IRON SULFIDE DISCOLORATION OF TUNA CANS[1/]

No. 2 - Analytical Methods

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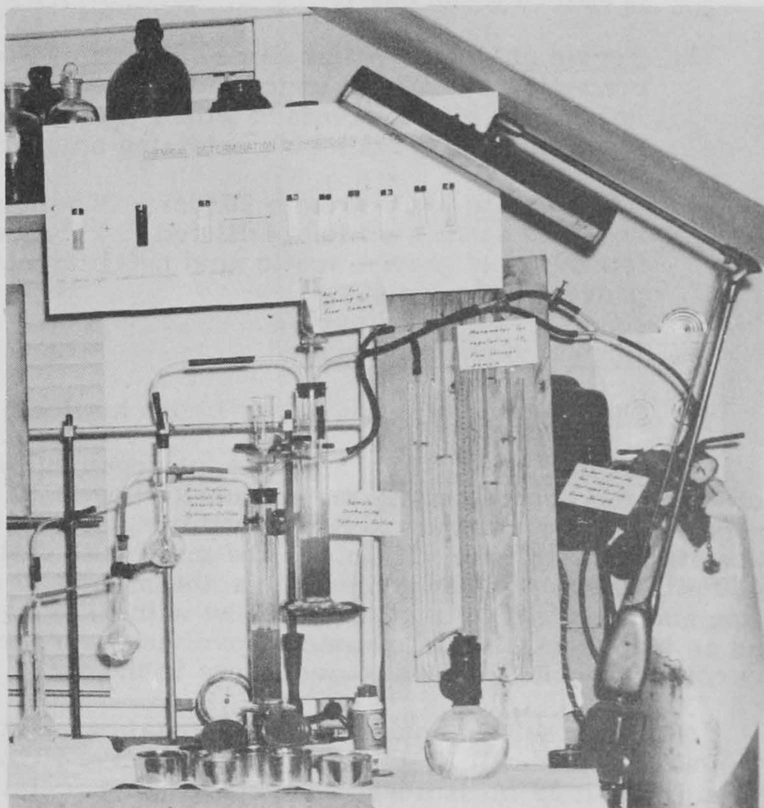
INTRODUCTION

During recent years, black deposits of ferrous sulfide have sporadically occurred in canned tuna on the inside surface of the can area adjacent to the headspace. This paper is the second in a series of six papers in which a study of the mechanism of iron sulfide discoloration is reported (Pigott and Stansby 1955).

The objective of this paper is to present the analytical methods that were used during the investigation. The sulfide analysis will be described in some detail, since the procedure has been improved and adapted for determining sulfide distribution in canned tuna.

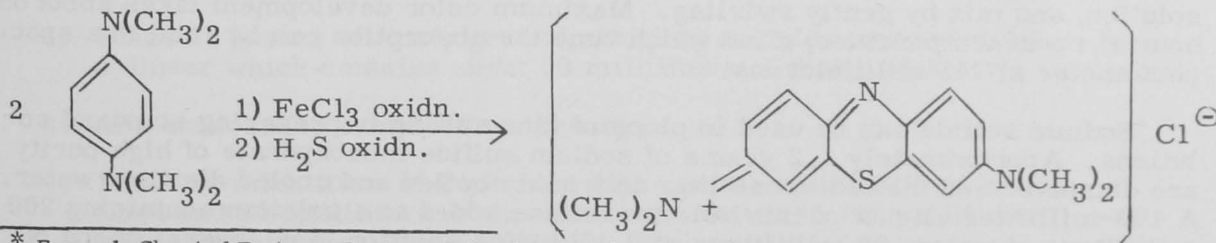
SULFIDE ANALYSIS

GENERAL: Sulfide was determined--as hydrogen sulfide--by a modification of Almy's method (Almy 1927) and (Brenner 1953). Inert gas is passed through an acidified suspension of the sample. The acid releases any free sulfide from the suspension as hydrogen sulfide. The gas is then passed through a zinc acetate solution where hydrogen sulfide is converted to zinc sulfide.



Apparatus used for the determination of hydrogen sulfide.

After the run, an oxidizing agent and p-aminodimethylaniline are added. A colorimetric reaction ensues which gives a blue-colored solution of oxidized methylene blue. The reaction can be considered qualitatively as:



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1/ This investigation, which was carried out at the Seattle Technological Laboratory, U. S. Fish and Wildlife Service, was jointly sponsored by the Continental Can Company and the U. S. Fish and Wildlife Service.

The intensity of the blue-colored solution resulting from this reaction is proportional to the amount of H_2S extracted from the sample. The amount of hydrogen sulfide can be determined by reading the percent of light transmission with a photoelectric spectrophotometer and comparing the results with a standard curve.

REAGENTS:

1. 1:1 hydrochloric acid.

2. 0.04 percent p-aminodimethylaniline hydrochloride.--Dissolve 40 milligrams of p-aminodimethylaniline in 1:1 hydrochloric acid and dilute to 100 milliliters with 1:1 hydrochloric acid. This solution should be prepared fresh daily.

3. Ferric chloride.--Dissolve 27 grams of $FeCl_3 \cdot 6H_2O$ in 500 milliliters concentrated hydrochloric acid and make to one liter. Before use, dilute 1 part of this standard with 4 parts of water giving an 0.02 normal solution of ferric chloride oxidizing solution.

4. Zinc acetate.--Prepare a 20-percent solution of zinc acetate. Before use, this stock solution is diluted to 2-percent zinc acetate solution. A few drops of glacial acetic acid per liter of dilute stock are added to prevent hydrolysis.

5. Carbon dioxide cylinder.

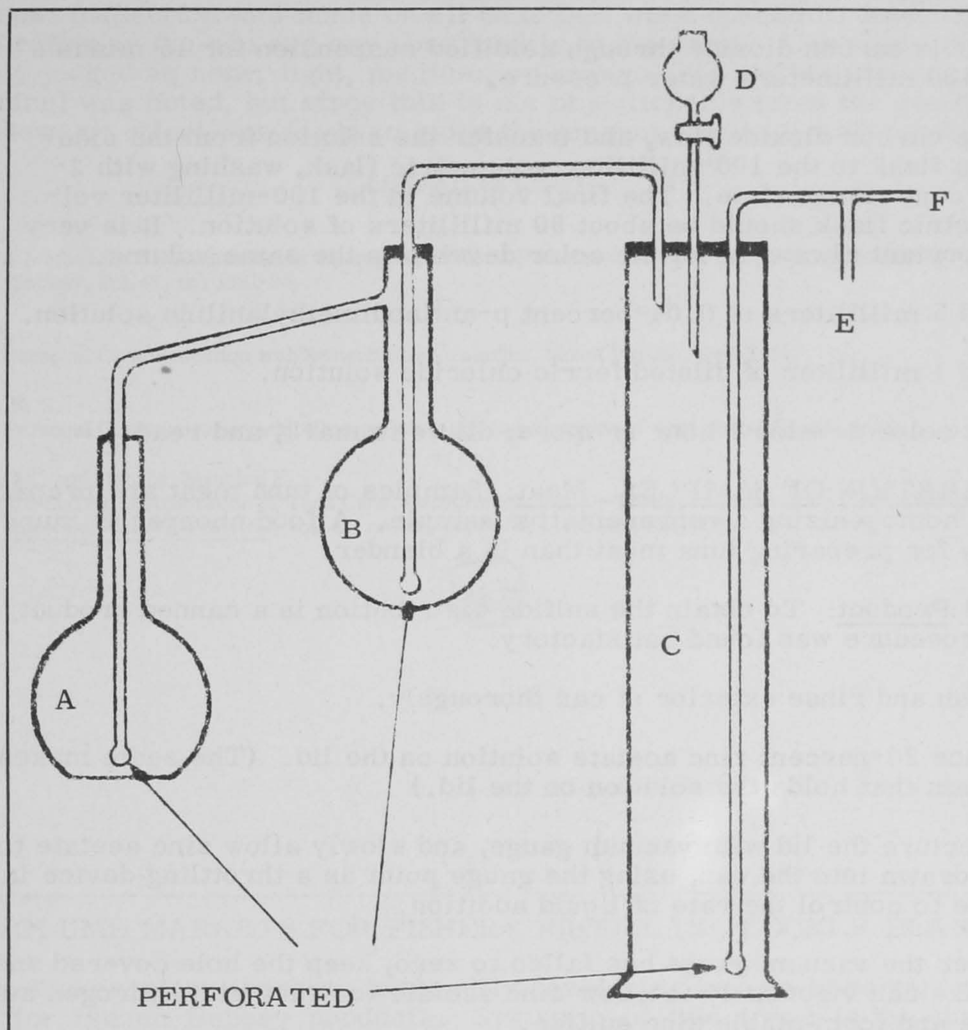
6. Antifoam agent. (Such as silicone antifoam spray.)

CALIBRATION CURVE: Bubble hydrogen sulfide gas through 500 milliliters of water for approximately one minute. Pipette 10 milliliters of this solution into a 100-milliliter volumetric flask containing about 10 milliliters of 20-percent zinc acetate stock solution. Dilute to the mark with distilled water. To the remaining 490 milliliters of hydrogen sulfide solution, add 20 milliliters of 0.1N iodine solution and back titrate the excess iodine with 0.1N sodium thiosulfate, using starch as an indicator. The above steps involving hydrogen sulfide solutions should be carried out quickly so as to avoid loss to the air.

The zinc sulfide solution should contain approximately 5 micrograms of hydrogen sulfide per milliliter. Add to each of five 50-milliliter volumetric flasks containing about 25 milliliters of 2-percent zinc acetate solution, aliquots of zinc sulfide solution containing 0, 5, 10, 25, and 50 micrograms of hydrogen sulfide, respectively. These standard solutions should be cooled in an ice bath before the color is developed so that a minimum of hydrogen sulfide will be lost. To the cooled solutions, add 5 milliliters of p-aminodimethylaniline and 1 milliliter of diluted ferric chloride solution. Dilute to the mark with 2-percent zinc acetate solution, and mix by gently swirling. Maximum color development takes about one hour at room temperature, after which time the absorption can be read in a spectrophotometer at 745 millimicrons.

Sodium sulfide can be used in place of zinc sulfide in preparing standard solutions. Approximately 1.2 grams of sodium sulfide monohydrate of high purity are dissolved and diluted to one liter in freshly boiled and cooled distilled water. A 100-milliliter aliquot of this solution is then added to a solution containing 200 milliliters of water, 20 milliliters of 0.1N iodine solution, and several drops of 1:1 hydrochloric acid. The excess iodine is then titrated with 0.1N sodium thiosulfate solution. The standard solutions are prepared as explained previously.

APPARATUS:



A. 100-milliliter volumetric flask.
B. 80- to 100-milliliter round bottom distilling flask.
C. Aerating cylinder about 5 centimeters diameter and 38 centimeters high.
D. Dropping funnel of at least 60 milliliters capacity.
E. Manometer (water).
F. CO_2 cylinder.

PROCEDURE:

1. Clean apparatus thoroughly and rinse in distilled water.

2. Place 25 grams of finely ground, weighed samples into aerating cylinder which contains about 50 milliliters of distilled water.

3. Add antifoam to sample if necessary.

4. Place 30 milliliters of 2-percent zinc acetate solution in side-arm flask and 20 milliliters of zinc acetate solution in 100-milliliter volumetric flask.

5. Apply glycerine to each rubber stopper to insure a good seal.

6. Place all stoppers in position, thus sealing apparatus from leaks.

7. Add 50 milliliters of 1:1 hydrochloric acid through dropping funnel, leaving a few drops in funnel to insure seal.

8. Bubble carbon dioxide through acidified suspension for 15 minutes at 400 millimeters water pressure.

9. Stop carbon dioxide flow, and transfer the solution from the side-arm flask to the 100-milliliter volumetric flask, washing with 2-percent zinc acetate. The final volume in the 100-milliliter volumetric flask should be about 90 milliliters of solution. It is very important always to let the color develop in the same volume.

10. Add 5 milliliters of 0.04-percent p-aminodimethylaniline solution.

11. Add 1 milliliter of diluted ferric chloride solution.

12. Let color develop 1 hour or more, dilute to mark, and read.

PREPARATION OF SAMPLES: Meat: Samples of tuna meat are prepared for analysis by homogenizing a representative sample. A food chopper is much more satisfactory for preparing tuna meat than is a blender.

Canned Product: To obtain the sulfide distribution in a canned product, the following procedure was found satisfactory:

1. Wash and rinse exterior of can thoroughly.

2. Place 20-percent zinc acetate solution on the lid. (The seam makes a dam that holds the solution on the lid.)

3. Puncture the lid with vacuum gauge, and slowly allow zinc acetate to be drawn into the can, using the gauge point as a throttling device in hole to control the rate of liquid addition.

4. After the vacuum gauge has fallen to zero, keep the hole covered and shake can vigorously to allow zinc acetate to react with hydrogen sulfide and form stable zinc sulfide.

5. Open can and homogenize sample in the usual manner.

The results obtained from analyzing this sample will give the total sulfide in the can. When determining the sulfide content of the meat plus liquid, the sample of meat and liquid is taken from the opened can after the headspace gas has escaped. The difference between the total sulfide and the sulfide in meat plus liquid is the amount of hydrogen sulfide in the headspace.

OTHER ANALYSES

Headspace gases were analyzed for volatile acids, volatile bases, oxygen, and hydrogen, using a modification of the Van Slyke manometric apparatus (Landgraf 1954).

Can vacuum was determined with a Bourdon-type can vacuum gauge. All vacuums were taken on the outer bead radii of the lid, in an effort to minimize the vacuum decrease due to pressing the top of the can.

The height of the headspace was measured with a Starrett depth gauge.

The pH was determined with a Beckman glass electrode.

A visual inspection was made on all cans that were opened to detect the extent of discoloration in the can and any abnormality in the meat. Can discoloration was arbitrarily judged as none, light, medium, or heavy. Tin sulfide staining (underfilm staining) was noted, but since this is not objectionable from the commercial point of view, no effort was made to judge the amount caused by different variables.

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VOLUME MARKETS FOR FISHERY PRODUCTS--LOCKER PLANTS

The locker-plant industry is steadily developing into an important volume market for frozen fishery products. Symbolic of this trend is the change in emphasis--a locker plant is now classified in the trade as a "Frozen Food Center."

In a survey of the frozen food centers or locker plants in New Jersey in 1954, a U. S. Fish and Wildlife Service fishery marketing specialist found that only 26 plants out of a total of 54 sold fishery products. Yet, these 26 plants sold 163,970 pounds of fishery products annually, an average of 6,300 pounds a plant each year, or about 525 pounds per plant a month. If each of the almost 11,000 locker plants in the United States were to sell 525 pounds of fishery products a month, the locker-plant industry would provide a market for $5\frac{3}{4}$ million pounds of fishery products a month or 69 million pounds annually. Because of this tremendous potential, the Service's educational and market development program includes working closely with members of this industry.