

Calcium citrate malate for calcium fortification and food supplements: A narrative review from a formulation perspective

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ABSTRACT

Different calcium salts often present a trade-off between high calcium content, bioavailability, solubility, and sensory properties, which limits their application. The settling of calcium is a significant problem in plant beverages; the calcium content in an unshaken beverage is often significantly lower than the labelled amount. Calcium citrate malate is a metastable calcium salt that was authorised for use in food in the EU in 2009. The calcium content of calcium citrate malate (24%) is significantly higher than that of other highly soluble calcium salts, such as calcium lactate (13%) or calcium gluconate (9%). It provides sufficient aqueous solubility for many beverage fortification and effervescent food supplement applications, enabling the dissolution of 500 mg of elemental calcium (contained in 2.1 g of calcium citrate malate) in 200 mL of water. To address the limited availability and high cost of commercial calcium citrate malate (CCM), a formulation for preparing a dry precursor that forms CCM upon reaction with water is provided.

KEYWORDS

calcium supplementation, calcium citrate malate, food fortification, beverage, supplements

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1. INTRODUCTION

Different calcium salts often present a trade-off between high calcium content, aqueous solubility, bioavailability, and sensory properties, which limits their application in various food and food supplement matrices. This narrative review provides an overview of calcium salts and compares them with calcium citrate malate (CCM), an underutilised calcium source with the potential to address some limitations in beverage fortification and effervescent food supplements. One of the limitations of CCM use is the limited availability and high cost of the commercial ingredient. Therefore, we also provide technical information on how to prepare a dry precursor that forms CCM upon reaction with water.

Literature was identified through searches of PubMed, Scopus, Google Scholar, and Google Patents, supplemented by regulatory opinions and technical handbooks. Searches covered the period up to July 2026, with no lower date limit. Preference was given to peer-reviewed publications. Patents and technical documents were included where peer-reviewed evidence was limited, particularly for formulation and technological aspects. No formal systematic review protocol or predefined inclusion or exclusion criteria were applied.

2. CALCIUM HOMEOSTASIS AND ABSORPTION

About 99% of calcium is found in the skeleton and teeth in the form of hydroxyapatite, where it provides rigidity and strength. The remaining calcium is involved in various metabolic processes, such as vascular and muscle contraction, nerve signal transmission, membrane transport, enzyme activation, and hormone regulation. Bone tissue also serves as a reservoir of calcium (Institute of Medicine, 2011).

Calcium homeostasis and absorption are tightly regulated by parathyroid hormone (PTH), $1,25(\text{OH})_2\text{D}_3$, and calcitonin, with circulating ionised calcium (iCa^{2+}) acting as a feedback signal (Jeon, 2008). In the stomach, inorganic calcium salts (e.g. calcium carbonate) are first ionised and solubilised by hydrochloric acid. Recker (1985) found that achlorhydria significantly impairs calcium carbonate absorption under fasting conditions, but absorption was similar to that of healthy subjects when calcium carbonate was taken with a normal breakfast (Recker, 1985). Similarly, calcium absorption from food was not impaired in patients taking proton pump inhibitors (Hansen et al., 2010).

The chemical form of calcium salts appears to have a relatively minor influence on calcium bioavailability compared with other factors. Apparent differences in bioavailability may partly reflect the methods used to assess absorption. Stable isotope tracer studies, which directly measure true intestinal calcium absorption, have shown that calcium carbonate and calcium citrate exhibit comparable absorption when administered with food at equivalent elemental calcium doses (Heaney et al., 1999; Heaney, 2001). In contrast, studies using indirect biomarkers of calcium bioavailability, including the serum calcium response, urinary calcium excretion, and PTH suppression, reported greater bioavailability of calcium citrate than calcium carbonate (Sakhae et al., 1999; Heller et al., 2000). Additionally, product formulation (e.g., coating, granulation, tablet hardness, and excipients) of tested products can substantially affect calcium bioavailability (Heaney, 2001).

Calcium is absorbed in the intestine via two complementary mechanisms: a $1,25(\text{OH})_2\text{D}_3$ -regulated transcellular active transport pathway, which predominates at low luminal concentrations, and an unregulated paracellular passive pathway, which becomes the principal route when luminal calcium is high (Bronner, 2003). Fractional calcium absorption decreases with increasing calcium intake, declining from 64.0% at a dose of 15 mg to 28.6% at a dose of 500 mg as part of the meal (Heaney et al., 1990b). Calcium is generally absorbed more efficiently with meals than in the fasting state, likely because delayed gastric emptying prolongs calcium solubilisation and intestinal residence time, whereas oxalate and phytate reduce absorption by forming insoluble complexes (Shkempi and Huppertz, 2021).

Calcium homeostasis is primarily regulated by parathyroid hormone (PTH). Hypocalcaemia stimulates PTH secretion, which upregulates renal 1α -hydroxylase, increasing the conversion of 25-hydroxyvitamin D to the active metabolite 1,25-dihydroxyvitamin D. This enhances intestinal calcium absorption *via* the $1,25(\text{OH})_2\text{D}_3$ -regulated transcellular active transport pathway (Goltzman et al., 2018). A linear relationship has been observed between true net calcium absorption and 1,25-dihydroxyvitamin D (Sheikh et al., 1988). In vitamin D deficiency, active intestinal calcium absorption is decreased, whereas passive paracellular absorption remains largely unaffected (Lips, 2012). Similarly, the decline in oestrogen levels after menopause reduces circulating 1,25-dihydroxyvitamin D concentrations, leading to decreased intestinal calcium absorption and increased bone loss (Gallagher et al., 1980). Prolonged hypocalcaemia and elevated parathyroid hormone (PTH) concentrations increase bone resorption and may contribute to bone loss (Goltzman et al., 2018). The intestine also adapts to habitual calcium intake by regulating active calcium transport. Individuals consuming low-calcium diets exhibit higher fractional calcium absorption, whereas high calcium intake reduces absorption efficiency (Heaney et al., 1989).

Calcium absorption in the colon accounts for <10% of total calcium absorption (Bronner and Pansu, 1999), but this proportion increases if there is malabsorption in the small intestine, for example after intestinal resection (Hylander et al., 1990). It can also be increased by colon acidification achieved through fermentation of indigestible carbohydrates such as lactulose (Van den Heuvel et al., 1999; Vičič et al., 2024) and some fermentable dietary fibre such as inulin (Abrams et al., 2005; Whisner et al., 2016; Nath et al., 2017). This approach could be used in food supplements, fortified foods, and calcium-containing medicines to improve absorption. Not all dietary fibre has this effect. A study on psyllium and cellulose added to a test meal reported no significant effect on calcium absorption in humans (Heaney and Weaver, 1995). Studies in rats fed diets containing high concentrations (5–10% of the diet) of psyllium or wheat bran, which are not expected in humans, reported reduced calcium absorption (Luccia and Kunkel, 2002).

In conclusion, assessment of calcium bioavailability in humans is inherently complex because absorption is influenced by multiple factors. Differences in calcium absorption among calcium salts appear to be relatively minor in healthy humans (Heaney, 2001). Therefore, the choice of calcium source should be primarily guided by the technological requirements of the intended application, while also considering nutritional, clinical, and economic factors.

3. RECOMMENDED AND ACTUAL CALCIUM INTAKE

The D-A-C-H recommended calcium intake for adults is 1,000 mg, the same amount is recommended for pregnant and lactating women (German Nutrition Society, 2013). IOM recommendations differ only slightly (Institute of Medicine, 2011).

Global data on calcium intake in adults reveal substantial variability between countries: average intake across 74 countries ranged from 175 to 1,233 mg day⁻¹. The authors also highlight the severe lack of nationally representative data; for half of the world's countries, no data were available. Considering only nationally representative studies, mean calcium intake in Europe ranged from 673 mg (Hungary) to 1,080 mg (Ireland) (Balk et al., 2017).

In practice, calcium is most often supplemented in postmenopausal women receiving osteoporosis treatment (Reymondier et al., 2013). However, adequate calcium intake is particularly important in children and young adults as peak bone mass is achieved at around 20 years of age and is influenced by lifestyle and nutrition (Weaver et al., 2016). There are also indications that calcium supplementation during pregnancy can reduce the risk of decayed, missing, or filled teeth in their 12-year-old offspring (Bergel et al., 2010).

The European Food Safety Authority (EFSA) has set a Tolerable Upper Intake Level (UL) for calcium at 2,500 mg per day for adults, applicable to total intake from both diet and food supplements (European Food Safety Authority, 2012).

4. TECHNOLOGICAL PROPERTIES OF DIFFERENT CALCIUM SALTS

Technological properties, including aqueous solubility, calcium content, sensory characteristics, bioavailability, and cost, must be considered when selecting a calcium source for food fortification or use in food supplements. These characteristics are summarised in Table 1.

4.1. Aqueous solubility of calcium salts

The aqueous solubility of calcium is crucial in beverage applications. Data on the aqueous solubility of calcium in water are provided in Table 1. Aqueous solubility increases substantially in acidic solutions (Goss et al., 2007). Beverages with a pH near neutral can be more problematic. In bovine milk, calcium phosphate is bound to casein micelles, which is crucial in preventing mammary gland calcification (Holt, 1997). Calcium content in unshaken bovine milk is less than 6% lower than in well-mixed samples (Smith et al., 2022). However, this is not the case when calcium is added to plant beverages. Heaney and Rafferty (2006) demonstrated that the labelled calcium content of fortified soy beverages does not reflect the amount of calcium actually consumed. In unshaken samples, measurable calcium averaged only 31% of the declared value, increasing to a mean of 59% after shaking. Significant inter-product variability was observed: two products reached calcium levels consistent with label claims when shaken, whereas one product failed to exceed 20% of the labelled calcium content even after agitation (Heaney and Rafferty, 2006). Consistent with these findings, Smith et al. (2022) reported that calcium content in unshaken coconut plant-based beverages (PBB) deviated by no more than 6% from well-mixed samples. In contrast, unshaken almond and soy beverages exhibited 14 and 18% lower calcium contents, respectively, while unshaken rice and oat beverages contained 96 and 97% less calcium than their well-mixed counterparts, indicating extreme sedimentation of added calcium salts (Smith et al., 2022).

Table 1. Aqueous solubility and required dose of selected calcium salts for 1,000 mg of elemental calcium

Calcium salt	Aqueous solubility in H ₂ O (g L ⁻¹)	Calcium concentration (%) [*]	Required mass for 1,000 mg of elemental calcium (g)	Key considerations
Calcium carbonate	<0.005 (20–22 °C) (Goss et al., 2007)	40.0	2.50	Low cost (Keller et al., 2002), high calcium concentration, good bioavailability when taken with meals (Recker, 1985). Low aqueous solubility
Tricalcium phosphate	0.020 (21 °C) (Kressel, 2010)	38.8	2.58	Significant source of phosphorus. Low aqueous solubility
Calcium chloride	745.0 (20 °C) (Tordoff, 1996)	36.1	2.77	Used as food additive (firming agent for tofu and other foods). Bitter and salty taste
Calcium citrate (CC)	0.96 (23 °C) (Haynes, 2016)	21.4	4.65	Low aqueous solubility
Calcium citrate malate (CCM, 6:2:3)	11.0 (25 °C) (Fox et al., 1993; European Food Safety Authority, 2007)	24.0	4.17	Sufficient aqueous solubility allows incorporation into beverages
Calcium lactate	64.1 (24 °C) (Kubantseva et al., 2004)	13.0	7.69	High aqueous solubility, low calcium concentration
Calcium gluconate	30 (21 °C) (Kressel, 2010)	9.0	11.11	High aqueous solubility, low calcium concentration
Calcium lactate gluconate	400.0 (20 °C) (Gerstner, 2002)	13.0	7.69	High aqueous solubility, low calcium concentration
Calcium lactate citrate	98.0 (21 °C) (Kressel, 2010)	16.2	6.17	High aqueous solubility
Calcium lactate malate	115.0 (21 °C) (Kressel, 2010)	18.1	5.52	High aqueous solubility

^{*}Typical values are presented as reported in the literature; differences in hydration state may affect elemental calcium content.

4.2. Calcium concentration of calcium salts

Calcium carbonate is usually a mined, finely milled mineral with the lowest cost (Keller et al., 2002) and a high elemental calcium content of 40% (Table 1). When consumed with food, it has good bioavailability (Recker, 1985), making it a preferred form for the fortification of wheat flour and baked products (Hackett et al., 1984; Romanchik-Cerpovicz and McKemie, 2007), where low aqueous solubility is not a technological limitation. In contrast, the high aqueous solubility of calcium gluconate and calcium lactate is advantageous for beverage applications; however, their low calcium content (9 and 13%, respectively) makes their use inefficient and economically unfavourable (Kubantseva et al., 2004; Kressel, 2010). Swallowable calcium tablets are predominantly based on calcium carbonate, as tablet size is inherently limited and large tablets significantly reduce adherence (Radhakrishnan et al., 2021). FDA adverse event reporting data indicate that most reported swallowing-related problems are associated with multivitamin products (72.9%) and calcium food supplements (17.3%) (Punzalan et al., 2019). However, given that multivitamins are the most commonly used food supplements, whereas calcium supplements rank only fourth among adults aged >60 years, calcium food supplements appear disproportionately problematic with respect to swallowing difficulties (Mishra et al., 2021). Because of its relatively low elemental calcium content (~21%), calcium citrate (CC) is rarely used in swallowable tablets. It is more commonly formulated as chewable products, where its low aqueous solubility can result in a gritty or chalky mouthfeel unless particle size is sufficiently reduced (Scheurer and McNamee, 1989). Calcium chloride (36% elemental calcium) has excellent aqueous solubility but its bitter and salty taste limits its application (Tordoff, 1996).

4.3. Calcium citrate malate

Calcium citrate malate (CCM) is a metastable complex of calcium, citrate, and malate (Fox et al., 1993). In 2007, EFSA conducted a review of the available evidence and concluded that CCM is a safe and bioavailable source of calcium for use in foods (European Food Safety Authority, 2007) and it was authorised for use in food in 2009 (European Commission, 2009). CCM provides a relatively high elemental calcium content (~24%) combined with adequate aqueous solubility; although its aqueous solubility is lower than that of some other calcium salts, it is sufficient for use in many calcium-fortified beverages (Fox et al., 1993; European Food Safety Authority, 2007) (Table 1). Sufficient aqueous solubility in practice is demonstrated by the following example: When a food supplement containing 2.3 g of calcium citrate (CC) (~500 mg of elemental calcium) is dissolved in 200 mL of water, the limited aqueous solubility of CC (0.96 g L^{-1}) results in only about 0.19 g of CC (41 mg of elemental calcium) remaining dissolved. The remaining 2.1 g of CC (459 mg of elemental calcium) forms a white, chalky sediment at the bottom. It is plausible that some users may discard the sediment, potentially reducing calcium intake, although this has not been investigated for calcium products. However, indirect evidence from one large therapeutic drug monitoring study compared plasma concentrations of the poorly soluble drug clozapine and its metabolite norclozapine in patients receiving crushed tablets or suspension ($n = 846$) versus intact tablets ($n = 6,065$). Although the median prescribed dose was higher in the crushed tablet/suspension group, the median plasma levels of both compounds were significantly lower. The authors attributed these findings to poorer adherence, sedimentation of the suspension before use, and incomplete dosage (Flanagan et al., 2022). In contrast, dissolving a supplement containing 2.1 g of calcium citrate malate (CCM) (~500 mg of

elemental calcium), which has a higher aqueous solubility (11.0 g L^{-1}), allows the majority of CCM to remain in solution (Table 1 and Fig. 1).

CCM is more soluble because its metastable form contains multiple hydration states and partially non-crystalline regions. These regions readily hydrate and behave like a pre-solubilised phase (European Food Safety Authority, 2007). Higher solubility of calcium salts by itself has only a limited effect on calcium bioavailability (Heaney et al., 1990a). Studies indicate that CCM is at least as bioavailable as conventional calcium sources, such as calcium carbonate and milk calcium (Martini and Wood, 2002), while some studies suggest that its absorption may be slightly greater than that of calcium carbonate (Smith et al., 1987; Miller et al., 1988).

The commercial availability of CCM remains limited and high prices limit its widespread use. According to EFSA, CCM can be a complex of calcium citrate and malate ligands, a mixture of calcium citrate with calcium malate, or a mixture of a calcium salt (e.g. calcium carbonate) with citric and malic acid (European Food Safety Authority, 2007). One patent presents preparation of calcium citrate malate (CCM) with a molar ratio of 6:2:3 (calcium: citrate: malate). Figure 2 presents a simplified scheme of the production and use of a dry precursor that forms

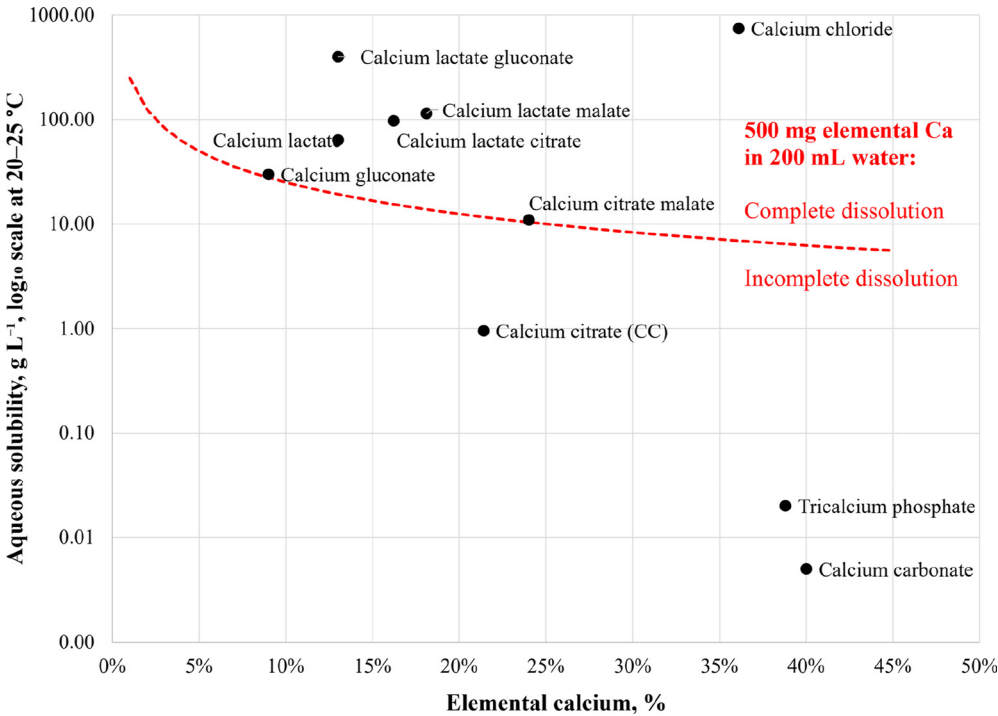


Fig. 1. Relationship between elemental calcium content and aqueous solubility of selected calcium salts. The red curve represents the minimum aqueous solubility required to dissolve the amount of calcium salt needed to provide 500 mg of elemental calcium in 200 mL of water (a common dosage). Calcium salts above the curve are expected to dissolve completely under these conditions. Actual solubility may vary with pH, temperature, and solution composition. Data compiled from the literature cited in Table 1

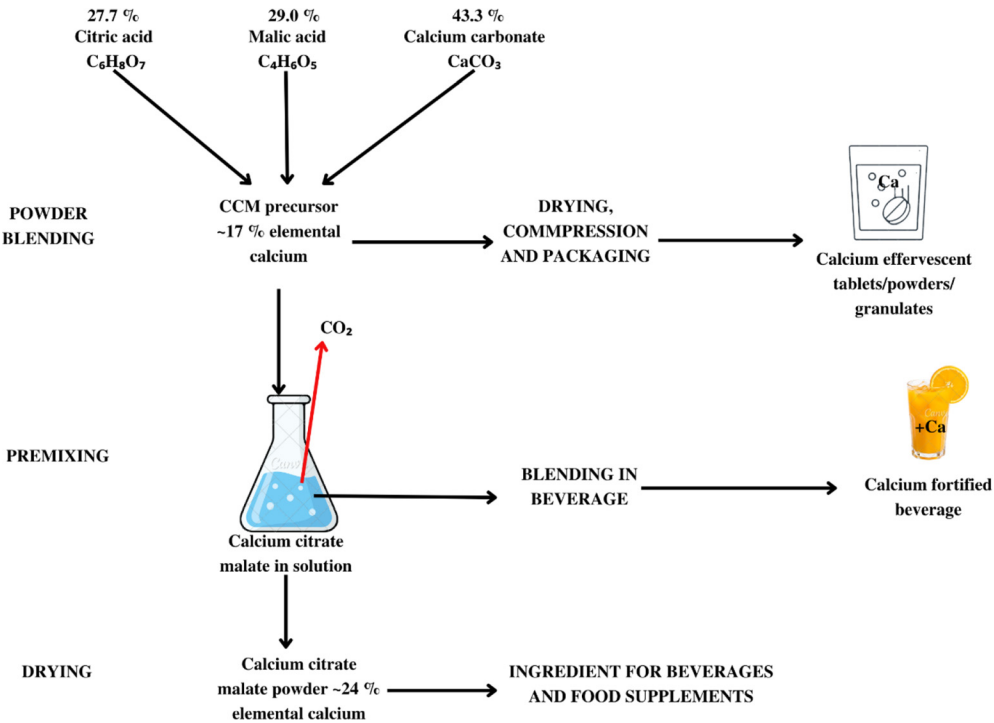


Fig. 2. Simplified scheme of production and use of calcium citrate malate (CCM). Source of images: Canva

CCM upon reaction with water. Based on the patent (Fox et al., 1993) and the authors' formulation experience, the practical example of a formulation for a dry precursor that forms CCM upon reaction with water is presented in Table 2. A commercial formulation based on this principle achieved a calcium dissolution percent of $88.65 \pm 0.90\%$, while spectroscopic analyses

Table 2. Formulation for preparation of dry precursor that forms CCM with molar ratio 6:2:3 upon reaction with water (calcium: citrate: malate) from common ingredients. CO₂ is released upon mixing with water.

This non-validated practical example is based on the patent by Fox et al. (1993) and the authors' formulation experience

Ingredient	Mass (%)	Amount for 1 kg of powder (g)	Elemental calcium concentration (%)
Calcium carbonate powder* (99.0% purity)	43.29	432.9	39.6
Citric acid anhydrous	27.71	277.1	0
DL-Malic acid anhydrous	29.00	290	0
CCM precursor mixture	100	1,000	17.14

*Particle size: D₅₀: 12–16 μm, D₉₈: 70 μm was found to be adequate.

were consistent with the conversion of calcium carbonate to CCM during the effervescent reaction (Zhang et al., 2026).

When the described dry mixture is added to water, it releases CO₂, making it suitable as a sodium-free ingredient for effervescent powders or tablets. Effervescent food supplements can be a relevant source of sodium. A recent Slovenian study reported that sodium content was not declared on 77% of effervescent food supplements, because such declaration is not mandatory under EU food supplement labelling legislation. The mean sodium content of calcium effervescent tablets was 136 ± 59 mg per tablet, which was significantly lower than that of effervescent products containing vitamins and minerals (314 ± 109 mg per tablet). This difference suggests that sodium hydrogen carbonate is already partially replaced with calcium carbonate in calcium formulations (Žmitek et al., 2026). Sodium intake from effervescent medicinal formulations has been linked to an increased risk of cardiovascular events (George et al., 2013).

4.4. Limitations of this review and future research needs

This review has several limitations. Published evidence on calcium citrate malate (CCM) remains limited compared with more widely used calcium salts. Consequently, some sections, particularly those addressing physicochemical properties, formulation, sensory characteristics, user adherence, and technological performance, rely on a limited number of studies, supplemented by patents, regulatory documents, technical literature, and, in some cases, indirect evidence.

Future research should generate data on the aqueous solubility of CCM across different pH conditions, temperatures, and food matrices. Further work should evaluate its stability during processing and storage, interactions with food components, sedimentation behaviour, beverage clarity, and consumer acceptability.

5. CONCLUSIONS

Calcium citrate malate (CCM) offers adequate aqueous solubility for beverage fortification and effervescent food supplement applications.

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AI (InstaText and ChatGPT) was used only to improve language and readability of text. These tools were not used for data analysis, interpretation of results, generation of scientific content, generation of images, or citation of references.

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