

Supplementary Data

Five tyrosines and two serines in human albumin are labeled by the organophosphorus agent FP-biotin

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Albumin residues labeled by chlorpyrifos oxon. The diethoxyphosphate adduct of human albumin was prepared by treatment with chlorpyrifos oxon (CPO). The labeled albumin was reduced, alkylated with iodoacetamide, and digested with trypsin. Peptides were purified by HPLC and analyzed by mass spectrometry.

Six tyrosines were labeled: Y138, Y150, Y161, Y401, Y411, and Y452.

The MS/MS spectra to support these assignments are in Figures S1-S5. Figure 7 in the text has the spectrum for the Y161 containing peptide.

Ions characteristic of CPO-labeled tyrosine are the 272 amu ion for diethoxyphosphoTyrosine and the 244 amu ion for monoethoxyphosphoTyrosine. The 272 ion is present in Figures S1, S2, S4, and S5. The 244 ion is present in figures S2 and S4. These ions may be useful as markers when searching for peptides labeled on tyrosine with chlorpyrifos oxon.

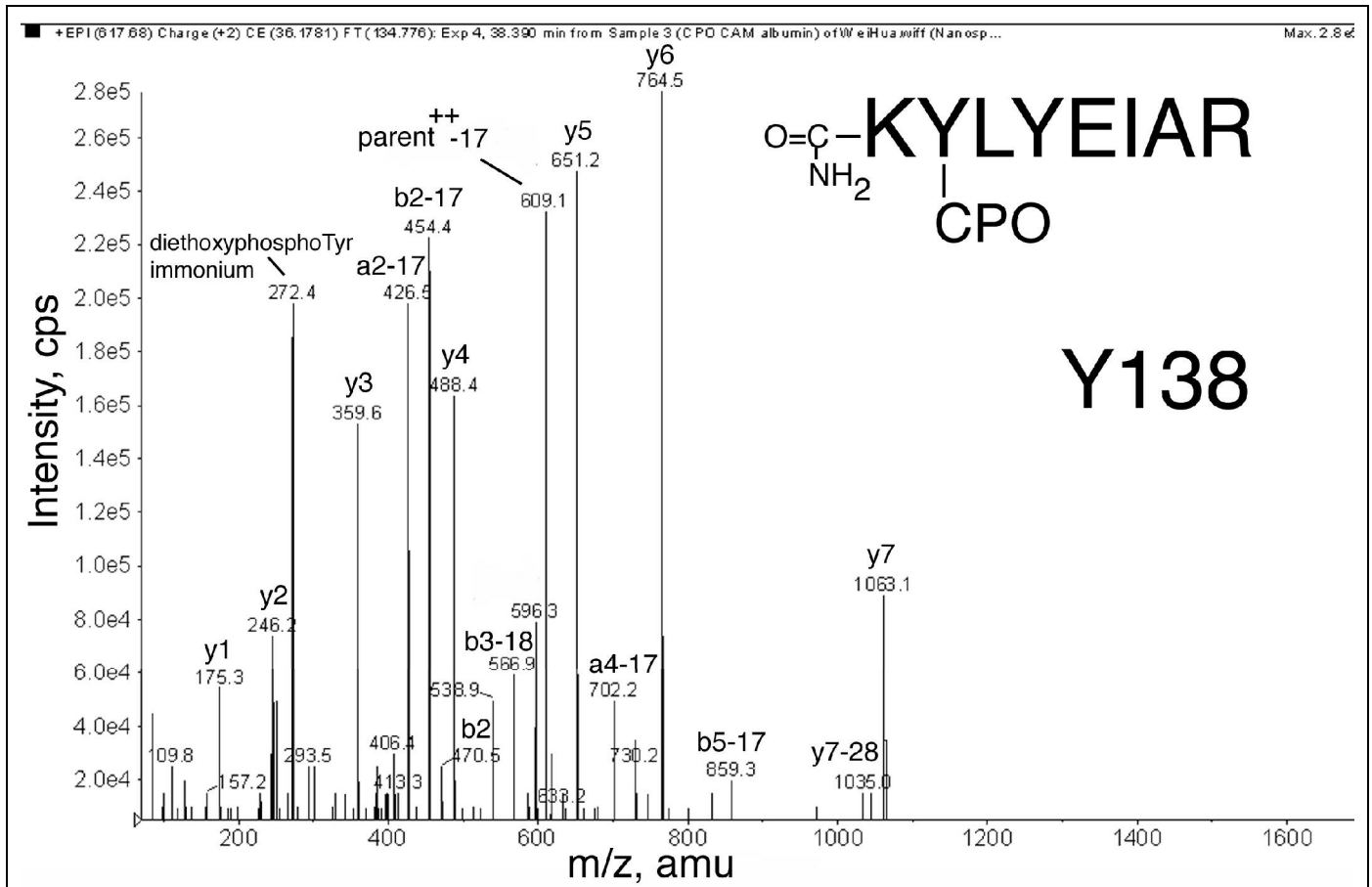
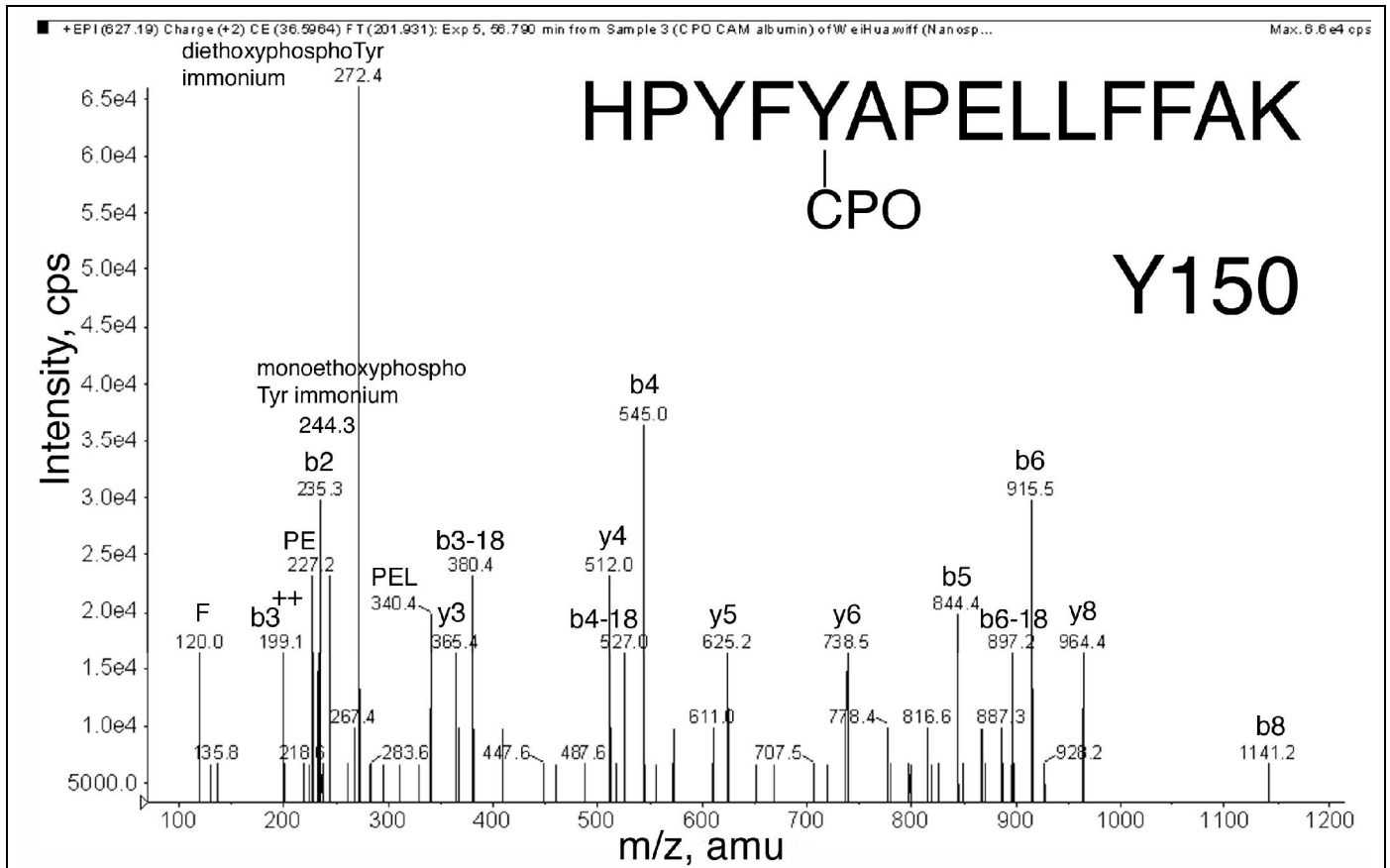


Figure S1. MS/MS spectrum for the tryptic peptide of human albumin labeled with CPO on Tyr 138. The ammonium cyanate on Lys is from urea used for denaturation. The added mass from ammonium cyanate is 43. The added mass from CPO is 136. The doubly charged parent ion has a mass of 617.7.

The diethoxyphospho-Tyrosine immonium ion is at 272.4. Its structure is shown below

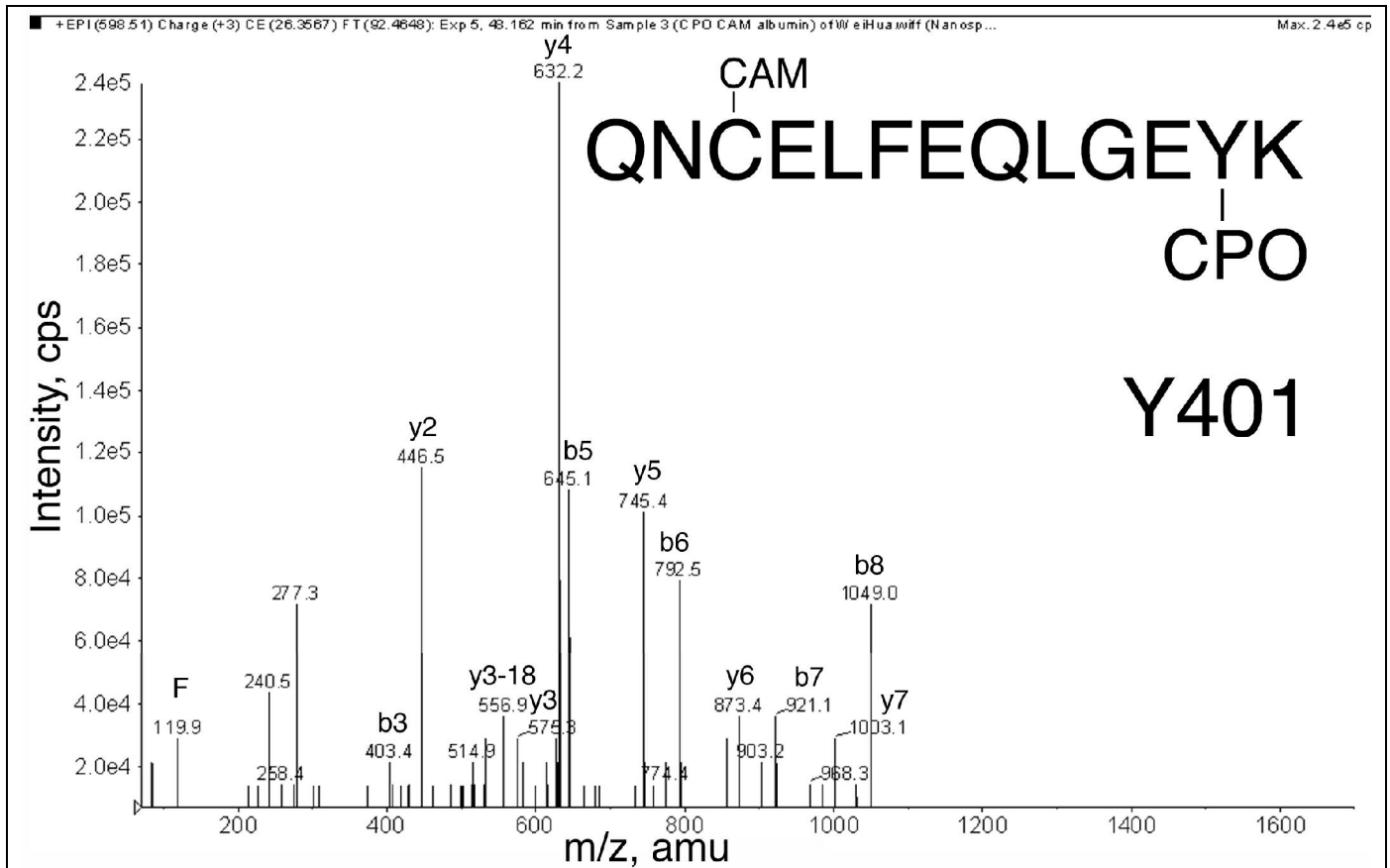
Mass	name	structure
272.0	diethoxyphosphoTyr immonium	$^+\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-C}_6\text{H}_4\text{-O-P(=O)(OCH}_2\text{CH}_3)_2$



Figures S2. MS/MS spectrum of the tryptic peptide of human albumin labeled with CPO on Tyr 150. The triply charged parent ion has a mass of 627. Internal fragmentation on the N-terminal side of proline yields a mass at 227.2 corresponding to PE and a mass at 340.4 corresponding to PEL.

The structure of the monoethoxyphospho-Tyrosine immonium ion at 244.3 is shown below.

Mass	name	structure
244.1	monoethoxyphosphoTyr immonium	$^+\text{NH}_2=\text{CHCH}_2\text{-C}_6\text{H}_4\text{-O-P(=O)(OH)-OCH}_2\text{CH}_3$



Figures S3. MS/MS spectrum of the tryptic peptide of human albumin labeled with CPO on Tyr 401. The triply charged parent ion has a mass of 598.5. The added mass from carbamidomethylation on cysteine is 57. The added mass from chlorpyrifos oxon is 136. The mass at 119.9 is the immonium ion of phenylalanine.

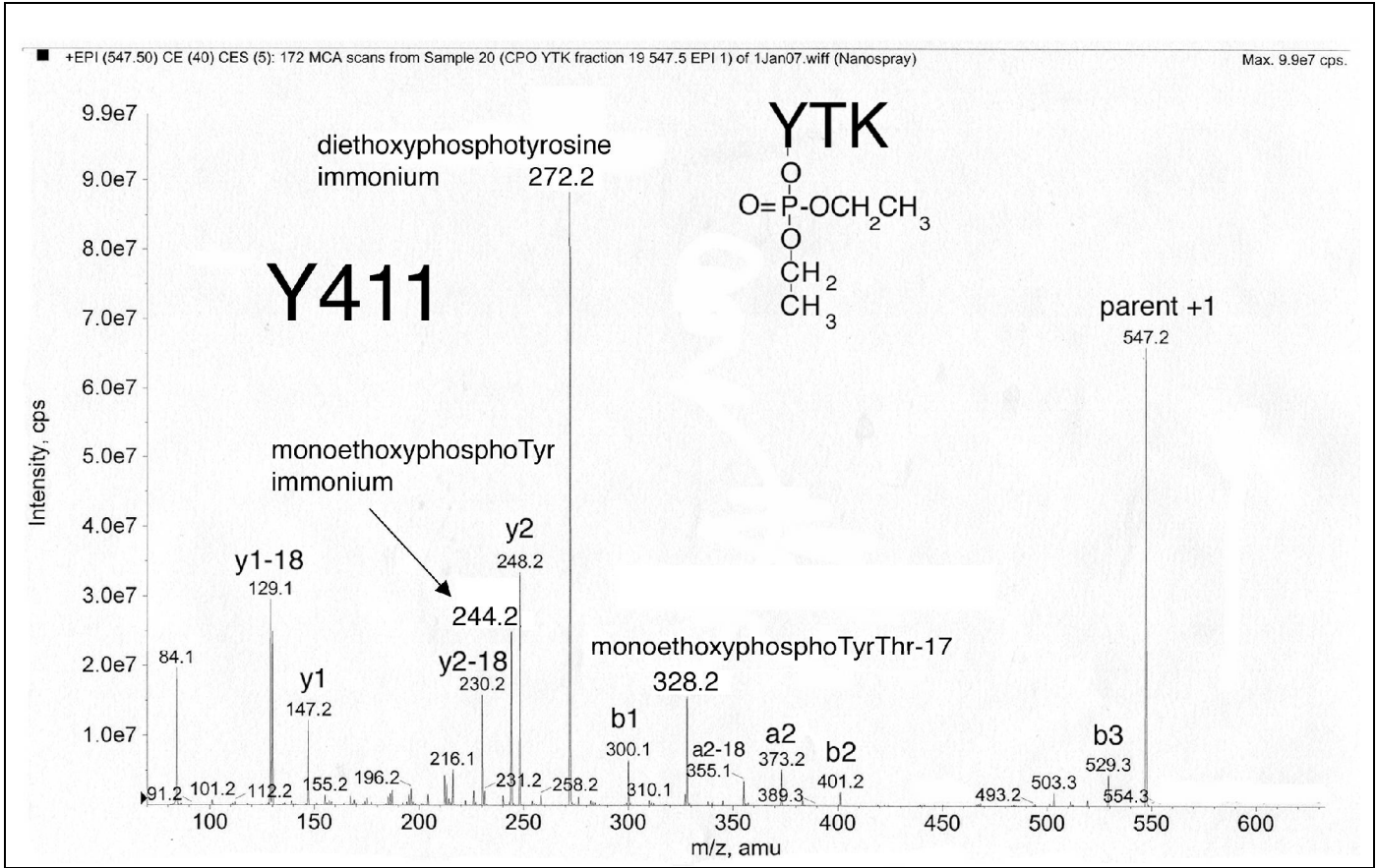


Figure S4. MS/MS spectrum of the tryptic peptide of human albumin labeled with CPO on Tyr 411. The mass at 328.2 is the dipeptide TyrThr carrying monoethoxyphosphate on Tyr minus 17 for loss of an amine. The singly charged parent ion has a mass of 547.2.

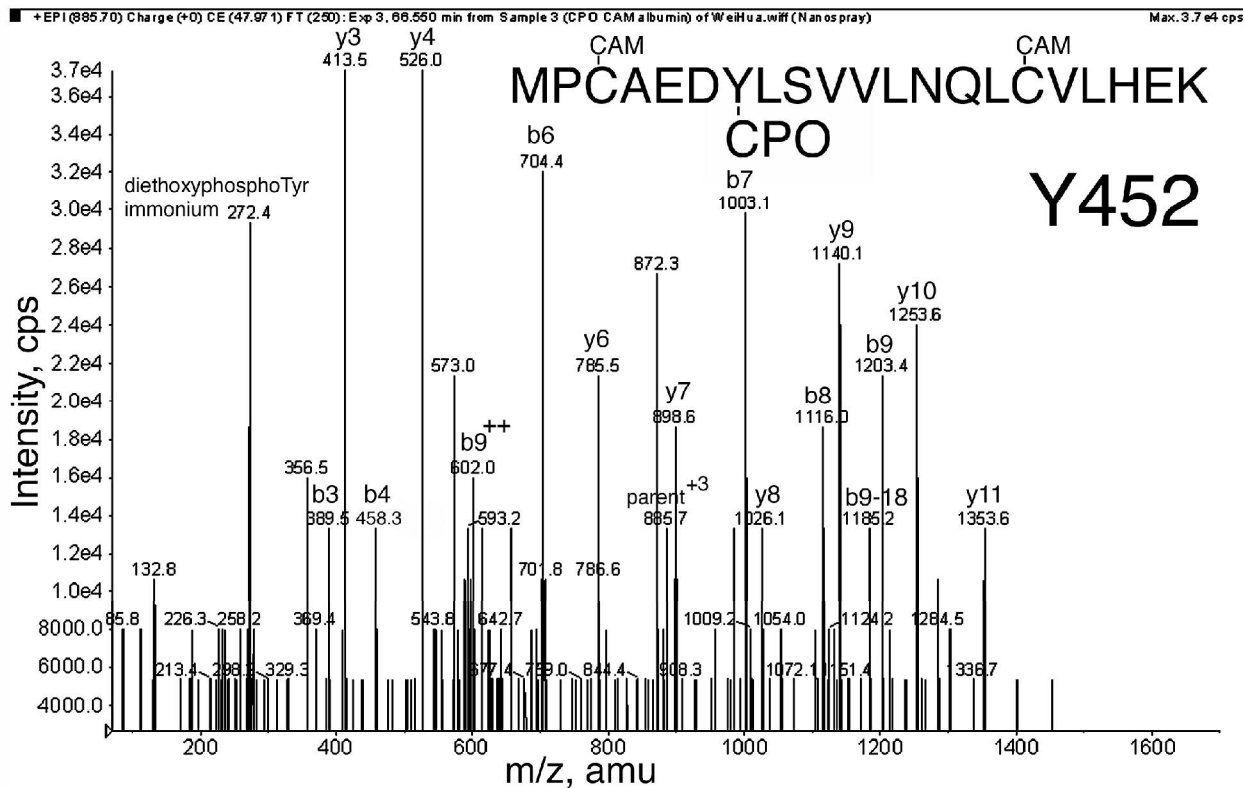


Figure S5. MS/MS spectrum of the tryptic peptide of human albumin labeled with CPO on Tyr 452. Cysteines were carbamidomethylated with iodoacetamide, designated as CAM. Each carbamidomethyl group adds a mass of 57 amu. The triply charged parent ion has a mass of 885.7.