## Metal Oxides Affinity Probe derived from MIL-125 (Ti) as for

## **Selective Enrichment of Endogenous Phosphopeptides**

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Tab.S1 List of phosphopeptides identified from  $\alpha$ -casein digest and  $\beta$ -casein in MALDI-TOF MS analysis

No.	Mass	Peptide sequence	Number
α1	1026.42	EKVNEL[PS]K	1
α2	1196.50	KNMAINP[PS]KENL	1
α3	1237.37	TVDME[PS]TEVF	1
α4	1253.36	TVD[Mo]E[PS]TEVF	1
α5	1410.80	EQL[PS]T[PS]EENSK	2
α6	1459.52	EQL[PS]TSEENSKK	1
α7	1466.51	TVDME[PS]TEVFIK	1
α8	1482.50	TVD[Mo]E[PS]TEVFTK	1
α9	1539.00	EQL[PS]T[PS]EENSKK	2
α10	1660.67	VPQLEIVPN[PS]AEER	1
α11	1832.00	YLGEYLIVPN[PS]AEER	1
α12	1847.59	DIGSE[PS]TEDQAMEDIK	1
α13	1864.40	DIGSE[PS]TEDQA[Mo]EDIK	1
α14	1927.55	DIG[PS]E[PS]TEDQAMEDIK	2
α15	1943.53	DIG[PS]E[PS]TEDQA[Mo]EDIK	2
α16	1951.81	YKVPQLEIVPN[PS]AEER	1
α17	1981.44	NMAINP[PS]KENLCSTFCK	1
α18	2079.88	KKYKVPQLEIVPN[PS]AEER	1
α19	2618.69	NTMEHV[PS][PS][PS]EE[PS]IISQE	4

α20	2634.67	NT[Mo]EHV[PS][PS][PS]EE[PS]IIS	4
		QETYK	
α21	2678.6	VNEL[PS]KDIG[PS]E[PS]TEDQAME	3
		DIK	
α22	2703.8	Q*MEAE[PS][PS][PS][PS]EEIVPN[PS]	5
		VEAQK	
α23	2720.69	QMEAE[PS][PS][PS][PS]EEIVPN[PS]	5
		VEAQK	
α24	2736.66	Q[Mo]EAE[PS][PS][PS][PS]EEIVPN	5
		[PS]VEAQK	
α25	2934.93	KEKVNEL[PS]KDIG[PS]E[PS]TEDQ	3
		AMEDIKQ	
α26	2951.93	KEKVNEL[PS]KDIG[PS]E[PS]TEDQ	3
		A[Mo]EDIKQ	
α27	3007.8	NANEEEYSIG[PS][PS][PS]EE[PS]AE	4
		VATEEVK	
β1	2061.32	FQ[PS]EEQQQTEDELQDK	1
β2	2355.60	FQ[PS]EEQQQTEDELQDKIHPF	1
β3	2555.94	FQ[PS]EEQQQTEDELQDKIHPF	1
β4	3122.27	RELEELNVPGEIVE[PS]L[PS][PS][PS]	4
		EESITR	
		1500	
		1000 -	
		500- 25	
		$\frac{1}{1000}$ (b)	

Fig. S2 MALDI-TOF MS spectra of standard phosphopeptides with different concentrartion: (a)  $5 \times 10^{-6}$  M (b)  $5 \times 10^{-7}$  M

0 -

 $m^{1250}/z$ 

(b)



Fig. S3 MALDI-TOF MS spectra of  $\beta$ -casein digest enriched by TiO<sub>2</sub>/C (a) for the first time, (b) for the third time, and (c) for the sixth time

 Tab.S2
 List of phosphopeptides identified from human serum in MALDI-TOF MS

analysis			
No.	Mass	Peptide sequence	Number
HS1	1389.33	D[PS]GEGDFLAEGGGV	1
HS2	1460.35	AD[PS]GEGDFLAEGGGV	1
HS3	1545.43	D[PS]GEGDFLAEGGGVR	1
HS4	1616.45	AD[PS]GEGDFLAEGGGVR	1

Tab.S3 List of phosphopeptides identified from human saliva in MALDI-TOF MS

analysis			
No.	Mass	Peptide sequence	Number
1	1055.4	ssEEKFL	2
2	1075.48	SsEEKFLR	1
3	1114.4	tDsDEKFI	2
4	1155.4	ssEEKFLR	2
5	1232.48	sEQFIDEER	1
6	1270.5	DssEEKFLR	2
7	1305.45	GGDsEQFIDEE	1
8	1443	HEKHHsHRGYR	1
9	1461.55	GGDsEQFIDEER	1
10	1589.61	GGDsEQFIDEERQ	1

11	2323.98	GGDsEQFIDEERQGPPLGGQQ	1
12	2439.01	DGGDsEQFIDEERQGPPLGGQQ	1
13	2526.04	sDGGDSEQFIDEERQGPPLGGQQ	1
14	2838.19	DGGDsEQFIDEERQGPPLGGQQSQPS	1