

Table S1. Phosphopeptides peaks identified from tryptic digests of α -casein and non-fat milk after captured by materials in MALDI- TOF/MS analysis.

Peak Label	Number of phosphorylation	Observed (m/z)	Peptide sequence	Type of material used
α -casein				
α_1	1	1237.267	TVDME[pS]TEVF	(1)(2)(3)
α_2	1	1253.142	TVD[Mo]ME[pS]TEVF	(1) (3)
α_3	1	1466.779	TVDME [pS]TEVF ^{TK}	(1)(2)(3)
α_4	1	1482.654	TVD[Mo]E[pS]TEVF ^{TK}	
α_5	2	1538.978	EQL[pS]T[pS]EENS ^{KK}	(1)(2)(3)
α_6	1	1660.949	VPQLEIVPN[pS]AEER	(1)(2)(3)
α_7	1	1833.197	YLGEYLIVPN [pS]AEER	(1)(2)(3)
α_8	1	1848.213	DIGSE[pS]TEDQAMEDIK	(1)(2)(3)
α_9	1	1864.366	DIGSE[pS]TEDQA[Mo]EDIK	(1)
α_{10}	2	1927.885	DIG[pS]E[pS]TEDQAMEDIK	(1)(2)(3)
α_{11}	2	1943.829	DIG[pS]E[pS]TEDQA[Mo]EDIK	(1)(2)
α_{12}	1	1952.109	YKVPQLEIVPN[pS]AEER	(1)(2)(3)
α_{13}	1	2080.00	KKYKVPQLEIVPNpSAEERL	
α_{14}	4	2619.391	NTMEHV[pS][pS][pS]EESII[pS]QETYK	
α_{15}	4	2635.332	NT[Mo]EHV[pS][pS][pS]EESII[pS]QETYK	
α_{16}	3	2678.944	VNEL[pS]KDIG[pS]E[pS]TEDQAMEDIK	
α_{17}	3	2695.032	VNEL[pS]KDIG[pS]E[pS]TEDQA[Mo]EDIK	
α_{18}	5	2703.758	Q*MEAE[pS]I[pS][pS] [pS]EEIVPN[pS]VEAQK	(1)(2)
α_{19}	5	2720.822	QMEAE[pS]I[pS][pS][pS]EEIVPNPN[pS]VEQK	(1)(2)(3)
α_{20}	4	2747.1	NTMEHV[pS][pS][pS]EE[pS]IISQETYKQ	(1)(2)(3)
α_{21}	3	2936.202	KEKVNEL[pS]KDIG[pS]E[pS]TEDQAMEDIKQ	(1)
α_{22}	4	3008.618	NANEEYSIG[pS][pS][pS]EE[pS]AEVATEEVK	(1)
α_{23}	5	3088.415	NANEEY[pS]IG[pS][pS][pS]EE[pS]AEVATEEVK	(1)
β -casein				
β_1	1	2061.985	FQ[pS]EEQQQTEDELQDK	(1)(2)(3)
β_2	1	2432.434	IEKFQ[pS]EEQQQTEDELQDK	
β_3	1	2556.473	FQ[pS]EEQQQTEDELQDKIHPF	(1)(3)
β_4	4	3122.746	RELEELNVPGEI[pS]L[pS][pS][pS]EESITR	(1)(3)

[pS]: Phosphorylated site; [Mo]: oxidation on methionine; *: Pyroglutamylation on the N-terminal Q;
Tryptic digests of non-fat milk was captured by (1) rGTZ; (2) rGT; (3) rGZ.

Fig. E1 MALDI-TOF/MS spectra of tryptic β -casein digest after enrichment by rGTZ using TFA in incubation with different contents of (A) 0.1%; (B) 0.5%; (C) 1%. The metastable losses of phosphoric acid were labeled by M*.

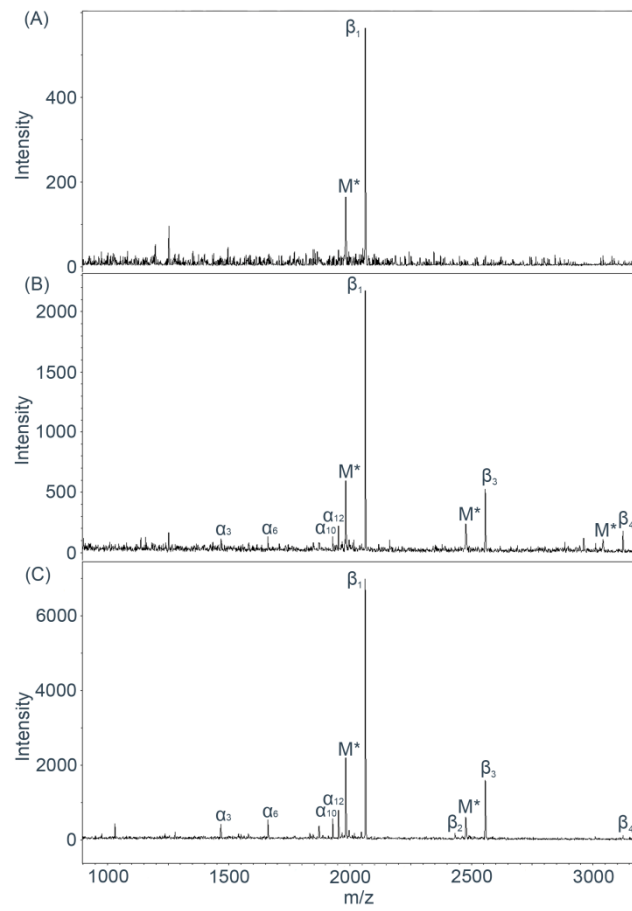


Fig. E2 MALDI-TOF/MS spectra of tryptic β -casein digest after enrichment by rGTZ using $\text{NH}_3 \cdot \text{H}_2\text{O}$ in eluent with different contents of (A) 5%; (B) 10%; (C) 15%. The metastable losses of phosphoric acid were labeled by M^* .

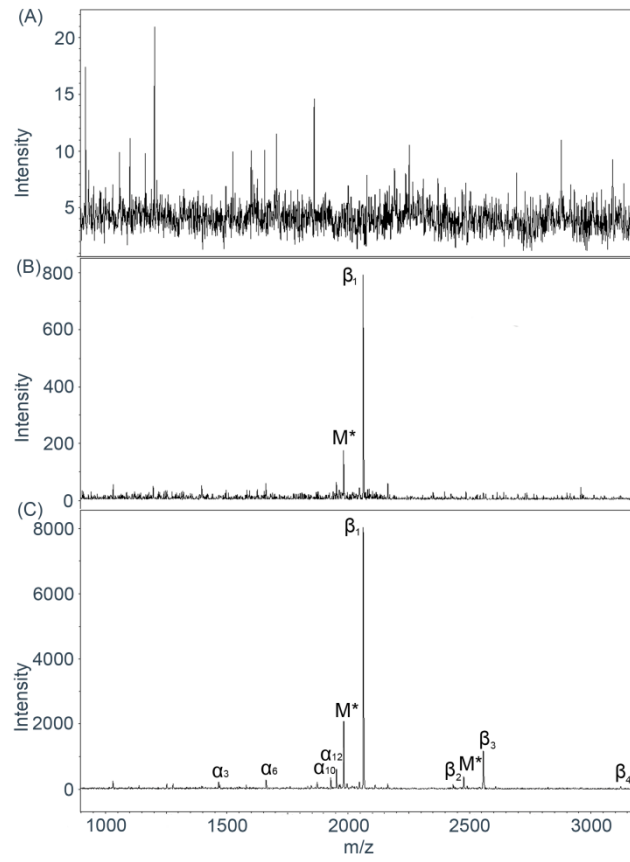


Fig. E3 MALDI-TOF/MS spectra of tryptic digest of α -casein without enrichment (A); enriched by rGTZ (B). The metastable losses of phosphoric acid were labeled by M*.

