Food Testing:

Using Automated Titration to Determine Salt and Acidity

HANNA® instruments

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Introduction

Analytical testing is a cornerstone of the food production process. Whether a hobbyist or food scientist, many are involved in food quality and safety using a variety of analytical techniques to create safe, stable and, most of all, great tasting foods.

We will take a look at:

1. How salt and acidity affect food quality.
2. Methods for testing salt and acidity in food.
3. Features to consider when choosing an automatic titration system.

Why Salt & Acidity Matters

Importance of Salt in Food

When we refer to "salt," most often we are referring to sodium chloride also known as table salt. However, there are many other types of salts including potassium chloride, calcium chloride, and sodium nitrate.

The most common form of salt found in food manufacturing is sodium chloride (NaCl). Sodium can also be added in other forms including sodium nitrite, sodium bicarbonate (baking soda), sodium benzoate, and monosodium glutamate (MSG).

Naturally occurring, as well as a common additive in food products, sodium is an important mineral required by the human body. Unfortunately, too much sodium in our diet can lead to an increase in blood pressure. Due to its hypertensive effects, it is one of the minerals that appear on product labels for people that must watch their dietary intake.

Sodium-containing compounds are added to:

1. Extend shelf life by inhibiting microbial growth.

2. Improve texture and appearance by retaining moisture and stabilizing chemical changes in finished products.

3. Improve flavor by promoting desired tastes while masking off-flavors.

Importance of Acidity in Foods

Acidity is the concentration of acid in food. Some foods naturally have a high acidity, such as citrus fruits or tomatoes. Acidity can also be produced through microbial fermentation, such as in yogurt. Frequently, acid is added directly to foods during production. The most common organic acids include citric, malic, lactic, tartaric, and acetic acids.

These organic acids play a primary role in:

1. **Taste:** Organic acids, such as citric acid, are often added to foods to promote a tart or sharp flavor.

2. **Consistency:** For food manufacturers, maintaining acidity concentrations is vital to maintaining a flavor that is associated with that brand.

For example, most ketchup brands promote their own unique flavor. The taste of that ketchup varies with the concentration of the predominant acid (i.e. acetic acid). It is important that titratable acidity (TA) be consistently maintained between production batches. After all, customers expect a certain taste when purchasing a particular brand of ketchup.

Regulations

The Code of Federal Regulations (CFR) is an annual edition of general and permanent rules produced by the FDA and other government agencies. 21CFR101.61 establishes clear criteria to nutrient content claims for the sodium content of foods.

In terms of titratable acidity, there are guidelines as to the type of acid expressed as well as the value allowed.

These exist primarily for fruit and dairy products, such as:

21CFR146.114
Which states that lemon juice must have a titratable acidity value ≥ 4.5% by weight expressed as anhydrous citric acid.

21CFR131.200
Which states that yogurt must have a titratable acidity of ≥0.9% expressed as lactic acid.

Methods of Analysis: Salt

The quality of analytical data depends on proper sampling, appropriate method selection, and effective execution. There are multiple methods for determining salt concentration. Which method to use depends on the specific application. For example, for a simple brine solution, a refractometer or conductivity meter could be used. For a sauce or semi-solid product, titration would be more applicable.

Here are common methods to measure salt:

Titration: A technique where a solution of known concentration is used to determine the concentration of an unknown solution. While it is an investment, automated titrations are the easiest way to obtain accurate results.

Refractometry: A measurement of the refractive index of a solution based on its composition. Refractometers are inexpensive and require little skill to operate.

Conductivity (EC): The measurement of a solution's ability to conduct an electrical current based on the number of total dissolved solids. As the level of dissolved solids increases, namely salts, conductivity increases.

Ion Selective Electrode (ISE): An electrochemical sensor that converts the activity of a specific ion in a solution into a mV response that can be measured with a meter. A sodium ISE will measure sodium salts, while a chloride ISE will measure chloride salts.

Potentiometric Method:

A potentiometric titration uses an electrochemical sensor, such as an ion selective electrode, to determine the equivalence point.

The equivalence point is the point where the greatest change in voltage for a specific volume of titrant added (mV/mL) to the sample is observed.

Titrators determine the endpoint by detecting an equivalence point. The equivalence point is the point during the titration at which the analyte and titrant are present in equal parts.

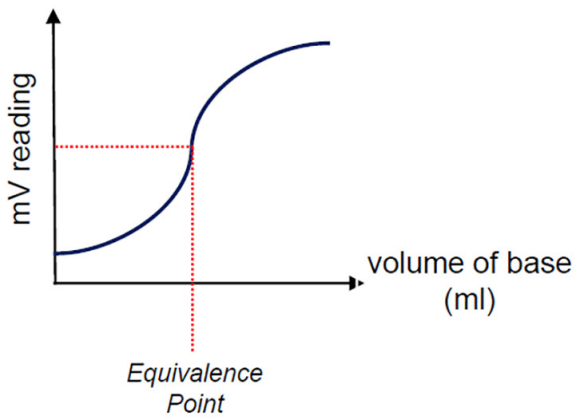
Mathematically, the equivalence point is the point where the slope of the titration curve is the steepest. That is the maximum mV response for a fixed volume of titrant that has been added. This can be seen in the left chart below.

The slope is determined by:

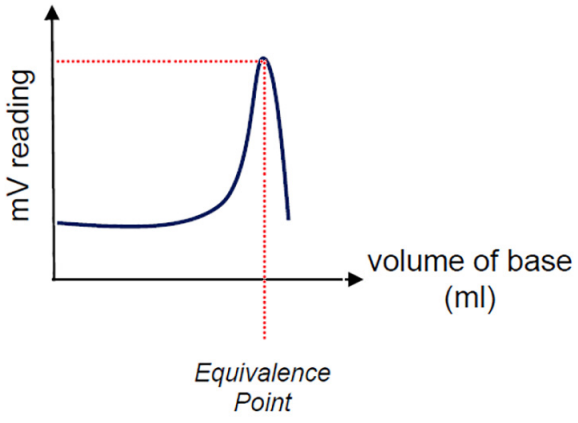
Slope = change in mV/change in mL

The slope calculation can be seen in the first derivative curve. This is a very important feature to have, especially when a titration curve is not steep, or when the curve is very noisy.

Titration Curve



First Derivative Curve



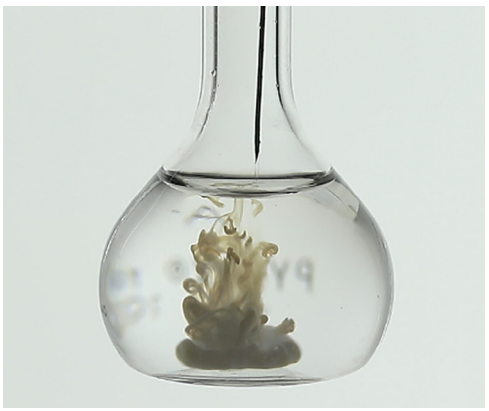
Salt

Potentiometric AOAC 983.14

The potentiometric method is a titration used to determine the chloride concentration in a solution. This method uses silver nitrate as a titrant. As silver nitrate is added to a solution containing chloride, a reaction takes place between the silver and chloride ions to form an insoluble silver chloride.

$$AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$$

When performing a salt titration with silver nitrate, it is assumed that any chloride present is from sodium chloride (NaCl). This allows us to infer the sodium content. This is the most common method for testing salt in food.



Silver chloride precipitation reaction

A chloride or silver-sulfide ion selective electrode (ISE) can be used to detect the equivalence point in a salt titration:

A chloride ISE measures the increase in mV as the chloride ions are removed.

A silver ISE measures the increase in mV as the silver ions become in excess since there are no more chloride ions to react with.

Hanna Note
Even though either ISE can be used, the preferred method is using the silver/sulfide ISE.

Acidity

Titratable acidity (TA) is a measurement of total titratable acids in a sample expressed as a concentration of the predominant acid present in the sample (i.e. citric acid in orange juice). TA titrations measure the overall amount of acid present and cannot differentiate between specific forms (i.e. citric versus malic).

TA is measured by titration in which a base, such as sodium hydroxide as the titrant, is added to the sample of a known quantity (weight or volume). The base will react with the acid to neutralize it.

Most food producers do not use an equivalence point to signal the end of an acidity titration. Instead a fixed endpoint is used to titrate the sample to a specific pH value. In most food and beverage acidity titrations, the endpoint is based on the point at which phenolphthalein, a color indicator, changes from colorless to pale pink. Depending on the sample and reference method, this corresponds to a pH value between 8.1 and 8.3.

A pH sensor, whether stand alone or as a titrator, is the preferred method for determining the fixed endpoint for the titration. It is not subject to chemical interferences or the subjectivity of seeing color. Color changes can be difficult to detect in color samples such as orange juice or milk.

Unreacted

Endpoint reached 8.3 pH

Hanna Note

The distinction between acidity and pH is very important. Acidity refers to titratable acidity (TA), or the concentration of acid in a solution, while pH refers to the strength of the acid present. TA is more useful as a predictor of how an acid will impact the flavor of a food product.

Food manufacturers use automated titration as their testing tool due to the consistent and accurate results it produces.

Here are three major advantages:

1. Automated

Make sure that the system offers the necessary features to maximize the benefits of automation.

2. Optimized

You do not want to have to figure out the best setup. The provider should develop the best configuration to achieve your objectives of throughput, accuracy, and ease of operation.

3. Fully Supported

There's no point in having amazing features if you are not using them correctly. Make sure that you are getting comprehensive setup, training, and support to guarantee that you get the most from your investment.

1) Automated

a) Why Automate

You should consider automating your titration processes if you have:

- High sample throughput - more than 10 samples per day
- High accuracy requirements
- Automatic reporting requirements

b. Key features to look for in an Automatic Titration System:

- Dual Analysis Setup
- Exchangeable Burettes
- Availability of Endpoint and Equivalence Titration
- Dynamic Dosing
- Automatic GLP Data Capture
- Sequential Linked Methods

What You Need

i. Dual Analysis Setup

Look for titration systems that can be set-up for both salt and acidity titrations at once. This means that the setup can be left in place without swapping out chemicals or electrodes.

Result: Save set-up time.

ii. Exchangeable Burettes

Additional titrations may require different types of titrants. Exchangeable burettes mean that you can switch between titrants without the need to purge and rinse the burette.

Result: Save time and reduce consumption of expensive chemicals.

iii. Availability of Endpoint and Equivalence Titration

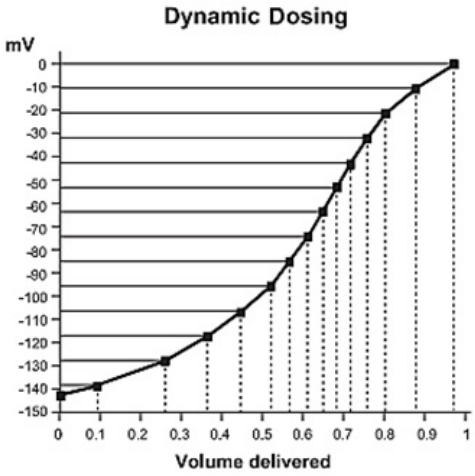
Acidity requires a fixed endpoint titration, while salt needs equivalence point titration. Your automated titration system needs to perform both to give you the flexibility that you need.

Result: One titrator for many types of titrations.

iv. Dynamic Dosing

Dynamic dosing adjusts the volume of titrant dose based on the mV response, speeding up the titration while increasing precision.

Result: Faster titration without compromising accuracy.



Hanna Note

Dynamic dosing allows for larger amounts of titrant to be dosed in the beginning and smaller amounts as the end point is neared. This is important since it allows for a fast titration without overshooting the end point.

vi. Automatic GLP Data Capture

Having the ability to record GLP (Good Laboratory Practice) data with every sample improves the integrity of traceability and record keeping processes. Look for data collection including company and operator name, sample ID, date, time, electrode ID codes, and calibration information.

Result: Save time with easy QC checks and auditing.

Easy Integration with Time Saving Equipment

Look for the ability of your titration system to easily integrate with other systems.

- Analytical Balance
- Printer
- Keyboard
- Monitor

Sequential Linked Methods

HANNA EXCLUSIVE FEATURE

Preparing samples takes time and also wastes valuable product. With Hanna's unique linked methods you can measure both your salt and acidity in one sample.

Result: One Sample + One Method = Two Results

See our video on linked titration for salt and acidity

2. Optimized

The optimal setup depends on your priorities, whether it be quantity, accuracy, sample efficiency, or operational simplicity. Make sure that your titration package includes expert help.

Check that the following is included:

a. Expert Consultation

It's important to have access to a technical expert experienced with titrations in food production environments.

The consultation should take place upfront so you can make sure that you get the right equipment and configuration for your needs.

b. Installation

You should get onsite setup and installation support. Make sure that this is included in your package!

c. Training

It is important to get onsite training for your startup process. Ensure that you have an option. The focus should be your success.

d. Ongoing Support

Insist that you get regular maintenance and calibration. You are likely to need calibration certificates from the vendor for SQF audits.

3. Fully Supported

Ongoing operational success is important to you. Work with a vendor who will support your needs. This means that you should have easy access to your entire team.

a. Support Standard Guarantees

Look for a dedicated 800 number and email address so you are not left unsupported.

b. Technical

You deserve a technical resource that knows your business and can quickly troubleshoot problems or help you make enhancements.

c. Executive Management

You do not want to be a nameless customer. Your titration process is important to you and should be important to your vendor. An executive sponsor shows that you are known and provides an escalation point if needed.

Determining Salt & Acidity

This procedure is an example for determining salt and acidity. Hanna Instruments will optimize the method to fit your specific needs. Always remember to consult the instruction manual or contact us for detailed instructions and customized support.

Before You Measure

1. Preparation and Calibration

a. Prepare the pH electrode (HI1131B).

- ☐ Remove the protective/storage cap from the electrode.
- ☐ If the pH bulb is dehydrated, place in storage solution for at least 3-4 hours.
- ☐ Remove the fill hole screw cap. Be sure to replenish with electrode fill solution HI7071 as needed.
- ☐ Connect the pH electrode and temperature probe to analog board 1 of the titrator.
- ☐ Enter pH mode by pressing "Mode", then "pH" making sure that analog board 1 is active.
- ☐ Once in "pH" mode, press "pH Calibr" to enter pH calibration mode.

b. Prepare the calibration buffers

- ☐ Fill a beaker with enough pH buffer solution 7.01 (HI7007C) to cover the pH electrode junction (approximately 75 mL in a 100 mL beaker).
- ☐ Repeat for pH 4.01 (HI7004C), and pH 10.01 (HI7010C) buffers.

c. Perform a three point calibration

- ☐ Rinse the pH electrode with deionized water.
- ☐ Use the "Next Buffer" and "Previous Buffer" buttons to select the pH 4.01 solution.
- ☐ Immerse the electrode, temperature probe, and propeller stirrer in pH 4.01 solution. (Verify that the propeller stirrer is plugged into board 1 and press "Stir" to turn on the stirrer.)
- ☐ Wait for the reading to stabilize
- ☐ Once the reading has stabilized, press "Accept" to update the calibration.
- ☐ Repeat this procedure for the pH 7.01 and pH 10.01 solutions.
- ☐ Press "Escape" to accept and exit calibration mode.

d. Prepare the silver-sulfide ISE (HI4115)

- ☐ Rinse the electrode stem with deionized water and assemble the electrode body. (See Manual)
- ☐ Fill the electrode with HI7072 fill solution.
- ☐ Connect the electrode to analog board 2 of the titrator.

2. Burette Preparation

a. Acidity - TA

- ☐ Install a 25 mL burette on pump one.
- ☐ Prime the burette with 0.1N sodium hydroxide (HI70456) 3 times. To do so, press "Burette" → "Prime Burette."

b. Salt

- ☐ Install a 25 mL burette on pump two.
- ☐ Prime the burette with 0.1N silver nitrate (HI70422) 3 times. To do so, press "Burette" → "Prime Burette."

How to Measure

3. Sample Preparation

The sample preparation procedure depends on the expected concentration and sample type. Use weight-based analysis for viscous/thick samples, and volume-based measurements for brines and low-viscosity samples.

Sample Size	Volume	Weight
Low Range (0-3% Acid), (0-4.5% NaCl)	2 mL	2 g
High Range (3-6% Acid), (4.5-9% NaCl)	1 mL	1 g

a. Analysis by Volume:

- ☐ Place pipette sample directly into a clean 150 mL beaker.
- ☐ Fill the beaker to the 100 mL mark with deionized water.

b. Analysis by Weight:

- ☐ Place a clean 150 mL glass beaker onto a balance and zero the balance.
- ☐ Weigh the sample and record the exact value.
- ☐ Fill the beaker to the 100 mL mark with deionized water.

4. Sample Titration

- ☐ Press "Select Method" to choose "Salt/TA Linked Volume" or "Salt/TA Linked Mass" based on your analysis type (by weight or by volume).
- ☐ Press "Start".
- ☐ Enter the exact analyte size (volume or mass) and press "Enter" to start the analysis.
- ☐ The titration will proceed automatically. Salt will be titrated first, followed by TA.
- ☐ At the end of the titrations, "Titration Complete" will appear. Results for salt content are displayed on top, with acidity on the bottom.
- ☐ Remove electrodes, temperature probe, and stirrer from the sample and rinse them thoroughly with deionized water.
- ☐ Ensure the pH electrode bulb is stored in HI70300L storage solution when not in use for extended periods. Disassemble and store the silver/sulfide ISE dry.

5. Salt and Acidity Video

Watch video here to find out how easy testing salt and acidity really is.

- ☐ Video: Salt and Acidity

6. Contact Us

- ☐ If you own a HI932 contact us for method files for Salt and Acidity
- ☐ Interested in more information? Call 800-426-6287 or email us at info@hannaints.com

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