JJH: ~~JGL~~: ~~TGG~~: RF
XF: Muriatic Acid

TO: Betsy Meyer, Jim Gibson, Wayne Hilgers, Nelson Borys, Kyle Resh

FROM: T. G. Grumbles
DATE: August 24, 1984

Interoffice Communication

SUBJ: VISTA RESPONSE TO FDA BY-PRODUCT ACID PROPOSAL

VISTA

Vista Chemical should continue to prepare comments regarding the proposed GRAS revocation for "by-product" muriatic acid. Following is a proposed general outline of our comments and discussion of each area.

1. Provide FDA process information for the Baltimore Plant. This has been done by the plant and is enclosed. It should be reviewed to assure that no information considered confidential is included.

2. Provide data on typical contaminant levels. This has also been supplied by the plant and more data should be forth coming.

3. Dispute FDA's approach of regulating by process and not setting specific contaminant levels. To do this we should offer suggested limits. This should be done by recommending the FDA incorporate the revised Food Codex specification. A draft of the new Food Codex monograph is attached. This should be carefully reviewed to determine if we could comply. The levels are what we expected, (0.05 ppm Benzene and 5 ppm total organics) but the analytical method specified is a bit of a surprise. The plant should review this method for feasibility.

4. Point out to FDA the potential indirect financial impact of the standard on the industry and Vista in particular. This would be qualitative and include such items as decreased price of non-food grade, potential environmental impact, and regional supply shortage. The FDA's threshold assessment is also enclosed.

We should attempt to have the draft comments completed by September 12. to allow legal review before sending to FDA. The deadline is September 24.

Thomas G. Grumbles

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Attachments

cc RAK, CFP, THH, OCK

VVV 000016327

Apr 23 1981

Threshold Assessment of the Proposed Rule to Affirm the GRAS Status of Hydrochloric Acid

I. PURPOSE

The purpose of this threshold assessment is to determine if the economic effects of this proposed rule to affirm the GRAS status of hydrochloric acid (HCl) would be of sufficient magnitude to warrant a Regulatory Impact Analysis (as specified in Executive Order 12291) or a Regulatory Flexibility Analysis (as specified in the Regulatory Flexibility Act, P.L. 96-354).

Guidance for determining the thresholds for a "major" impact under Executive Order 12291 includes the criteria in Section 1b of the Executive Order itself, and informal supplementary guidance provided by FDA's Office of Planning and Evaluation dated March 31, 1981. Guidance for determining the thresholds for "a significant impact on a substantial number of small entities" under P.L. 96-354 includes definitions in Section 601 of the Act and informal supplementary guidance provided by FDA's Office of Planning and Evaluation dated March 31, 1981.

II. OBJECTIVE OF THE REGULATION

The objective of this proposed rule is to affirm the GRAS status of HCl as a direct human food ingredient. The safety of this ingredient has been evaluated as part of a comprehensive safety review of GRAS ingredients being conducted by the agency.

III. NATURE OF ECONOMIC IMPACT

Currently, food manufacturers who use HCl in their production process use ~~food-grade HCl~~ obtained from chlorine and salt (prime or non-byproduct HCl) or food-grade HCl obtained primarily as a byproduct of various chlorination processes (byproduct HCl). The Food Chemical Codex, 3rd Ed., 1981 (FCC-III) specifies that the manufacturer, vendor, or user of HCl (prime or byproduct) is responsible for identifying specific organic contaminants and for establishing the suitability of the acid for its intended use.*

FDA has insufficient data to conclude that any byproduct HCl is safe for use in food. Consequently, in this proposed rule, the agency is

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* The monograph for HCl in the earlier editions of the FCC in 1965 and 1972 contained a note that HCl produced during the manufacture of chlorinated hydrocarbon insecticides is not considered food grade. In contrast, the FCC-III does not prohibit the use of HCl from this source.

not endorsing the requirements for HCl in the FCC-III and is not affirming any byproduct HCl as GRAS. The restriction of food uses to non-byproduct HCl conceivably could produce price premiums for the non-byproduct acid in some market areas depending on local supply and demand conditions.

The agency is aware of efforts by the Committee on Codex Specifications of the NRC/NAS to develop definitive specifications for the organic contaminants of byproduct HCl. FDA will consider any new specifications as a comment to this proposal and will make appropriate modifications in the final rule.

IV. IMPACT ASSESSMENT

Hydrochloric acid (HCl) is commonly referred to as muriatic acid (aqueous solution). "Pure hydrogen chloride is a colorless, pungent, poisonous gas at ordinary temperatures and pressures. The standard commercial strength has a Baume of 21 degrees (31.4% HCl) and is slightly yellowish in color."[1]

In 1980, food processing accounted for approximately 10% of all uses for HCl.[2] It is used as a processing aid in the food industry for the hydrolysis of protein and starch, the inversion of sugar and the manufacture of edible gelatin.[3] During recent years, the largest growth area for food use has been in the manufacture of high fructose corn syrup.[4]

As can be seen in the following table, the majority of the HCl supplied for all uses in the U.S. in 1980 was byproduct HCl.

U.S. PRODUCTION OF HCL[5]
(THOUSANDS OF SHORT TONS - 1980)

Source	Tons	%
Byproduct	2490	89
From Chlorine	191	7
From Salt	97	4
TOTAL	2778	100

1. "Outlook for Cresylics", Chemical Purchasing, Nov. 1981. p. 60.
2. Chemical Manufacturing Review, 233:44, April 25, 1983.
3. "Outlook for Cresylics", Chemical Purchasing, Nov. 1981. p 60.
4. Chemical Manufacturing Review 222:31, Dec. 13, 1982.
5. Chemical Purchasing, p. 63.

FDA has no information as to exactly what pecentage of food manufacturers use byproduct HCl although, as HCl use is determined primarily by regional availability, it is believed that the use of byproduct HCl in food has become significant.

As a result of short supply of byproduct acid, production of prime (non-byproduct from chlorine and salt) has increased in recent years, i.e., an increase of 21% in 1979.[6] This trend may act to mitigate potential availability problems.

The price of HCl is governed by region, transportation costs, demand for primary products which use chlorine, supply of HCl, and Baume (20° or 22°). The agency believes that non-byproduct and byproduct HCl currently are competitively priced within a range of about $60-100 per short ton depending on location. It appears that price premiums for non-byproduct HCl could occur as a result of the regulation in given market areas if local food use exceeds local production. However, it is unlikely that the entire food use of HCl would acquire such premiums, and their size would be limited by transportation costs from markets where non-byproduct HCl availability exceeds food uses. We may illustrate the general magnitude of possible impact with the assumption that half the food use (say 150,000 tons) generates a price increment averaging half the maximum range of current prices ($20 per ton). This would imply a cost impact on food manufacturers of $3 million per year. Advice from several HCl suppliers indicates that sales for food processing use are mainly to large firms. It is evident from this example that under no plausible assumptions could the proposal constitute a major rule requiring a regulatory impact analysis under Executive Order 12291 nor one with sufficient impact on small entities to warrant a regulatory flexibility analysis.

V. Summary

The Food and Drug Administration has examined the economic consequences of this proposed rulemaking for purposes of Executive Order 12291 and the Regulatory Flexibility Act of 1980. Of U.S. production of hydrochloric acid (HCl) amounting to about 2.8 million tons per year, non-byproduct acid accounts for a rising share believed to be in excess of 10 percent recently. Food use represents a similar 10 percent share but its distribution between byproduct and non-byproduct acid is not known. Because uses of the two types of product are strongly influenced by relative regional availabilities, it is possible that a significant proportion of food use by now may be byproduct. The agency believes that non-byproduct and byproduct HCl currently are competitively priced within a range of about $60-100 per short ton depending

6. Ibid.

on location. Conceivably, the proposed restriction of food uses to non-byproduct HCl could produce price premiums for this substance in some areas depending on local supplies and demands. Because it is unlikely that the entire food use of HCl would acquire such price premiums, the magnitude of potential impact, if any, may be illustrated with the assumption that half the food use (say 150,000 tons) becomes subject to a price increment averaging half the maximum range of current prices ($20 per ton). On the basis of this example, the cost impact on food manufacturers would be $3 million per year, affecting mainly large scale producers. The agency concludes that the proposed rule does not require a regulatory impact analysis under Executive Order 12291 and further certifies that it would not have a significant economic impact on a substantive number of small entities and hence does not require a regulatory flexibility analysis.

REVISED 2/21/84 DRAFT

RCVD 8/81

Hydrochloric Acid

HCl Mol wt 36.46

DESCRIPTION

A water solution of hydrogen chloride of varying concentrations. It is a clear, colorless or slightly yellowish, corrosive liquid having a pungent odor. It is miscible with water and with alcohol. Concentrations of hydrochloric acid commercially available are usually expressed in Baume degrees (Be°) from which percentages of HCl and specific gravities can readily be derived. (See Hydrochloric Acid Table, page 514). The usually available concentrations are 18°, 20°, 22°, and 23° Be. Concentrations above 8.5° Be (12.5%) fume in moist air, lose hydrogen chloride, and create a corrosive atmosphere. Because of these characteristics, suitable precautions must be observed during sampling and analysis to prevent losses.

Note: Hydrochloric acid is produced, for example, by the salt cake process, the burner process, and as a by-product during the manufacture of a variety of organic compounds. Trace amounts of organic compounds might be present as impurities in hydrochloric acid from any source. The

manufacturer, vendor, or user is responsible for identifying the specific organic compounds which are present and for meeting the Requirements for Extractable Organic Compounds. Methods are given below for their determination. In applying the procedures such standards as are necessary should be utilized to quantitate the organic compounds present in each specific product.

The variety of organic impurities that might conceivably be found in hydrochloric acid is such that it is impossible to provide a comprehensive and accurate list here. Therefore, the manufacturer, vendor, or user is responsible for establishing the suitability of such hydrochloric acid for its intended application in foods or food processing in accordance with the provision on Trace Impurities, page 3.

REQUIREMENTS

Identification

It gives positive tests for Chloride, page 516.

Assay Not less than the minimum or within the range of Baume degrees claimed or implied by the vendor.

Arsenic (as As) Not more than 1 mg/kg.

Color Passes test.

Concentration of HCl Not less than the minimum or within the range specified or implied by the vendor.

Extractable Organic Compounds

Total Organic Compounds (Non-Fluorine Containing)

Not more than 5 mg/kg, including:

Benzene Not more than 0.05 mg/kg.

Vinyl Chloride Not more than 0.05 mg/kg.

Fluorinated Organic Compounds (total) Not more than 25 mg/kg.

Heavy Metals (as Pb) Not more than 5 mg/kg.

Iron Not more than 5 mg/kg.

Nonvolatile Residue Not more than 0.5%

Oxidizing Substances (as Cl_2) Not more than 30 mg/kg.

Reducing Substances (as SO_3) Not more than 70 mg/kg.

Specific Gravity Not less than the minimum or within the range specified or implied by the vendor.

Sulfate Not more than 0.5%.

TESTS

Extractable Organic Compounds Analyses are to be carried out by gas-liquid chromatography employing Vapor Partitioning or Solvent Extraction, depending upon the characteristics of the compound being determined. It is necessary, however, to use the Vapor Partitioning method for benzene and vinyl chloride, in order to determine them at the levels specified above.

Vapor Partitioning Method This method is suitable for the determination of extractable organic compounds in the range of 0.05 mg/kg to 100 mg/kg, but is most appropriate for those organic compounds having a vapor pressure greater than 10 mm Hg at 25°.

Use a gas chromatograph equipped with a flame ionization detector and a 4-m x 3-mm (id) by stainless steel column packed with 15% by weight of methyl trifluoropropyl silicone (DCFS 1265, QF 10, OV 210) stationary phase on 80/100 mesh Gas Chrom R. A newly packed column should be conditioned at 120° and 30 ml/min helium flow for at least two h (preferably overnight) before attaching it to the detector. For analysis the column is maintained

isothermally at 105°; the injection port and detector are maintained at 250°; the carrier gas flow rate is set at 11 ml/min; fuel gas flows should be optimized for the gas chromatograph and detector in use. The experimental conditions may be changed as necessary for optimum resolution and sensitivity. The minimum signal to noise ratio should be 10:1.

Preparation of Standards Prepare a standard solution of the organic compounds to be quantitated in hydrochloric acid (known to be free of interfering impurities) at levels of about 5 mg/kg, or within an order of magnitude of the levels in the samples to be analyzed.

Place a stirring bar in a 1 L volumetric flask equipped with a ground glass stopper and tare the combination. Fill the flask with reagent grade HCl so that no air space is present when the flask is stoppered and determine the weight of the HCl. Calculate the volume of each organic component to be added from the formula:

$$V = \frac{C \times W}{D \times 1000}$$

where V is the volume in microliters, C is the desired concentration in mg/kg, W is weight of the HCl, and D is density of the organic compound. Add the calculated amount of each component to the HCl by means of a syringe; stopper the flask and stir the solution for at least two h using a magnetic stirrer.

Calibration Treat the standard in the same way as a sample as described under Procedure (below). Determine a blank for each lot of reagent grade hydrochloric acid. To determine response factors divide the concentration (C) of each component in mg/kg in the standard by the area for that component.

$$R = \frac{C}{A - \text{Area of Blank}}$$

where R is the response factor and A is the area for the component.

Gaseous compounds present special problems in the preparation of standards. Therefore, to determine response factors for gaseous compounds use the method of multiple extractions, as follows:

> Dilute a sample of hydrochloric acid known to contain the gaseous compound of interest with an equal volume of water. Draw 20 ml of this solution into a 50 ml glass syringe, then draw 20 ml of air into the syringe, cap with a rubber septum, and place the syringe on a shaker for five min. Withdraw 1 ml of the vapor through the septum and inject it into the chromatograph. Expel the vapor phase from the 50 ml syringe, draw in another 20 ml of air, repeat the extraction, and inject another one ml vapor sample into the chromatograph. Repeat the

extraction and GLC analysis on the same sample of acid a total of six times. For each impurity plot the area (A_n) determined for extraction n versus the difference between An and the area determined for extraction (n + 1); that is, A_n versus [A_n - A_{n+1}]: the slope of this line is the extraction efficiency (E) for that impurity into the air.

Inject into the chromatograph one ml of a 0.1% (by volume) standard gas sample of each impurity in air and determine the absolute factor F_a in grams per area (A) by the following formula:

$$F_a = \frac{4.0816 \times 10^{-8} \times M}{A}$$

where M is the molecular weight of the compound.

Then the concentration (C) in mg/kg of the component in the original sample is calculated by the formula:

$$C = \frac{A \times F_a \times 1.6949 \times 10^6}{E}$$

Where A is the area corresponding to the compound (as above), F_a is the absolute factor, and E is extraction efficiency. This formula assumes a 10 ml sample size as in the Procedure below (20 ml of 1:1 dilution of HCl).

The response factor is then calculated as:

$$R = C/A$$

Procedure Dilute a 10 ml sample of hydrochloric acid to be analyzed with an equal volume of water. Draw this solution into a 50 ml glass syringe. Then draw 20 ml of air or nitrogen into the syringe, cap with a rubber septum, and place the syringe on a shaker for five min. Draw 1 ml of the vapor through the septum and inject it into the gas chromatograph. Approximate elution times for some specific organic compounds are as follows:

Methane and acetylene	1.70 min.
Methyl chloride	2.21
Vinyl chloride	2.29
1,1,1-Trichlorofluoromethane	2.62
Ethyl chloride	2.90
Vinylidene chloride	3.20
Methylene chloride	3.64
Chloroform	4.49
1,1-Dichloroethane	4.53
Carbon tetrachloride	4.86
1,1,1-Trichloroethane	5.50
Benzene	6.00
Trichloroethylene	6.22
Ethylene dichloride	6.61
Propylene dichloride	8.41
Perchloroethylene	9.73

Other columns may be required to resolve certain combinations of components. Methyl chloride and vinyl chloride are resolved by a 3.7-M Squalane column at 45° and 10 ml/min helium flow. Chloroform and 1,1-dichloroethane are resolved by a 4-m x 3-mm (id) DC 550R column at 110° and a helium flow of 12 ml/min.

Calculation Calculate the concentration (C) in mg/kg of each compound by multiplying the corresponding area found by the appropriate response factor (R) determined in the Calibration protocol.

$$C = R \times A$$

Precision The relative standard deviation at 5 mg/kg should be no greater than 15% for five analyses.

Solvent Extraction Method The solvent extraction technique is suitable for the determination of extractable organic compounds in the range of 0.3 to 100 mg/kg, but is most appropriate for those organic compounds having vapor pressures less than 10 mm Hg at 25°.

The conditions for the gas chromatograph are the same as for the Vapor Partitioning method except that the column temperature is 120° and the carrier gas flow is 21 ml/min.

Preparation of Standards Prepare the standard solution as described under Vapor Partitioning.

Calibration Extract a sample of the standard solution as directed under Procedure (below) and inject it into the chromatograph. Determine a blank for each lot of reagent grade hydrochloric acid and perchloroethylene by extracting the HCl in the same way as the standard. Determine a response factor R by dividing the concentration (C) in mg/kg for each component by the area (A) for that component.

$$R = \frac{C}{A - \text{Area of Blank}}$$

Procedure Accurately transfer 90 ml of the hydrochloric acid sample and 10 ml of perchloroethylene (free from interfering impurities) into a narrow-mouth, four-ounce bottle. Place the bottle in a mechanical shaker for 30 min. Separate the two phases (perchloroethylene on the bottom) and inject 3 microliters of the perchloroethylene extract into the gas chromatograph. Approximate elution times for a number of chlorinated organic compounds are as follows:

Vinylidene chloride	2.94 min.
Methylene chloride	3.27
Chloroform	3.83
Carbon tetrachloride	4.07
1,1,1-Trichloroethane	4.50
Trichloroethylene	4.97
Ethylene dichloride	5.26
Propylene dichloride	6.36

Perchloroethylene	6.95
1,1,1,2-Tetrachloroethane	10.12
1,1,2,2-Tetrachloroethane	13.70
Pentachloroethane	16.19

In order to determine perchloroethylene and higher boiling impurities, substitute methylene chloride (free from interfering impurities) for perchloroethylene in the extraction step. For higher boiling impurities such as monochlorobenzene and the three dichlorobenzenes use a 2.74 m x 2.1 mm (id) stainless steel column packed with 10% carbowax 20M/2% KOH on 80/100 chromasorb W (acid washed) at 150° and a nitrogen flow of 35 ml per min.

Calculation Calculate the concentration (C) in mg/kg of each compound by multiplying the corresponding area (A) found by the appropriate response factor (R) determined in the calibration protocol step.

$$C = R\ (A - \text{Area of Blank})$$

Precision The relative standard deviation at 5 mg/kg should not exceed 15% for five analyses.