim milk and fermented milk products. In cheese industry, NIRS has been successfully used to determine proteins, moisture, lactose and fat [165, 166]. Since food waste also comprises the same constituents, this opens up the possibility of using NIRS for food waste composition analysis as well.

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