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A COMPREHENSIVE REVIEW ANALYSIS ON ORGANIC ACIDS IN FRUIT JUICES BY USING VARIOUS ANALYTICAL METHODS

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ABSTRACT

In this article discuss on varied extraction and analytical strategies used for quantifying organic acids gift in fruit juices. Recent times food commodities emerges varied new technology to developed food merchandise by adding food additives to increasing their period and different organoleptic properties. At constant time, it needs the determination of safety and quality aspects. Organic acid analysis is crucial once assessing the legitimacy of fruit juices. By utilising varied extraction ways are often wont to analyze samples. associate degree analytical methodology plays a serious role to work out or quantifying the presence of organic acids in fruit juices. In analytical strategies preponderantly natural action techniques, combined techniques and action techniques. By mistreatment these analytical techniques at the same time we will simply verify completely different organic acids in fruit juices.

Keywords: Analytical methods; Organic acids; chromatographic; Hyphenated and electrophoretic.

INTRODUCTION

Fruit juice is taken into account to be one in every of the healthiest foods in human diet, because of their well-known according health edges (source of natural vitamins and antioxidants, anti-inflammatory properties, bar of chronic diseases, etc.). during this sense, business ready juices claim to preserve these nutritionary and healthy effects. For these reasons, fruit juices demand higher costs compared to different styles of liquid refreshments and that they are often targets of adulteration. Dilution with water, addition of sugars or different additions, or mixing with cheaper drinks area unit the foremost rife types of adulteration within the fruit juice business. because of inherent selection in cultivars, storage conditions, and process procedures, sleuthing and preventing adulteration may be a troublesome operation. thanks to the range of adulteration techniques, a spread of analytical ways supported the identification and quantification of a spread of compounds (carbohydrates, phenolic resin compounds, amino acids, inorganic anions, etc.) are planned, with organic acid measure forever taken into consideration. Thus, organic acids in fruit juices displayed numerous profiles, that seemingly influence the organoleptic (e.g., flavours, freshness, or spoilage) and chemical (e.g., pH, total acidity) characteristics of the juice, giving in addition relevant Fingerprints for legitimacy functions[1].

Organic acids area unit chemicals found naturally in fruits and vegetables. as a result of organic acids have such an outsized impact on the organoleptic qualities and stability of fruit juices, the character and concentration of organic acids in fruits area unit of nice interest. The profile and concentration of organic acids in fruits and vegetables area unit influenced by factors like species, soil, and therefore the stress conditions to that the fruit was exposed. they are additionally wide used within the production of beverages, fruit and vegetable drinks, and juices as food additives. Organic acids area unit gift naturally in fruits and vegetables, and that they will be created through methods like fermentation or accessorial to food throughout the assembly

process. Water or solvent extraction, vapour distillation, or precipitation with lead or different components will all be accustomed take away organic acids from food. Solvent extraction is that the preferred technique for extracting organic acids found in fruits and vegetables presently. the amount and kinds of organic acids contained in numerous fruits area unit tormented by their maturation stage and geographical origin. For food and drink technology and quality assessment, the identification and chemical analysis of key organic acids in fruits is crucial. Organic acids area unit a useful indicator of fruit believability as a result of they're less prone to amendment throughout process and storage than different fruit parts. as a result of every fruit features a completely different pattern of organic acids, correct understanding of organic acid levels (and ratios) could also be valuable for activity the share juice also as detective work misbranding and/or adulteration in fruit juices. owing to its impact on sensory qualities, the organic acid composition of fruits is additionally of importance.[2,3]

Organic acid identification and detection in fruit juices is important for quality and method management. Organic acid concentrations in fruits area unit essential as a result of they need an effect on the organoleptic qualities of fruit juices, significantly in terms of flavour, colour, and scent. Organic acid level in fruit juices affects not solely the organoleptic aspects of the liquids, however conjointly their stability, nutrition, satisfactoriness, and quality. Natural and industrial fruit juices have varied levels of organic acids, additions, and preservatives. many natural action ways are developed for distinguishing and quantifying severally organic acids in several matrixes[4].

It is important to work out the presence of organic acids in foods. In reality, their presence and relative quantitative relation would possibly alter the chemical and sensory options of the matrix (e.g., pH, total acidity, microbic stability, sweetness, international acceptability) and supply valuable data on food quality or the way to improve sure technical processes[5].

Importance of organic acids in fruit juices[6-15]

Organic acids plays vital roles in juices owing to their influence on the organoleptic properties (flavour, color & aroma) additionally because the stability & microbiological management of the products.

Acetic acid
It is employed as Anti-microbial activity, Acidulant and Flavouring agent.

Ascorbic acid
It shows inhibitor impact for preventing injury from free radicals and alternative reacting oxygen species. It is employed as Preservative, Acidulants & Stabilizer.

Benzoic acid
It is employed as Antibacterial activity and Preservative in beverages.

Citric acid
It is employed as flavourer, Preservative, Stabilizer, opposing oxidiser and conjointly hydrogen ion concentration regulator. And also firming agents & sequestrants.

Formic acid
It is employed as Antimicrobial activity and hydrogen ion concentration regulator agent.

Fumaric acid
It is utilized as Microbiological activity, Acidulant and conjointly pH stabilizer. It can even used as pH management agents, firming agents, flavour enhancers, emulsifiers, synergists & preservatives.

Galacturonic acid
It is employed as acidifying agent.

Iso citric acid
It is utilized as Acidulant In pharmaceutical trade used as raw materials for synthesis of chemicals.

Lactic acid
It is utilized as natural action, Flavour sweetening & microorganism inhibitors in foods. it's a probiotic

L-ascorbic acid
It is employed as preservative & Antioxidant.

Malic acid
It is employed as acidulant, a buffering agent, anti oxidant, flavouring, a chelating agent & stabilizer. It inhibits the growth of yeast and some bacteria.

Malonic acid
It is utilized as fixings agent and cross linking agent. It controls the acidity.

Oxalic acid
It inhibits bowing of fresh apple juice.

Pyro glutamic acid
It is utilized as cope with brain operate thanks to its role in supporting the healthy production of neurotransmitters. and sometimes wont to support memory and learning additionally to managing anxiety.

Quinic acid
It is used as Anti oxidant agent.

Shikimic acid
It is used as flavonoids.

Succinic acid
It is employed as Bio stimulant and anticoagulant medication. conjointly used as enhancers, pH control agents, preservatives, flavour and in baking.

Tartaric acid
It is employed as Flavour sweetening, Preservative, Chelating and conjointly pH regulator. Similarly, as humectants, firming agents, baking additives & emulsifiers.

These are the organic acids present in fruits
Table-1: organic acids present in fruits
The goal of this review is to enhance and validate a fast technique for deciding the first organic acids in natural or commercial juices of varied fruits. The circumstances of various extraction methods which will be wont to analyse materials and analytical ways, particularly activity, hyphenated, and electrophoretic procedures, are compiled in a very table during this review. Various knowledge bases were used for this review, together with MEDLINE, Google, Scopus, Pubmed and article searches were performed with none year limit. This paper provides a scientific review of various literature sources.

MATERIALS AND METHODS

Different extraction methods for the analysis of organic acid[6,16-19]
Table-2: Different extraction methods for the analysis of organic acid

Various Analytical Techniques Were Tabled Below
HPLC: High performance liquid chromatography; UV: Ultraviolet; DAD: Diode array detector; M.P: Mobile phase; r2: regression coefficient; LOD: limit of detection; LOQ: limit of quantification
Table-3: Various Analytical techniques

CONCLUSION

In this literature we tend to closing that the sample extraction method was terribly easy, reliable and economical by using solid phase extraction. This approach will be used to confirm the organic acids in fruits. they will be detected at terribly low quantities, demonstrating their sensitivity. Organic acid extraction may be a easy and fast methodology. This approach may be accustomed confirm alternative organic acids. SPE, LLE, UAE, MAE, ALE, SFE, and ESE are samples of new techniques that cover a large vary of analytes and sample matrices and supply important enhancements over previous procedures. as compared to LLE, SPE yields higher recoveries and a purer analyte. LLE is long and regularly necessitates the employment of unsafe organic solvents. In any case, in comparison to alternative approaches activity separation procedures are terribly effective and fast.

Table 1: organic acids present in fruits

Organic acids	Fruits and Fruit juices
Acetic	Grape and Orange
Ascorbic	Apple, Cranberry, Guava, Grape, Lemon, Lime, Orange, Pomelo and Tangerine
Benzoic	Cranberry, Orange and Plums
Citric	Apple, Cranberry, Clementine, Grape, Lemon, Lime, Minneola, Mandarin, Orange, Pomelo, Pineapple, Pomegranate, Raspberry, Sweetie and Tangerine
Formic	Apple, raspberries and strawberries
Fumaric	Apple, Cranberry, Grape and Orange
Galacturonic	Apple
Iso-citric	Apple, Grape, Mandarin, Orange and Pineapple
Lactic	Cashew apple, Orange and Pomegranate
L-ascorbic	Cranberry
Malonic	Apple, Berries and Grapes
Malic	Apple, Cranberry, Grape, Lemon, Mandarin, Orange, Pineapple, Peach, Pear and Raspberry
Oxalic	Apple, Cranberry, Grape, Orange, and Raspberry
Pyro glutamic	Some of citrus fruits
Quinic	Apple, Cranberry, Peach, Pear and Plums
Shikimic	Apple, Cranberry, Grape and Orange
Succinic	Grape and Peach
Tartaric	Apple, Cranberry, Grape, Lemon, Orange, Raspberry and Tangerine

Table 2: Different extraction methods for the analysis of organic acid[6,16-19]

Various sample preparation for analysis	Procedure
Solid-Liquid	20 gms of fruit sample ↓ Mashed well in mortar ↓ Add 10 ml of Water**:** Methanol (75:25v/v) ↓ Centrifuged at 25^{o}C, 3500 rpm/min for 30 min ↓ Filtration ↓ Centrifugation was repeated 3 times & filtrates were collected ↓ Combine filtrates were again through supelco discovery DSC-18 filter ↓ Ready to injection
Liquid-liquid	Sample + Alkaline solution ↓ If required then adjust pH ↓ Sample extraction were by two immiscible solvents/extraction solvent(non-polarity) ↓ Collect the supernatant liquid and evaporate it with nitrogen gas until it is completely dry. ↓ Dissolve the residue in suitable solvents ↓ Filtration ↓ Ready to inject
Ultrasound-assisted extraction	Fruit sample ↓ Drying ↓ Grinding & Seiving(Particle size:250-500 µmol/L) Solvent:Ethyl acetate Solvent/sample ratio(80:1ml/g) Power: 150W, 200W,250W

	↓ Filtering ↓ Analysing(Total carotenoid and Antioxidant capacity)
Microwave- assisted extraction(MAE)	Fruit sample ↓ 19.355-19.718 g of solvent system(0%, 40% &80%)various concentrations of ethanol ↓ Stirring the mixture for 5 mins ↓ MAE input variables(Power, Temperature, Liquid-Solid ratio & Ethanol concentration) ↓ Centrifugation at 4000 rpm for 20 mins ↓ Residue & Supernatant: MAE extract ↓ Aqueous extract were stored in refrigerator at 4^{o}C ↓ Obtaining & Quantifying the extract did not exceed 24 hrs
Accelerated liquid extraction	Fruit sample ↓ Pre-treatment(Physical, Chemical & Biological) ↓ Phytochemical extraction (Solvent extraction, Soxhlet extraction, Centrifugation, Hydro distillation, Cold pressing & Hand pressing) ↓ Separation, Isolation & Purification ↓ Identification & Determination of compounds ↓ Structure elucidation & Data analysis

Supercritical fluid extraction	Fruit sample ↓ Pre-treatment (physical, chemical & biological) ↓ Supercritical fluid extraction ↓ Saponification ↓ Separation ↓ Analysis (spectroscopic & chromatographic)
Enzyme assisted extraction	Fruit sample ↓ Mix dried power in Water/Buffer ↓ Enzyme hydrolysis ↓ Centrifugation(discard precipitation) ↓ Filtration ↓ Purification ↓ Juice ↓ Spray drying(Natural compounds-power) Pasteurization(Natural compounds-liquid) Concentration(Natural compounds-concentrate)

Table 3: Various Analytical techniques

Analytical techniques	Methods	Determination of acids	Applications	parameters	References
Chromatography:					
HPLC	**Column:** PerkinElmer Brownlee Validated Aqueous C18, 5 µm, 4.6 x 250-mm **M.P:** Isocratic; 25-mM K-phosphate buffer; pH 2.4 **Detector:** UV, λ= 210 nm **Run Time:** 8.0 min.; wash/equilibration time = 6.0 min **Flow Rate:** 1.5 mL/min. (~3000 psi; 200 bar) **Oven Temp.:** 30 ºC **Injection Volume:** 20 µL	Oxalic Tartaric Malic Shikimic Citric Succinic Fumaric	Grape juice	Robust Repeatability linearity	20
		Oxalic Malic Ascorbic Shikimic Citric Fumaric	Orange juice		
		Malic Ascorbic Shikimic Citric Fumaric	Apple juice		
		Quinic Malic Ascorbic Shikimic Citric	Cranberry juice		
UPLC	**Reversed phase UPLC method** **Column:** Hypersil Gold a Q Analytical, RP chromatography on a 150 mm x 4.6 mm i.d.,5µm particle ZORBAX Eclipse XDB-C18 **M.P:** potassium dihydrogen orthophosphate buffer (pH 3.1) **Detector:** DAD, λ=254 & 214 nm **Run time:** **Flow Rate:** 1.2 mL/min **Oven Temp.:** +4 ºC **Injection Volume:** 5 µL	Oxalic Tartaric Malic Lactic Citric Ascorbic	Sweet orange Red apple White apple Lime Lemon Grape fruit (pink & white)	Linearity LOD LOQ Precision	3
HPLC/DAD	**Reversed phase HPLC method** **Column:** Inertsil ODS-4 C18 column (250 x 4.0 mm, 5µm). **M.P:** 10 mM KH2PO4 aqueous solution adjusted to pH 2.2 **Detector:** UV, λ=210 and 245 nm **Run time**: 10 mins **flow rate:** 1 mL/min-1 within 10 min **Injection Volume:** 20 µL	Oxalic Tartaric Malic Ascorbic Lactic Acetic Citric Fumaric	Orange	Linearity LOD LOQ Precision Accuracy	4
HPLC/Post-column method	**Column:** 5cm x 8.0 mm i.d. Shorex RS pack KC-LG guard column **M.P:** 3 mm perchloric acid solution **Detector:** UV, λ=440 nm **Run time:** 30 mins **Temp:** 80ºC **flow rate:** 0.7 mL/min	Citric Tartaric Malic Succinic Lactic Formic Acetic Pyroglutamic	Orange Mandarin Grape Mango Tomato Apple Pear Mulberry Blueberry	LOD LOQ	21
HPLC	**Reversed phase HPLC method** **Column:** Hypersil Gold a Q Analytical **M.P:** potassium dihydrogen orthophosphate buffer (pH 2.8) **Detector:** DAD, λ=214 & 254 nm **Run time:** 20 mins **flow rate:** 0.7 ml/min **Injection Volume:** 5 µL	Oxalic Tartaric Malic Lactic Citric Ascorbic	Citrus fruits ⬇ Sweet orange Minneola Clementine Mandarinorange Pomelo Lemon Lime Sweetie grapefruit	LOD LOQ Linearity Precision	22
Ion exclusion liquid chromatography	**Column:** resin based Aminex HPX 87H (300 7.8mm i.d.) at 25 ºC **M.P:** diluted 1:10 (v/v) with the M.P, were filtered through a 0.22mm cellulose acetate **Detector:** (UV 970), λ=210nm **Run time:** 20 mins **Injection Volume:** 20 µL	Citric Galacturonic Malic Quinic Succinic Fumaric	Apple Peach Pear Apricot	Precision Linearity LOD LOQ	5

HPLC	**Method validation and characterization** **Column:** PL Hi-Plex H (5×3mm) guard **M.P**: 4.0mML−1H2SO4 in ultrapure water **Detector**: DAD, λ=210nm **Run time:** 20min **Oven Temp**: 70°C **flow rate**: 0.5mL/min	Tartaric Malic Citric Acetic Lactic	Grape	Linearity Accuracy LOD LOQ Precision Recovery	23
HPLC	**Column**: Shim-Pack VP-ODS (25034.6 mm I.D.) guard (GVP-ODS, 1034.6 mm I.D.) **M.P**: sulphuric acid solution, 0.35 ml/min of pH 2.5 **Detector**: DAD,UV spectra, λ=200–600 nm **Run time:** 75 mins **Injection volume**: 20 ml **Oven Temp**: 40 ºC **Flow rate:** 0.35 ml/min	Tartaric Quinic Oxalic Malic L-Ascorbic Malonic Lactic Acetic Citric Fumaric	Apple juice Also include- raspberry, cranberry, grape	Precision Accuracy LOD	24
HPLC	**Column**; AMINEX HPX-87H **M.P**: single solution of H2So4 0.008 mol.L-1 in isocratic **Detector**: DAD **Run time**: 20 mins **Temp**: 45 °C **Flow rate**: 0.6 mL/min	Citric Tartaric Malic Ascorbic	Orange Grape Apple Tangerine	LOD LOQ Precision	25
HPLC	**Column:** 2 RP- C18 columns in series **M.P:** 100mM phosphate buffer, pH 2.5 **Detector:** UV @ 226nm **Run time:** 40 mins **Flow rate:** 0.5mL/min **Temp:** ambient **Injection volume**: 10µL	Tartaric	Grape juice	Retention Selectivity	26
		Quinic Malic Citric Fumaric	cranberry juice		
Ion chromatography	**Gradient** **Column:** Dionex Corp: Om- niPac Pax-500 Guard Column 50 × 4 mm I.D., **M.P: A**-0.60 mM NaOH in water-ethanol-methanol (66.5:20:13.5, v/v); **B**- 20 mM NaOH in water-ethanol (65:35, v/v); **C**-60 mM NaOH in water-ethanol (65:35, v/v) **Detector**: UV **Run time:** 30 mins **Flow rate :** 2 ml/min **Injection volume**: 20µL	Malic Ascorbic Citric Iso citric	orange juice	Reproducibility LOD	27
		Galacturonic Malic Ascorbic Citric	Apple		
		Malic Tartaric Ascorbic Citric	Grape		
HPLC	**Column:** RP-C18 column (3 µm particle size, 150 4.6 mm I.D., kept at 25 ºC) **M.P:** 0.01 mol L1 KH2 PO4 buffer solution (pH = 2.60 adjusted with o-phosphoric acid) **Detector:** UV–Visible diode array detector (DAD), λ=210 nm,250nm **Run time:** 90 mins **Flow rate:** 0.5 mL/min **Injection volume:** 20 µL	Malic Ascorbic Citric	Apple	Linearity Reproducibility Repeatability LOD LOQ	2
		Tartaric Malic Ascorbic Citric	Orange		
		Tartaric Malic Ascorbic Citric	Lemon		
RP LC	**Column:** Agilent Poroshell 120 EC-C18, 4.6 × 100 mm, 2.7µm **M.P:** 20 mM monobasic phosphate buffer (KH2PO4), pH 2.5 adjusted by o-phosphoric acid **Detector:** DAD, λ= 210, 230 & 243.5 nm **Run time:** 13 mins **Flow rate:** 1.0 mL/min **Injection volume:** 5 µL	Benzoic Citric Ascorbic	Orange	LOD LOQ Linearity range Precision Robustness Accuracy	28
UHPLC	**Column:** Agilent Poroshell 120 EC-C18, 4.6 × 100 mm, 2.7µm **M.P:** 20 mM monobasic phosphate buffer (KH2PO4), pH 2.5 adjusted by o-phosphoric acid **Detector:** DAD, λ= 210, 230 & 243.5 nm **Run time:** 5 mins **Flow rate:** 1.5 mL/min **Injection volume:** 4 µL	Benzoic Citric Ascorbic	Orange	LOD LOQ Linearity range Precision Robustness Accuracy	28

HPLC-UV Method	**Column:** Restek Allure Organic Acids 5µm, 300 x 4.6mm **M.P:** 50mM potassium phosphate, pH 2.5, 2% methanol in HPLC H2O &Acetonitrile **Detector:** Waters 2996,PAD **Run time:** 50 min **Flow rate:** 0.8 mL/min **Injection Volume:** 20µL	Citric Quinic Malic Tartaric	Apple Lemon Orange Cranberry White grape Pomegranate	Specificity LODS	29
Hyphenated Techniques:					
LC-MS	**Column:** 10X 4.6mm(5µm)guard column at 30 °C **M.P:** water containing 0.5% formic acid, delivered at 0.7 mL/min **Detector:** (RP or ion exchange) coupled to UV detection **Run time**:20 mins **Flow rate:** 0.7 mL/min **Injection volume** : 10 µL	Citric Malic Quinic Tartaric	Apple Orange Cranberry white grape Red grape pomegranate	Precision LOD LOQ	30
UPLC-MS Method	**Column:** Waters BEH C18 1.7µm, 2.1 x 100mm **M.P:** Deionized H2O ,1% Formic Acid in H2O & Acetonitrile **Detector:** Waters Xevo TQD **Run time:** 12 min **Flow rate:** 0.35 mL/min **Injection Volume:** 1µL	Citric Quinic Malic Tartaric	Apple Lemon Orange Cranberry White grape Pomegranate	Selectivity Linearity range	29
Electrophoresis:					
Capillary electrophoresis	**Capillaries:** uncoated fused-silica capillaries of 112.5 cm length (104 cm effective length) × 75 µm id (375 µm o.d.) **M.P:** 1 and 0.1 M NaOH and water at 60 °C for 10 min each. **Detector:** UV & DAD, λ= 214 and 271 nm **Run time:** 20 mins	Fumaric Malic Citric	Apple	Linearity Precision LOD LOQ	1
		Malic Tartaric Citric	Grape		
		Iso citric Malic Citric	Mandarin		
		Iso citric Malic Citric	Orange		
		Iso citric Malic Citric	Pineapple		
Capillary zone electrophoresis	**Capillaries:** 2 fused-silica capillaries: a PVA-coated 64.5 cm length (56 effective length) 50 µm id (375 lm o.d.) (Agilent). **M.P:** NaoH & NaH2Po4 **Detector:** UV, λ=200+20 nm **Run time:** 12 mins	Fumaric Iso citric Malic Tartaric Citric	Pine apple Grape Orange	Repeatability Linear range Sensitivity r 2 LOD LOQ	31

HPLC: High performance liquid chromatography; UV: Ultraviolet; DAD: Diode array detector; M.P: Mobile phase; r2: regression coefficient; LOD: limit of detection; LOQ: limit of quantification

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