Supplementary Information

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Keratin adducts in human hair prove exposure to sulfur mustard in a real case of poisoning and indicate exposure to sesquimustard and O-lost *in vitro*

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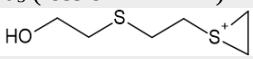
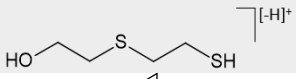
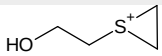
Table SI 1

MS/HR MS data of the double protonated AE(-*HETETE*)IRSDL biomarker peptide

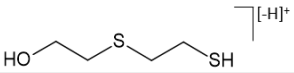
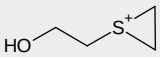
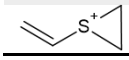
ion	**elemental composition**	***m/z* theoretical**	***m/z* measured**	**Δ *m/z* [mmu]**	**Δ *m/z* [ppm]**
AE(-*HETETE*)IRSDL $[M+2H]^{2+}$	$C_{39}H_{72}N_{10}O_{14}S_2$	484.2330	484.230	-3.0	-6.2
b_6	$C_{36}H_{58}N_9O_{12}S_2$	836.3641	836.365	+0.9	+1.1
AEIRSDL (loss of *HETETE*)	$C_{33}H_{59}N_{10}O_{13}$	803.4258	803.426	+0.2	+0.2
b_6 (loss of *HETETE*)	$C_{27}H_{46}N_9O_{11}$	672.3311	672.335	+3.9	+5.8
y_5 (loss of *HETETE*)	$C_{25}H_{47}N_8O_9$	603.3461	603.346	-0.1	-0.2
y_4 (loss of *HETETE*)	$C_{19}H_{36}N_7O_8$	490.2620	490.263	+1.0	+2.0
a_3 (loss of *HETETE*)	$C_{13}H_{24}N_3O_4$	286.1761	286.176	-0.1	-0.3
	$C_6H_{13}OS_2$	165.0402	165.042	+1.2	+7.3
	$C_4H_9OS_2$	137.0089	137.009	+0.1	+0.7
	C_4H_9OS	105.0369	105.037	+0.1	+1.0

HETETE: hydroxyethylthioethylthioethyl-moiety

Data were extracted from the biomarker peak (t_R 7.1 min, Fig. 2B) obtained from μLC-ESI MS/HR MS (PIS) analysis of hair incubated with sesquimustard (25 mM) followed by pepsin-catalyzed proteolysis. A triple TOF mass spectrometer was used. The corresponding MS/HR MS spectrum is shown in Figure 3A. The exact mass of the single protonated biomarker is *m/z* 967.4587.

Table SI 2

MS/HR MS data of the double protonated FKTIE(-*HETETE*)EL biomarker peptide

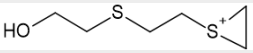
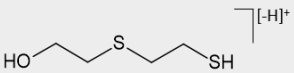
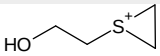
ion	**elemental composition**	***m/z* theoretical**	***m/z* measured**	**Δ *m/z* [mmu]**	**Δ *m/z* [ppm]**
FKTIE(-*HETETE*)EL $[M+2H]^{2+}$	$C_{47}H_{80}N_8O_{14}S_2$	522.2612	522.261	-0.2	-0.4
FKTIEEL (loss of *HETETE*)	$C_{41}H_{67}N_8O_{13}$	879.4822	879.479	-3.2	-3.6
y_7 (loss of *HETETE* and H_2O)	$C_{41}H_{65}N_8O_{12}$	861.4717	861.467	-4.7	-5.5
b_6 (loss of *HETETE*)	$C_{35}H_{54}N_7O_{11}$	748.3876	748.392	+4.4	+5.9
b_5 (loss of *HETETE*)	$C_{30}H_{47}N_6O_8$	619.3450	619.348	+3.0	+4.8
$[M+2H]^{2+}$ (loss of H_2O)	$C_{47}H_{78}N_8O_{13}S_2$	513.2559	513.258	+2.1	+4.1
b_3	$C_{19}H_{29}N_4O_4$	377.2183	377.219	+0.7	+1.9
b_2	$C_{15}H_{22}N_3O_2$	276.1707	276.173	+2.3	+8.3
y_2-18	$C_{11}H_{19}N_2O_4$	243.1339	243.134	+0.1	+0.4
	$C_4H_9OS_2$	137.0089	137.010	+1.1	+8.0
	C_4H_9OS	105.0369	105.037	+0.1	+1.0
	C_4H_7S	87.0263	87.027	+0.7	+8.0

HETETE: hydroxyethylthioethylthioethyl-moiety

Data were extracted from the biomarker peak (t_R 10.7 min, Fig. 2D) obtained from μLC-ESI MS/HR MS (PIS) analysis of hair incubated with sesquimustard (25 mM) followed by pepsin-catalyzed proteolysis. A triple TOF mass spectrometer was used. The corresponding MS/HR MS spectrum is shown in Figure 3B. The exact mass of the single protonated biomarker is *m/z* 1043.5152.

Table SI 3

MS/HR MS data of the double protonated LE(-*HETETE*)TKLQF biomarker peptide

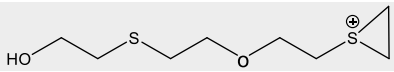
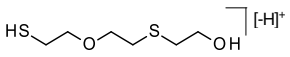
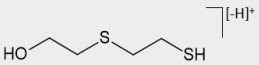
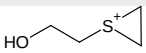
ion	elemental composition	*m/z* theoretical	*m/z* measured	Δ *m/z* [mmu]	Δ *m/z* [ppm]
LE(-*HETETE*)TKLQF $[M+2H]^{2+}$	$C_{47}H_{81}N_9O_{13}S_2$	521.7692	521.767	-2.2	-4.2
y_6	$C_{41}H_{69}N_8O_{12}S_2$	929.4471	929.447	-0.1	-0.1
LETKLQF (loss of *HETETE*)	$C_{41}H_{68}N_9O_{12}$	878.4982	878.496	-2.2	-2.5
y_7 (loss of *HETETE* and H_2O)	$C_{41}H_{66}N_9O_{11}$	860.4876	860.487	-0.6	-0.7
y_6 (loss of *HETETE*)	$C_{35}H_{57}N_8O_{11}$	765.4141	765.410	-4.1	-5.4
b_6 (loss of *HETETE*)	$C_{32}H_{57}N_8O_{10}$	713.4192	713.418	-1.2	-1.7
y_5	$C_{30}H_{50}N_7O_8$	636.3715	636.371	-0.5	-0.8
b_5 (loss of *HETETE*)	$C_{27}H_{49}N_6O_8$	585.3606	585.359	-1.6	-2.7
b_5 (loss of *HETETE* and H_2O)	$C_{27}H_{47}N_6O_7$	567.3501	567.350	-0.1	-0.2
y_4	$C_{26}H_{43}N_6O_6$	535.3239	535.326	+2.1	+3.9
b_4 (loss of *HETETE*)	$C_{21}H_{38}N_5O_7$	472.2766	472.277	+0.4	+0.8
b_4 (loss of *HETETE* and H_2O)	$C_{21}H_{36}N_5O_6$	454.2660	454.262	-4.0	-8.8
y_2 (loss of NH_3)	$C_{14}H_{17}N_2O_4$	277.1183	277.119	+0.7	+2.5
b_2 (loss of *HETETE*)	$C_{11}H_{19}N_2O_4$	243.1339	243.134	+0.1	+0.4
y_1	$C_9H_{12}NO_2$	166.0863	166.086	-0.3	-1.8
	$C_6H_{13}OS_2$	165.0402	165.041	+0.8	+4.8
	$C_4H_9OS_2$	137.0089	137.009	+0.1	+0.7
	C_4H_9OS	105.0369	105.037	+0.1	+1.0
a_1	$C_5H_{12}N$	86.0964	86.096	-0.4	-4.6

HETETE: hydroxyethylthioethylthioethyl-moiety

Data were extracted from the biomarker peak (t_R 9.8 min, Fig. 2F) obtained from μLC-ESI MS/HR MS (PIS) analysis of hair incubated with sesquimustard (25 mM) followed by pepsin-catalyzed proteolysis. A triple TOF mass spectrometer was used. The corresponding MS/HR MS spectrum is shown in Figure 3C. The exact mass of the single protonated biomarker is *m/z* 1042.5312.

Table SI 4

MS/HR MS data of the double protonated AE(-*HETEOETE*)IRSDL biomarker peptide

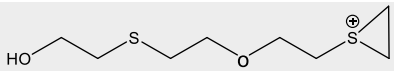
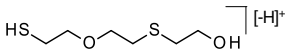
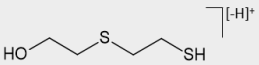
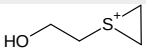
ion	**elemental composition**	***m/z* theoretical**	***m/z* measured**	**Δ *m/z* [mmu]**	**Δ *m/z* [ppm]**
AE(-*HETEOETE*)IRSDL $[M+2H]^{2+}$	$C_{41}H_{76}N_{10}O_{15}S_2$	506.2461	506.247	+0.9	+1.8
$[M+H]^+$ (loss of *HETE*)	$C_{37}H_{67}N_{10}O_{14}S$	907.4553	907.456	+0.7	+0.8
$[M+H]^+$ (loss of *HETE* and H_2O)	$C_{37}H_{65}N_{10}O_{13}S$	889.4448	889.443	-1.8	-2.0
AEIRSDL (loss of *HETETE*)	$C_{33}H_{59}N_{10}O_{13}$	803.4258	803.426	+0.2	+0.2
y_6 (loss of *HETEOETE*)	$C_{30}H_{54}N_9O_{12}$	732.3887	732.385	-3.7	-5.1
b_6 (loss of *HETEOETE*)	$C_{27}H_{46}N_9O_{11}$	672.3311	672.326	-5.1	-7.6
y_5 (loss of *HETEOETE*)	$C_{25}H_{47}N_8O_9$	603.3461	603.342	-4.1	-6.8
$[M+2H]^{2+}$ (loss of H_2O)	$C_{41}H_{74}N_{10}O_{14}S_2$	497.2408	497.243	+2.2	+4.4
y_4 (loss of *HETETE*)	$C_{19}H_{36}N_7O_8$	490.2620	490.261	-1.0	-2.0
b_2 (loss of *HETE* and H_2O)	$C_{12}H_{19}N_2O_4S$	287.1060	287.104	-2.0	-7.0
	$C_8H_{17}O_2S_2$	209.0664	209.068	+1.6	+7.7
	$C_6H_{13}O_2S_2$	181.0354	181.035	-0.4	-2.2
	$C_4H_9OS_2$	137.0098	137.009	-0.8	-5.8
	C_4H_9OS	105.0369	105.037	+0.1	+1.0

HETEOETE: hydroxyethylthioethyloxyethylthioethyl-moiety

Data were extracted from the biomarker peak (t_R 7.2 min, Fig. 4B) obtained from μLC-ESI MS/HR MS (PIS) analysis of hair incubated with O-lost (T, 25 mM) followed by pepsin-catalyzed proteolysis. A triple TOF mass spectrometer was used. The corresponding MS/HR MS spectrum is shown in Figure 5A. The exact mass of the single protonated biomarker is *m/z* 1011.4849.

Table SI 5

MS/HR MS data of the double protonated FKTIE(-*HETEOETE*)EL biomarker peptide

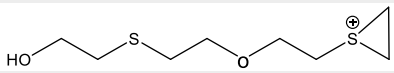
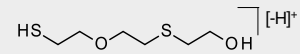
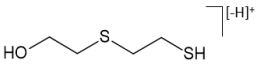
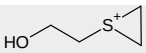
ion	**elemental composition**	***m/z* theoretical**	***m/z* measured**	**Δ *m/z* [mmu]**	**Δ *m/z* [ppm]**
FKTIE(-*HETEOETE*)EL $[M+2H]^{2+}$	$C_{49}H_{84}N_8O_{15}S_2$	544.2743	544.275	+0.7	+1.3
$[M+H]^+$ (loss of *HETE*)	$C_{45}H_{75}N_8O_{14}S$	983.5118	983.506	-5.8	-5.9
$[M+H]^+$ (loss of *HETE* and H_2O)	$C_{45}H_{73}N_8O_{13}S$	965.5012	965.508	+6.8	+7.0
FKTIEEL (loss of *HETEOETE*)	$C_{41}H_{67}N_8O_{13}$	879.4822	879.481	-1.2	-1.4
b_6 (loss of *HETEOETE*)	$C_{35}H_{54}N_7O_{11}$	748.3876	748.388	+0.4	+0.5
b_5 (loss of *HETEOETE*)	$C_{30}H_{47}N_6O_8$	619.3450	619.350	+5.0	+8.1
$[M+2H]^{2+}$ (loss of H_2O)	$C_{49}H_{82}N_8O_{14}S_2$	535.2691	535.270	+0.9	+1.7
$[M+H]^{2+}$ (loss of *HETE* and H_2O)	$C_{45}H_{74}N_8O_{13}S$	483.2543	483.256	+1.7	+3.5
b_3 (loss of *HETEOETE*)	$C_{19}H_{29}N_4O_4$	377.2183	377.219	+0.7	+1.9
y_2 (loss of *HETEOETE* and H_2O)	$C_{11}H_{19}N_2O_4$	243.1339	243.133	-0.9	-3.7
	$C_8H_{17}O_2S_2$	209.0665	209.067	+0.5	+2.4
	$C_6H_{13}O_2S_2$	181.0352	181.035	-0.2	-1.1
	$C_4H_9OS_2$	137.0089	137.009	+0.1	+0.7
	C_4H_9OS	105.0369	105.037	+0.1	+1.0

HETEOETE: hydroxyethylthioethyloxyethylthioethyl-moiety

Data were extracted from the biomarker peak (t_R 11.5 min, Fig. 4D) obtained from µLC-ESI MS/HR MS (PIS) analysis of hair incubated with O-lost (T, 25 mM) followed by pepsin-catalyzed proteolysis. A triple TOF mass spectrometer was used. The corresponding MS/HR MS spectrum is shown in Figure 5B. The exact mass of the single protonated biomarker is *m/z* 1087.5414.

Table SI 6

MS/HR MS data of the double protonated LE(-*HETEOETE*)TKLQF biomarker peptide

ion	elemental composition	*m/z* theoretical	*m/z* measured	Δ *m/z* [mmu]	Δ *m/z* [ppm]
LE(-*HETEOETE*)TKLQF $[M+2H]^{2+}$	$C_{49}H_{85}N_9O_{14}S_2$	543.7823	543.784	+1.7	+3.1
$[M+H]^+$ (loss of *HETE*)	$C_{45}H_{76}N_9O_{13}S$	982.5278	982.529	+1.2	+1.2
$[M+H]^+$ (loss of *HETE* and H_2O)	$C_{45}H_{74}N_9O_{12}S$	964.5172	964.527	+9.8	+10.2
LETKLQF (loss of *HETEOETE*)	$C_{41}H_{68}N_9O_{12}$	878.4982	878.501	+2.8	+3.2
b_6 (loss of *HETEOETE*)	$C_{36}H_{65}N_8O_{11}S$	817.4488	817.452	+3.2	+3.9
y_6 (loss of *HETEOETE*)	$C_{35}H_{57}N_8O_{11}$	765.4141	765.406	-8.1	-10.6
b_6 (loss of *HETEOETE*)	$C_{32}H_{57}N_8O_{10}$	713.4192	713.423	+3.8	+5.3
y_5 (loss of *HETEOETE*)	$C_{30}H_{50}N_7O_8$	636.3715	636.369	-2.5	-3.9
b_5 (loss of *HETEOETE*)	$C_{27}H_{49}N_6O_8$	585.3606	585.361	+0.4	+0.7
$[M+2H]^{2+}$ (loss of H_2O)	$C_{49}H_{83}N_9O_{13}S_2$	534.7770	534.778	+1.0	+1.9
b_4 (loss of *HETEOETE*)	$C_{21}H_{38}N_5O_7$	472.2766	472.274	-2.6	-5.5
b_2 (loss of *HETEOETE* and H_2O)	$C_{15}H_{25}N_2O_4S$	329.1530	329.153	0.0	0.0
y_2 (loss of *HETEOETE*)	$C_{14}H_{20}N_3O_4$	294.1448	294.143	-1.8	-6.1
	$C_8H_{17}O_2S_2$	209.0665	209.067	+0.5	+2.4
	$C_6H_{13}O_2S_2$	181.0352	181.036	+0.8	+4.4
	$C_4H_9OS_2$	137.0089	137.009	+0.1	+0.7
	C_4H_9OS	105.0369	105.036	-0.9	-8.6

HETEOETE: hydroxyethylthioethyloxyethylthioethyl-moiety

Data were extracted from the biomarker peak (t_R 10.5 min, Fig. 4F) obtained from μLC-ESI MS/HR MS (PIS) analysis of hair incubated with O-lost (T, 25 mM) followed by pepsin-catalyzed proteolysis. A triple TOF mass spectrometer was used. The corresponding MS/HR MS spectrum is shown in Figure 5C. The exact mass of the single protonated biomarker is *m/z* 1085.5500.