# Chemical Examination of Food

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### How to Determine the Nutritional Value of Food

- · Chemical examination of food products :-
  - 1-Nutritive Value

Example: Protein ,fat,minerals....etc.

• 2-Keeping Quality Tests

Example:

- TVN (total volatile nitrogen)
- TBA (Thiobarbabturic acid)
- PH
  - 3-Chemical Residues

# **1-Nutritive Value**

#### Labeling the nutritional value

Within the European Union there is legislation stating how and when the nutritional value should be labeled on food products. The labeling is regulated through the <u>EU 1169/2011 directive</u>. This is a very extensive piece of regulation on how food products should be labeled. The regulation defines things such as the name of products (e.g. you're not allowed to call something 'strawberry yogurt' if it contains no strawberries), but also weight, shelf life dates, etc.

It also describes the nutrition labeling. It describes which nutritional values have to be on the label, how they have to be determined, etc.

Once a manufacturer knows which data has to be put on a label it is time to determine the values for the label. So let's dig into how these numbers are determined, starting with the energy content.

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	Mass in product (g)	Energy content of molecules (kcal/g)	Energy in product (kcal)
Fats	5	9	45
Proteins	8	4	32
Carbohydrates	3	4	12
Total			89 kcal

Table 1: Calculating the energy content of 50g of an imaginary product A.

This simple calculation has now told us that 50g of product A contains 89 kcal. Whether this is a healthy product or not, no idea! That will depend on all the other nutrients present in this product.

Determining fat, carbohydrate & protein content

So now we know how to calculate the energy content of a product. But in order to do that we needed the quantities of energy containing ingredients such as fats, proteins, etc.

There are two ways to determine these quantities:

- 1. The analytical route
- 2. The literature route

#### Option 1: Literature analysis

Let's start with the 2nd option: the literature route. In this case, no analysis of the actual final product is done. Instead, databases which contain a lot of data on nutritional values of all sorts of products are used.

The <u>USDA</u> has a very extensive database. It contains the nutritional value of a lot of different products, both processed and unprocessed foods. In the Netherlands, a database exists as well, from the <u>RIVM</u>.

In the case of unprocessed food, chances are pretty high you will find the nutritional value of your product in one of the tables. If you have a processed food though (e.g. a muffin you baked or a salad you made) your product will not be there, especially if you invented a new recipe!

So, you have to start calculating, in a same way as we calculated energy content. Make a list of all the ingredients in your product. Write down how much of each is in there. Look up the nutritional values of each ingredients per gram of ingredient. Now multiply the amount of material with the nutritional values and you've got your values!

#### **Option 2: Analytics**

Of course, when there is no available literature data, another way has to be used, that of analyzing the food. This can de done using various chemical analysis techniques.

But, before doing any analysis it is important to consider one thing. Foods are very heterogeneous, that is, they are not identical throughout the whole product. Also, every item is just a little different. For instance, milk milked in summer is often very different from milk milked in winter. The same goes for a lot of other products. Therefore, it is impossible to determine the carbohydrate, protein and fat content of every food to the tenth of a gram. There is always some variety and therefore inaccuracy of the results.

#### Protein analysis – Determining nitrogen content

Foods can contain a lot of different proteins. Each of these is slightly different therefore it is virtually impossible to analyze all the different proteins in a food. Luckily, for labeling only the overall protein content has to be given.

For determining this content a work-around is used. Instead of analyzing protein content, the amount of nitrogen in a sample is analyzed. Proteins contain quite a bit of nitrogen. Moreover, most of the molecules in food that contain nitrogen are actually proteins. Nevertheless, the methods aren't 100% perfect. Not all proteins contain the same fraction of nitrogen, which causes the calculation of protein content from the nitrogen content to be off at times.

There are two main analysis techniques used for this: the Kjeldahl method and the Dumas method. For some further reading on the details of this method, <u>here</u> are <u>here</u> are two nice articles.

#### Carbohydrate analysis

Carbohydrate analysis is actually even harder than protein analysis. In most cases, the carbohydrate concentration is simply determined by taking

the total mass of a product and subtracting all the other components (fats, protein, water, ash & alcohol).

Since there are so many carbohydrates (think of the <u>mono-, di-, oligo- and</u> <u>polysaccharides</u>) there is no general overlaying analysis method. There are methods to identify individual (groups of) carbohydrates though. However, in a lot of cases the method mentioned above is used.

Feel like some more chemistry? The <u>FAO</u> and the <u>University of</u> <u>Massachutes Amherst</u> have written about it in more detail.

Fat content analysis

Most of the fats in foods are the so-called <u>triglycerides</u>. These can be analyzed in foods pretty accurately using a technique call gas chromatography. This is however a more expensive and completx technique. There are other methods as well. Near infrared radiation for instance is used, although more for a process control reason, than an analytical method.

Also, since fats do not dissolve in water a commonly used method is that of extraction. This uses the fact that carbohydrates, proteins, etc. prefer to sit in water, whereas fats do not and prefer another type of solvent. This way the fats can be <u>extracted</u> from the product and their quantity can be analyzed.

# 2-Keeping quality tests

- <u>TVN</u>

#### ANALYSIS OF TMA/TMA-N-O AND TVB-N

#### 1 Direct methods

Biogenic amines are commonly determined using chromatography (Galgano et al., <u>2009</u>), colorimetric (Khulal et al., <u>2016</u>), or combined methods, such as gas chromatography-mass spectrometry (Wojnowski

et al., 2019). Each of these methods involve derivatization during sample preparation. Saccani et al. (2005) proposed an underivatized sample method for the detection of total biogenic amine in fresh and frozen meat. The method was based on separation by cation-exchange chromatography and suppressed conductivity coupled with mass spectrometry. TVB-N determination measures the concentration of ammonia, TMA, and DMA (Choe et al., 2017) and is generally perceived as a reflection of the level of protein decomposition and therefore quality deterioration of meat. Several methods have been reported for the measurement of TVB-N, including organoleptic and distillation techniques. The distillation technique involves the generation and trapping of volatiles using a Conway cell in either high temperature, reduced pressure, or distillation at a temperature slightly higher than temperature (Saenz-Garcia et al., **2020**; room Senapati&Sahu, 2020; Tantratian&Kaephen, **2020**; Wang & Duncan, 2017). A common distillation technique involves the heating of muscle tissues with an alkali to form ammonia from amides. Due to the likely erroneous results from steam distillation, the liberation of TVB-N at room temperature through the mixing with an alkali is captured by an acid placed in a microdiffusion cell "Conway cell." This latter method has the advantage of being carried out at a low temperature, which perhaps contributes to its widespread application in fish studies for the measurements of TVB-N and TMA (Howgate, 2010a). However, a steam distillation method using the Kjeldahl system has been adopted as the standard by many laboratories (Cai et al., 2011; Chen et al., 2019c; Huang et al., 2015a) and as the baseline test for the developed TVB-N regulations. While the use of meat samples has been the most common, the use of meat juice was suggested as a better alternative than the raw meat for the detection of biogenic amines (Bota& Harrington, 2006). The reported TVB-N results are affected by the analytical procedure, especially those involving the use of a distillation step where the use of high temperature and strong alkali causes decomposition of nitrogen-containing substances (Howgate, 2010a, 2010b). These include the use of high-performance liquid chromatography (HPLC), gas chromatography-flame ionization detection, GC-MS, capillary electrophoresis, flow-injection analysis (FIA), ion mobility spectrometry, amperometric bi-enzyme electrodes, and metalloporphyrins-coated quartz microbalance sensor array (electronic

nose) (Chang et al., 2015; Huang et al., 2015b; Karpas et al., 2002; Sun et al., 2018). FIA is based on partitioning the bases generated from an alkalized extract through a polytetrafluoroethylene membrane into a carrier stream containing bromothymol blue indicator (Sadok et al., 1996). The techniques listed above are collectively regarded as conventional methods, which exhibit reduced detection efficiency, owing to the possible decomposition of TVB-N, for example, during high-temperature distillation and a lack of standardization. Also, these methods are time-consuming, labor-intensive, and involve destructive procedures. In recent years, much effort has been directed toward the development of rapid determination and nondestructive monitoring techniques for TVB-N detection. For example, Xia et al. (2016) used rat muscles to compare steam distillation using the Kjeldahl method and a new conductometric titration using a conductivity meter for determination of TVB-N in the skeletal muscles. The study showed that TVB-N values could successfully predict the postmortem protein decomposition of animal tissues after 24 hr storage at 24°C and 80% relative humidity. Analytical methods involving chemical sensors (e.g., e-nose, e-tongue, electrical conductivity, and computer vision) with an ability to detect and quantify a group of related chemical species have also been developed (Gil et al., 2011; Gil et al., 2008; Gil-Sánchez et al., 2016).

#### 2 Indirect/rapid methods for the determination of TVB-N

Unlike conventional methods used for the determination of TVB-N, noninvasive and nondestructive methods have attracted much interest due to their high reliability, being used directly on the sample without the need to conduct sample preparation, and because of their fast and simultaneous determination of several properties. Several technologies have been reported for this purpose, including computer vision, infrared spectroscopy (VIS–near-infrared, mid-infrared, far-infrared spectroscopy, and short-wave near-infrared), E-nose, NMR spectroscopy, Raman spectroscopy, and hyperspectroscopy (Cheng et al., **2017**; Kamruzzaman et al., **2015**; Su et al., **2017**; Taheri-Garavand et al., **2019**; Xiong et al., **2017**). Due to the high interest in the biological effects of TVB-N and TMA on the quality of food products and on health, a new generation of rapid methods of determination have been proposed (Table <u>4</u>). Many of these methods have

been described as inexpensive, safe, rapid, and nondestructive options for rapid detection of TVB-N and unsafe levels of bacteria spoilage. Since loss in meat quality due to bacterial activity also causes changes in the internal and external physicochemical attributes (chemical changes, such as pH value, structural modification, such as texture/tenderness, and color change), they collect information on changes in multiple properties, which could provide a better strategy for the measurement of freshness. Therefore, sensors that are capable of detecting certain substances and products of biochemical/microbial activities have been developed to measure the freshness of meat (Shi et al., 2018). Table 4 shows the integration of digital imaging and spectrometry for the rapid and accurate description of TVB-N levels in meat. The main advantage of such combined methods is the acquired ability for real-time monitoring, reduced detection limit, and high correlation ( $R^2$  prediction > 0.93) between the detected TVB-N value and the control spoilage factor. Some of the fast and nondestructive analytical methods are described hereafter.

#### - <u>TBA</u>

#### TBA as an Index of Oxidative Rancidity in Muscle Foods

The most common chemical measurement of lipid oxidation in muscle foods is the thiobarbituric acid (TBA) assay. The widespread use of the TBA assay is primarily due to its simplicity. However, the TBA test may pose many challenges due to its relative nonspecificity and varying sensitivity. These problems can negate any advantages of simplicity, and can lead to a misinterpretation of results unless the factors which influence the TBA reaction are thoroughly accounted and understood. The TBA assay is based on the reaction between TBA and carbonyls to form red, fluorescent adducts under acidic conditions. The assay can be conducted on ground muscle, muscle extracts, and muscle distillates; and adduct formation can be conducted under a number of varying temperature (25 to 1000 C) and time (15 min to 20 hr) protocols. The compound often attributed to be the primary lipid oxidation product detected by TBA is malonaldehyde (MDA) whose TBA adduct absorbs strongly at 532 nm. MDA is a dialdehyde produced by a two step oxidative degradation of fatty acids with three or more double bonds. This means that MDA yield during the oxidation of lipids is dependent on fatty acid composition with highly unsaturated fatty acids producing high amount of MDA. TBA can also react with aldehydic lipid oxidation products other than malonaldehyde. The most notable of these products are unsaturated aldehydes including 2-hexanal, 2-nonenal, and 2,4-decadienal. Since the type of oxidation products produced is dependent on fatty acid composition, the sensitivity of the TBA reaction is dependent on species and dietary history of muscle. Therefore, attempts to use TBA to compare oxidation between muscles with different fatty acid compositions is inappropriate. The nonspecificity of the assay is also due to interfering compounds which react with TBA. Examples of such compounds include ascorbic acid, sugars, and nonenzymic browning products. These compounds can form TBA adducts which absorb over the range of 450-540 nm. In addition, several compounds containing amine and sulfhydryl groups can interact with MDA and other aldehydes thus decreasing their ability to react with TBA. Since many compounds can interfere with the TBA reaction, a thorough knowledge of the meat product formulation is necessary for the interpretation of TBA numbers. Often it is more appropriate to refer to TBA reactive substances or TBARS to acknowledge that compounds in addition to MDA can generate pink chromophores. TBA results are also dependent on the method type, with each method having its own advantages and disadvantages. Formation of TBA adducts with non-MDA aldehydes is temperature dependent, with increasing temperature resulting in decreased formation of TBA-non-MDA aldehydes adducts. Formation of interfering TBA adducts also increases with increasing assay temperature. Therefore, while high temperature TBA tests are quicker, they are more susceptible to interference from nonoxidation products but they can be more selective for MDA. Additional factors which should be considered when choosing a TBA method include the relationship between sample homogeneity and sample size, time required for analysis in relation to oxidation rate, and how assay conditions will impact additional oxidation of the sample during analysis. The TBA assay can be a useful method for analysis of lipid oxidation in muscle foods. However, the nonspecificity of method requires an understanding of the test limitations so improper comparisons and conclusions are not made.

In order to minimize potential misinterpretation of TBA analysis it is suggested that analysis of fresh, nonoxidized samples be conducted to obtain baseline data for each meat product. In addition, lipid oxidation measurements should routinely include the measurement of a second oxidation product to support TBA results.

## - <u>PH</u>

#### The Role of pH Measurement in Food & Drink

In relation to food and cooking, pH may be most commonly known as a measure to ensure food safety. For example, in water-bath canning, foods must have a pH below 4.6 to ensure safety and prevent growth of harmful bacteria.<sup>2</sup> Foods with a low pH are resistant against dangerous microbiological growth and spoilage.

While food safety is a crucial consideration, understanding the pH of an ingredient can also help to achieve balance of flavors. Acidity, or sourness, is as essential as salt or seasoning in achieving balance of flavor, something all good chefs know.

Example Applications of pH Measurement in Food

The following are a few quick examples of the application of pH measurement in a variety of food products.

#### **Quality of Meats**

pH levels can be used to determine the quality of meats. For example, pork with a pH of 5.6 to 6.0 is indicative of a pig raised well and stress free, while pork with a pH of 4.9 to 5.5 indicates a pig raised poorly and/or stressed at slaughter.<sup>3</sup>

#### Salami

Meat used to make fermented products should be below pH 5.8.<sup>4</sup> Salami should be fermented to pH 5.3 or below to protect against the growth of Staphylococcus aureus.<sup>5</sup> pH can also be utilized to achieve and measure the desired sourness and resulting flavor in a finished product.

#### Litmus Paper

pH can be measured one of two ways: By litmus paper, (sometimes referred to as pH test strips) or by a pH meter and electrode.

#### Test Strips vs. pH Meter

Litmus is a water soluble mixture of different dyes extracted from lichens. Litmus paper test strips work by dipping the paper strip into a solution and comparing the change in color to a reference chart. The reference chart maps a color to a particular pH level: green-to-blue-to-purple for basic, and yellow-to-orange-to-red for acidic. Test strips are inexpensive, disposable and easily portable. They are a great solution for those on a tight budget where accuracy is not a factor of safety.

#### Manual Temperature Compensation

Measurement of pH is dependent on the temperature of the sample. As a temperature increases or decreases, ionic mobility increases and decreases respectively. The majority of test strips are standardized at 25°C (77°F). Compensation must be made for temperatures other than 25°C.

To manually calculate pH readings, use an adjustment of 1.9% pH per 1 degree Celsius above or below 25°C. For example, a test strip reading of pH 6.0 at a temperature of 24°C would be adjusted to an actual pH of 5.89; and a reading of pH 6.0 at a temperature of 26°C would be adjust to an actual pH of 6.11.

#### The Problem with Test Strips

In many cases, test strips do not provide the accuracy necessary. Measurement relies on visually matching colors to a printed reference chart, which assumes accuracy in the printing of reference colors. Further, the color difference in a 1 point range (e.g. pH 4 to 5) can be difficult to determine by eye. And to compound the issue, 1 in 12 men and 1 in 200 women have a certain level of colorblindness.<sup>10</sup> In applications like waterbath canning, where a pH of 4.6 or lower is necessary to prevent c. botulinum toxin growth (botulism)2, a pH meter and electrode should be used, as test strips do not provide the precision required.

#### Tools for Measuring pH

Assuming that litmus test strips will not suffice, the following outlines mandatory and optional tools for a proper setup to measure pH.

#### Mandatory Tools

These tools should be considered necessary for a proper pH measurement setup.

- pH meter
- Electrode(s) (aka probe or sensor) (if not integrated or included with meter)
- Electrode fill solution (for re-fillable electrodes)
- Calibration buffer solutions
- Cleaning solution(s)
- Storage solution
- Deionized/Distilled water
- <u>KimWipes®</u>

#### **Optional Tools**

These tools should be considered optional. They are beneficial, but not strictly necessary.

- <u>Glass beakers;</u> 250-500mL and 50-100mL
- Laboratory wash bottle
- Magnetic stirrer

# **3- Chemical Residues in Food**

Veterinary drugs and pesticides are used routinely in animal production to manage diseases and control parasites, and crop protection chemicals are used in production of animal feeds. It is possible, therefore, for foodstuffs of animal origin to be adulterated with residues of veterinary drugs and pesticides, and for animal fibers to be contaminated with residues of ectoparasiticides. Veterinarians must consider the implications of both possibilities when providing for the health and welfare of animals. First, animals and animal products destined for human consumption must not contain residues of drugs or pesticides that exceed legally permitted concentrations. Second, pesticide residues in fiber have potential implications for public health, occupational health and safety, and environmental safety.

Chemical Residues in Foodstuffs of Animal Origin

Chemical residues can be found in animal tissues, after administration of veterinary drugs and medicated premixes, application of pesticides to animals, or consumption of stockfeeds previously treated with agricultural chemicals.

Residues Resulting from Veterinary Drugs, Medicated Feeds, or Application of Pesticides:

Extensive regulatory and monitoring systems have been established to ensure that chemical residues in food do not constitute an unacceptable health risk. The premarket approval process undertaken by regulatory authorities for new veterinary drugs and medicated feeds evaluates the quality, safety, and efficacy of these products. For veterinary medicines intended for administration to food-producing animals, an additional consideration is the safety of edible tissues and products (milk, honey, eggs) derived from treated animals. Regulatory authorities establish maximum residue limits (MRLs) or tolerances and set withdrawal times that ensure residues of the active constituent will not exceed the MRL when the label instructions for the product are followed.

Residue programs consist of two principal activities: monitoring and surveillance. Residue-monitoring programs randomly sample food commodities from animals. Samples are assayed for residues of specific veterinary drugs, pesticides, and environmental contaminants, and the residues are assessed for compliance with the applicable MRL or environmental standard. The number of samples taken for monitoring purposes typically provides a 95% probability of detecting at least one violation when 1% of the animal population contains residues above the MRL. Surveillance programs, by comparison, take samples from animals suspected of having violative residues on the basis of clinical signs or herd history. Food from animals identified with violative residues of veterinary drugs or pesticides do not enter the food chain.

Residue monitoring is also a trade requirement, either mandatory or as an expectation, of importing countries allowing market access to food products derived from animals. Compliance with the national standards of importing countries becomes more difficult when the health standards, regulatory policies, and MRL-setting approaches of the exporting country and importing country differ. The situation is further exacerbated when patterns of use differ across countries or when the minor status of a disease or pest in a country does not warrant product registration, in which case MRLs are unlikely to be established.

Regulatory authorities undertake premarket approval assessments of applications in support of new veterinary drugs and medicated feeds.

These assessments consider scientific data submitted by the sponsor. In the case of veterinary medicines proposed for use in food-producing animals, the data must demonstrate the safety of any residues remaining in the edible tissues or products from treated animals. These data describe the compound's toxicology, metabolism, pharmacokinetics, residue depletion, and dietary exposure. The key parameters derived in the safety and residue evaluations are defined below.

The **acceptable daily intake (ADI)** is the amount of a veterinary drug, expressed on a body weight basis, that can be ingested daily over a lifetime without an appreciable risk to human health. The ADI is established based on a review of animal studies on toxicologic, pharmacologic, or microbiologic effects as appropriate. Conservative safety factors are built into the ADI.

The **safe concentration** is the maximal allowable concentration of total residues of toxicologic concern in edible tissue. The safe concentration is calculated from the ADI and considers the weight of an average person and the amount of meat, milk, honey, or eggs consumed daily by a high-consuming individual.

An **MRL**, or **tolerance**, is the maximal concentration of residue resulting from the use of a veterinary drug (expressed in mg/kg or mcg/kg on a fresh-weight basis) that is legally permitted as acceptable in or on a food. It is based on the type and amount of residue considered to be without any toxicologic hazard for human health as expressed by the ADI. Other relevant public health risks and aspects relating to food technology, good practice in the use of veterinary drugs, and analytical methodologies are also considered when establishing the MRL.

The **marker residue** is the parent drug, its metabolites, or any combination of these, with a known relationship to the concentration of the total residue in the last tissue to deplete to the safe concentration. When the marker residue in the target tissue has depleted to the MRL, the total residue will have depleted to the safe concentration in all edible tissues.

The **target tissue** is the edible tissue with residues that deplete to a concentration below the MRL at a slower rate than that in other edible tissues. It is considered suitable for monitoring compliance with the MRL of each edible tissue from a treated animal. The target tissue is frequently liver or kidney for the purpose of domestic monitoring and muscle or fat for monitoring meat or carcasses in international trade.

The **withdrawal time** is the period of time between the last administration of a drug and the detection of residues of that drug to levels below the MRL in food from a treated animal. Compliance with the preslaughter withdrawal time ensures the total residues deplete to below the safe concentration, and the marker residue depletes to below the MRL. Failure to observe the correct withdrawal time is the most common cause of violative residues of veterinary drugs in food.

Regulatory authorities determine withdrawal times based on residue depletion data that has been generated using healthy animals representative of those typically treated with the specific product. The drug formulation used in these trials is identical to the market formulation, which is administered at the maximal label rate. The withdrawal time is usually determined statistically, taking into account variability among animals in drug disposition.

Unlike an MRL, which applies to a veterinary drug regardless of the dosage form, route of administration, or dosage regimen, the withdrawal time stated in the product labeling applies only to that particular formulation when administered by the recommended route and in accordance with the dosage regimen. Altering any of these factors modifies the pharmacokinetic behavior of the drug in the animal and invalidates the stated withdrawal time. In addition, a range of physiologic and pathologic factors may modify the drug's disposition in the animal and prolong drug elimination.

In the USA, some veterinary or human drugs can be used extra-label (offlabel) in food-producing animals under the Animal Medicinal Drug Use Clarification Act, provided certain conditions are met (more information can be obtained on the <u>FDA website</u>). Veterinarians must be mindful, however, that the extra-label use of a small number of veterinary drugs is prohibited by the FDA. Extra-label use refers to use in a species not included in the product labeling or at a dosage rate higher than that stated in the product labeling. For drugs used in this manner, data are inadequate to demonstrate the safety of food products derived from the treated animal. An understanding of pharmacokinetic principles allows extended withdrawal times to be estimated both when veterinary drugs are used in an extra-label manner and in situations that may lead to changes in the kinetic behavior of a drug in an individual animal. The pharmacokinetic principles involved as well as two relevant practical examples that demonstrate such occurrences are discussed below.

The elimination **half-life** is the time required for the concentration of a drug to be reduced by 50%. Therefore, 99.9% of an administered dose is eliminated over 10 half-lives. In food-producing animals, the residues of drugs with longer terminal elimination half-lives take longer to deplete to below the MRL. The pharmacokinetic behavior of the drug determines whether the elimination half-life in tissues will exceed the elimination half-life in plasma. In food-producing animals, the terminal elimination half-life for the slow elimination phase, or  $\gamma$  phase, of the residue concentration versus time profile determines the withdrawal time. Half-life is determined by both clearance (CI) and volume of distribution (Vd).

**Clearance** is the blood volume cleared of drug per unit time and refers to the irreversible elimination of a drug from the body. The principal organs of elimination are the liver and kidneys; organ clearance is related to blood flow and the efficiency of drug removal. To determine hepatic clearance.

**Volume of distribution** relates the amount of drug in the body to the concentration of drug in plasma. For a drug administered IV.

Vd is a characteristic property of the drug rather than the biologic system. A drug confined to the vascular compartment has a minimal value of Vd equal to plasma volume. Factors influencing Vd include the size of the drug molecule, lipid solubility, drug pKa, and tissue blood flow. Certain disease states effect changes in the Vd of a drug, particularly changes in drug binding.

If it is necessary to administer a drug to a healthy animal at twice the recommended rate, the elimination half-life of the drug is unchanged. Assuming the pharmacokinetic behavior of the drug demonstrates first-order kinetics, which is generally the case, doubling the administered dose will increase the depletion time by one half-life. Thus, the withdrawal time should be extended by one half-life to arrive at the same concentration as observed for the recommended rate. However, if a drug is administered to an unhealthy animal with impaired drug excretion in which clearance is reduced by 50%, it can be seen from the relationship for half-life shown above that reducing clearance by 50% will double the half-life. Accordingly, the withdrawal time should be doubled to arrive at

the same concentration as seen in an animal with a fully functional excretory system.

The predicted result should always be verified using a rapid-screening test. The detection of residues is likely to signal that the withdrawal time should be extended and the rapid-screening test repeated.

Residues Resulting from Consumption of Stockfeeds Treated with Agricultural Chemicals:

The use of agricultural chemicals can result in residues in crops and pastures that are subsequently consumed by animals. During drought conditions, the feeding of potentially contaminated crop byproducts, such as stubbles and fodder, and processed fractions, including grape marc, citrus pulp, fruit pomace, and cannery wastes, is likely to become more prevalent. In all cases, chemical residues may result in the edible tissues, milk, honey, or eggs derived from these animals.

For approved uses of crop protection chemicals that are likely to result in dietary exposure of food-producing animals, regulatory authorities establish animal commodity MRLs. The approach adopted for establishing these MRLs is fundamentally different from the one that applies to veterinary drugs. Animal transfer studies, which allow determination of the relationship between the level of chemical in the animal diet and the concentration of residue found in edible tissues, milk, honey, and eggs, are pivotal in determining MRLs. MRLs for animal tissues, milk, honey, and eggs are established at concentrations that cover the highest residues expected to be found from the estimated livestock dietary exposure. Human dietary exposure assessments are also performed to verify that food complying with MRLs is safe for consumption. In animal production systems, compliance with animal commodity MRLs relies on adherence to a stipulated period to allow residues in the crop to deplete before it is fed to animals, a stipulated period to allow residues in the animal to deplete before slaughter, or a combination of both.

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