Food and Agriculture Organization of the United Nations

87th JECFA - Chemical and Technical Assessment (CTA), 2019

METATARTARIC ACID

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1. Summary

This Chemical and Technical Assessment (CTA) summarises data and information on metatartaric acid (MTA) submitted to the 84th and 87th meetings of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) upon request by the 48th and 50th session of Codex Committee on Food Additives (CCFA, 2016, 2018). At the 84th meeting, JECFA was asked to evaluate all data necessary for the assessment of safety, dietary intake and specifications related to the use of MTA as a stabilizer in wine, to prevent growth and precipitation of potassium bitartrate and calcium tartrate crystals. At the 87th meeting, JECFA was asked to evaluate all data necessary for the characterization of the product and for the removal of the tentative status of the specifications. Metatartaric acid is approved for use in red and white wines in the European Union, Argentina, Australia, Brazil, Chile, New Zealand, Norway, Paraguay, Uruguay, Russia, South Africa, and Turkey. This document discusses published information relevant to metatartaric acid, the production methodology, and the specifications.

New specifications were prepared for metatartaric acid at the 84th JECFA and made tentative requiring information on the characterization of the product (content of free tartaric acid, degree of esterification and molecular weight distribution), IR spectrum and data on above parameters. The Committee at its 87th meeting received the requested information, and the specifications were revised and the tentative status was removed.

2. Description

Metatartaric acid (CAS No. 56959-20-7/ 39469-81-3) is a polydisperse polymer mixture. It consists of a polymerized compound formed by the intermolecular esterification between the carboxylic group of one L-tartaric acid unit and the secondary alcohol group of another molecule of L-tartaric acid (Ribéreau-Gayon et al. 2006; Sprenger et al. 2015). The primary components of MTA are the di- tartrate monoester and diester, L-tartaric acid monomer, and polyester chains of varying degrees of polymerization.

3. Methods of Manufacture

Metatartaric acid is produced by heating L-tartaric acid, from naturally occurring sources such as grapes, at 150-170 ºC at atmospheric or reduced pressure for up to one hour. This produces a colourless liquid which is cooled, dried and ground into an off-white powder. Variations in production temperature, pressure, and time will allow manufacturers to control the degree of esterification in the final product.

4. Chemical Characterization

4.1 Composition

Metatartaric acid is a polydisperse polyester of L-tartaric acid. Primary components include the monoester and diester of di-tartaric acid, the monomeric L-tartaric acid, and polyester chains of varying degrees of

esterification and polymerization. The exact composition of the final polymeric material has not been well characterized. The structural formulas of selected metatartaric acid components are found in Figure 1.

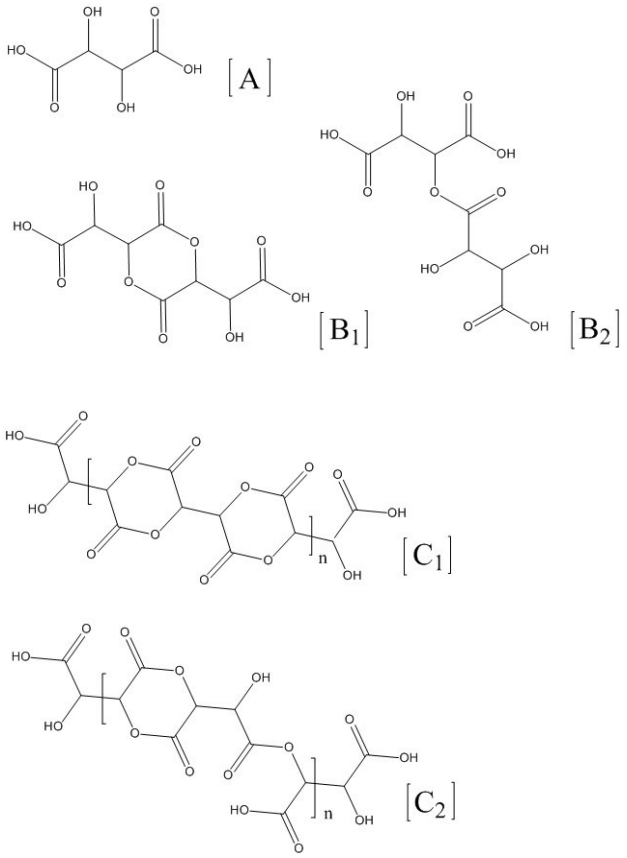

Figure 1. Structural formula of metatartaric acid components. [A] L-tartaric acid, [B1] di-tartaric monoester, [B2] ditartaric diester, [C1] polymer with diester ring, [C2] polymer with monoester ring. The final product has a degree of esterification of above 32% and upon hydrolysis must contain not less than 105% total tartaric acid.

The reported range of the molecular weight of MTA in the products of commerce is wide (Table 1 & Table 2). The weight average molecular weight (Mw) is in the range of 1.2–8.9 kDa, the low molecular weight (Mn) is in the range of 0.25-3.52 kDa and the high molecular weight (Mz) is in the range of 3.4-40.9 kDa with the polydispersity index (PDI, Mz/Mn) ranged from 1 to 50. The optical rotation of an aqueous solution of metatartaric acid (5 g/100 ml) ranged from -34 to -41º.

Table 1. Summary of analytical results for molecular weight for five commercial batches of metatartaric acid (AWRI, 2018)

Sample	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz/Mn
A	3521 (+/-6%)	5707 (+/-7%)	8380 (+/-16%)	2
B	603 (+/-1%)	4147 (+/-1%)	17800 (+/-1%)	30
C	2915 (+/-5%)	3207(+/-4%)	3.489 (+/-8%)	1
D	246 (+/-13%)	1248 (+/-7%)	3674 (+/-15%)	15
E	803 (+/-3%)	2317 (+/-1%)	5024 (+/-2%)	6

Table 2. Molecular mass (in Daltons) of MTA samples determined by size-exclusion chromatography combined with UV, refractive index and multiangle light scattering detection (Sprenger, S., 2015). Molecular masses presented below represent: M_N - low, M_W - medium, M_Z - high. M_Z/M_N is the polydispersity index.

Sample	M_N	M_W	M_Z	M_Z/M_N
A	451 ± 20	3124 ± 754	8532 ± 2938	19
B	466 ± 355	2378 ± 245	6277 ± 352	34
C	588 ± 42	5854 ± 98	22025 ± 935	37
D	430 ± 232	2838 ± 134	9097 ± 266	30
E	851 ± 137	8873 ± 251	40883 ± 3123	50
F	746 ± 258	4446 ± 601	14610 ± 1870	21
G	445 ± 90	2233 ± 174	5889 ± 301	14

The solid-state transmission spectrum of metatartaric acid (Figure 2), is obtained by using a FT-IR spectrophotometer, by putting 20 grams of sample directly in the spectrophotometer at a wavelength from 500 to 4000 cm^{-1}.

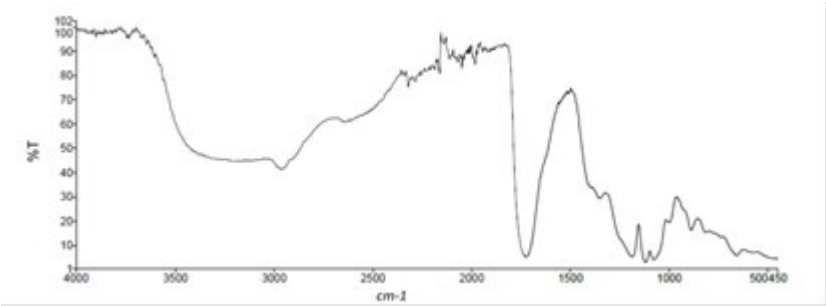

Figure 2. FTIR spectrum of metatartaric acid.

4.2. Possible impurities (including degradation products)

Possible impurities of metatartaric acid include (i) any inorganic impurities and heavy metals, and (ii) unreacted L-tartaric acid. Analytical data of products in commerce indicated that loss on drying ranged from 0.73-1.62% and loss on ignition was almost 100%. Metallic impurities met the following limits: lead <2 mg/kg, arsenic <2mg/kg, cadmium <0.13 mg/kg and mercury <0.1 mg/kg. L-tartaric was above 73 %.

4.3. Analytical methods

The proposed assay for the determination of metatartaric acid is based on hydrolysis of metatartaric acid components using sodium hydroxide to form tartaric acid. This allows the calculation of the degree of esterification. Addition of an excess of sodium hydroxide solution followed by back titration with sulfuric acid using bromothymol blue indicator allows the calculation of the total free and esterified acid present in the original sample. (OIV, 31/2000)

5. Functional uses and reactions and fate in food

5.1. Technological function

Metatartaric acid is intended for use as stabilizer and is used to prevent the growth and precipitation of potassium bitartrate and calcium tartrate crystals in wine.

Metatartaric acid hydrolyses to tartaric acid in solution over time with the rate dependent on both pH and

temperature. In wine, complete hydrolysis has been reported to be as short as a few minutes at 45º and as long as several years at 10º (Table 3) (Peynaud and Guimberteau, 1961).

The sensitivity of metatartaric acid to high temperatures is the main limit for its use in enology. This is the reason for its use only for ready-to-drink wines that are stored for few months in bottle. When MTA was used in white wine at different pH values (3.0, 3.2, 3.5, 3.7, 3.9) and temperatures (12ºC, 20ºC and 35ºC, during a ten-week storage study, showing that the highest instability was found for the highest pH (3.9), thus the lowest inhibition of tartrates precipitation. A high linear correlation was also found between temperature and tartaric acid stability that decreased at higher temperatures (35ºC) (Morello, A., 2012)

Table 3. Reported Stability / Hydrolysis of metatartaric acid in wine

Temperature, °C	Observation
<0 – 0	Stable for several years
10 – 12	At least 2 years
10 – 16	At least 18 months
12 – 18	At least one year
20	Stable for three months
25	Stable for one month
30	Complete hydrolysis in one week
35 – 40	Complete hydrolysis in few hours
45 – 50	Complete hydrolysis in few minutes

6. Food categories and use levels

Metatartaric acid is an approved EU food additive (E353) as an acidity regulator. It is also an approved EU winemaking additive in accordance with Regulation (EU) 1129/2011. Use levels are at or below 100 mg/L.

Metatartaric acid has also been for use as an additive in wine making in the following countries: Argentina, Australia, Brazil, Chile, New Zealand, Norway, Paraguay, Uruguay, Russia, South Africa, and Turkey.

7. References

Report of the 48th meeting of the Codex Committee on Food Additives (CCFA48, REP16,_FA) http://www.fao.org/fao-who-codexalimentarius/sh-proxy/en/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252FMeetings%252FCX-711-48%252FReport%252FREP16_FAe.pdf ,2016

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