SPE-UPLC-MS/MS for Determination of 36 Monomers of Alkylphenol Ethoxylates in Tea

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Table S1. Mass spectrometric parameters for monitoring $OPEO_{3-20}$ and $NPEO_{3-20}$.

Analyte	Retention time	Precursor ion (m/z)	Product Ion (m/z)	Cone Voltage (V)	Collision voltage (V)	Analyte	Retention time	Precursor ion (m/z)	Product Ion (m/z)	Cone Voltage (V)	Collision voltage (V)
$OPEO_3$	6.11	356.3	227.2*	15	10	$NPEO_3$	6.77	370.1	121.3*	30	30
			121.2		15				227.1		10
$OPEO_4$	6.11	400.3	271.2	15	25	$NPEO_4$	6.77	414.1	397.2*	30	10
			383.2*		10				270.9		15
$OPEO_5$	6.11	444.3	427.3*	15	14	$NPEO_5$	6.77	458.1	315.0*	30	15
			315.3		16				441.6		10
$OPEO_6$	6.10	488.3	89.1*	22	29	$NPEO_6$	6.76	502.2	133.1*	30	18
			471.4		15				485.4		15
$OPEO_7$	6.08	532.4	89.1*	25	30	$NPEO_7$	6.74	546.3	529.1	30	15
			515.3		15				132.9*		28
$OPEO_8$	6.06	576.4	89.1*	25	30	$NPEO_8$	6.71	590.3	291.1	30	26
			133.2		25				133.3*		30
$OPEO_9$	6.04	620.4	89.1*	23	40	$NPEO_9$	6.68	634.4	291.1	30	30
			133.2		28				133.3*		30
$OPEO_{10}$	6.01	664.4	89.1	25	40	$NPEO_{10}$	6.65	678.5	291.1*	30	30
			133.2*		28				133.3		30
$OPEO_{11}$	5.99	708.5	89.1*	25	40	$NPEO_{11}$	6.62	722.4	177.1	50	30
			133.2		30				133.2*		30
$OPEO_{12}$	5.97	752.5	89.1*	25	40	$NPEO_{12}$	6.60	766.6	290.6	30	30
			133.2		30				132.7*		30
$OPEO_{13}$	5.94	796.6	89.1*	25	40	$NPEO_{13}$	6.56	810.6	793.2	30	20
			277.2		30				133.4*		38
$OPEO_{14}$	5.92	840.6	89.1*	25	40	$NPEO_{14}$	6.54	854.6	177	30	30
			133.2		35				133.0*		40
$OPEO_{15}$	5.90	884.7	89.1*	25	40	$NPEO_{15}$	6.51	898.7	291.1	30	30
			133.2		40				133.2*		40
$OPEO_{16}$	5.88	473.2	89.0*	30	30	$NPEO_{16}$	6.48	479.8	89.3*	30	24
			408.8		10				133.3		20
$OPEO_{17}$	5.85	495.3	89.1*	10	30	$NPEO_{17}$	6.46	986.6	88.9*	28	60
			133		30				133.0		20
$OPEO_{18}$	5.83	517.3	89.1*	10	30	$NPEO_{18}$	6.43	523.8	133.0	10	22
			133.2		30				89.1*		30
$OPEO_{19}$	5.81	539.4	89.3*	10	30	$NPEO_{19}$	6.40	1074.7	89.1*	20	50
			133.2		30				133.2		50
$OPEO_{20}$	5.79	561.4	89.5*	10	35	$NPEO_{20}$	6.34	568.0	132.9	20	27
			132.6		20				89.0*		30

* indicates quantitative ion.

Table S2. Validated parameters of APEO$_{3-20}$ in spiked tea samples.

Analyte	Spiked level (μg/kg)	Matrix standard curve	R²	Recovery %	RSD% (n=5)	LOQ (μg/kg)	Analyte	Spiked level (μg/kg)	Matrix standard curve	R²	Recovery %	RSD% (n=5)	LOQ (μg/kg)
OPEO$_3$	0.024	y = 263254 x + 2715	0.9989	98.6	3.4	0.024	NPEO$_3$	2.79	y = 49852 x + 30818	0.9993	110.7	6.3	2.79
	0.24			83.0	2.8			27.85			79.8	5.1	
	0.47			88.4	6.9			55.70			83.0	3.5	
OPEO$_4$	0.092	y = 109203 x + 2934	0.9980	101.4	8.1	0.092	NPEO$_4$	5.01	y = 20380 x + 19496	0.9993	107.1	6.7	5.01
	0.92			87.0	3.1			50.10			85.2	4.6	
	1.84			92.8	6.0			100.20			90.5	4.4	
OPEO$_5$	0.54	y = 23913 x + 2570	0.9990	103.3	10.8	0.54	NPEO$_5$	4.99	y = 12188 x + 15110	0.9993	101.3	2.9	4.99
	5.37			88.7	4.3			49.90			87.2	4.4	
	10.73			93.7	5.8			99.80			93.7	2.0	
OPEO$_6$	1.31	y = 12685 x + 8309	0.9949	104.1	11.9	1.31	NPEO$_6$	3.75	y = 12123 x + 1432	0.9999	98.4	7.5	3.75
	13.13			87.8	4.8			37.50			91.9	5.0	
	26.26			89.2	5.0			75.00			86.3	3.2	
OPEO$_7$	2.39	y = 11890 x + 6313	0.9988	92.2	5.9	2.39	NPEO$_7$	3.86	y = 8074 x + 10458	0.9982	99.5	2.4	3.86
	23.88			86.6	2.9			38.60			92.3	4.6	
	47.76			91.9	4.9			77.20			84.9	4.3	
OPEO$_8$	3.29	y = 263254 x + 2715	0.9989	95.0	4.6	3.29	NPEO$_8$	3.54	y = 10035 x + 4451	0.9997	104.5	4.3	3.54
	32.90			91.2	4.9			35.35			83.0	6.2	
	65.80			89.0	7.6			70.70			87.9	6.6	
OPEO$_9$	5.16	y = 8207 x + 10957	0.9987	97.5	4.2	5.16	NPEO$_9$	4.29	y = 7291 x + 6178	0.9996	100.4	4.1	4.29
	51.61			88.7	4.2			42.85			89.6	6.4	
	103.22			90.9	5.7			85.70			88.3	4.6	
OPEO$_{10}$	5.83	y = 8009 x + 11700	0.9987	93.5	5.5	5.83	NPEO$_{10}$	4.64	y = 7108 x + 3919	0.9997	100.1	6.8	4.64
	58.26			90.7	5.7			46.35			86.7	5.3	
	116.52			93.3	3.9			92.70			92.2	5.8	
OPEO$_{11}$	6.27	y = 7754 x + 15942	0.9973	98.5	7.7	6.27	NPEO$_{11}$	4.13	y = 6815 x + 5285	0.9992	98.6	7.8	4.13
	62.69			87.4	5.3			41.25			89.4	6.6	
	125.38			90.8	6.5			82.50			89.2	4.1	
OPEO$_{12}$	5.86	y = 8177 x + 15620	0.9974	93.3	5.6	5.86	NPEO$_{12}$	3.74	y = 6052 x + 3328	0.9991	96.9	3.9	3.74
	58.57			88.0	7.4			37.35			82.0	5.6	
	117.13			91.9	6.5			74.70			92.9	3.6	
OPEO$_{13}$	5.36	y = 9044 x + 10924	0.9986	95.3	5.4	5.36	NPEO$_{13}$	3.06	y = 3212 x + 1279	0.9999	99.6	13.0	3.06
	53.62			85.6	5.3			30.55			88.1	6.4	
	107.24			93.2	8.9			61.10			91.2	5.4	
OPEO$_{14}$	5.20	y = 263254 x + 2715	0.9989	93.6	5.5	5.20	NPEO$_{14}$	2.46	y = 1878 x + 660	0.9998	98.3	4.2	2.46
	52.00			84.3	4.3			24.60			79.1	3.9	
	104.00			87.8	7.4			49.20			89.4	6.2	

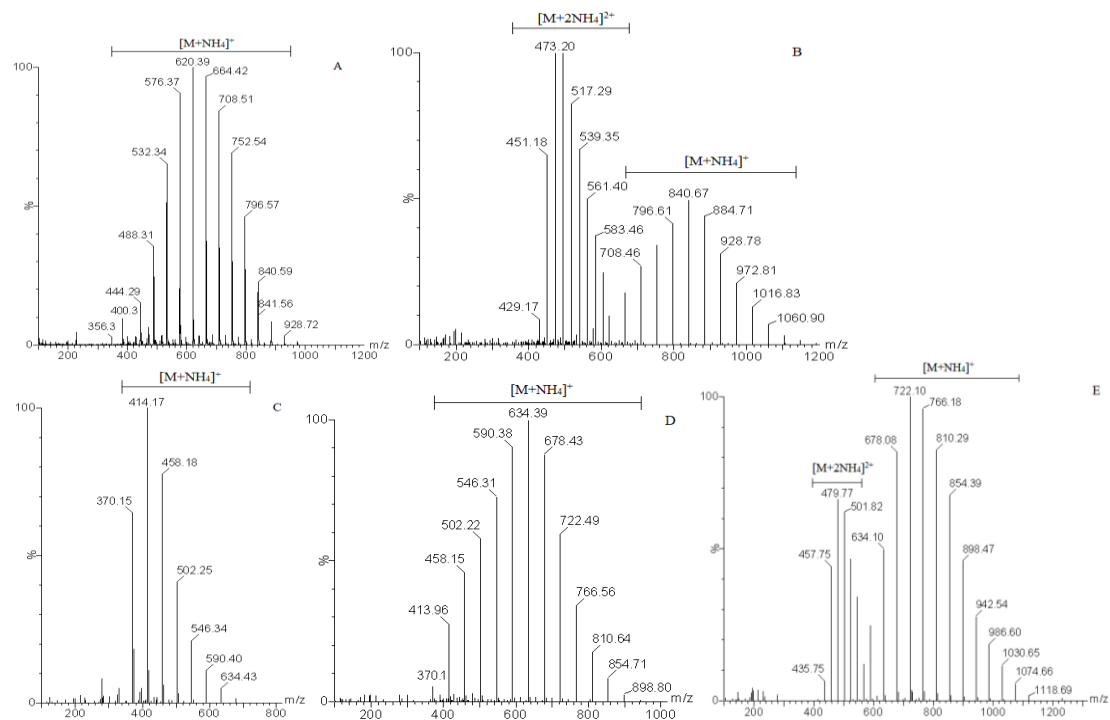|											
OPEO$_{15}$	3.81	y = 9334 x 0.9992 + 6486	89.2	6.9	3.81	NPEO$_{15}$	1.48	y = 5867 x 0.9999 + 233	107.2	9.8	1.48
	38.07		83.8	7.0			14.80		85.5	4.0	
	76.13		88.8	6.6			29.60		91.3	5.2	
OPEO$_{16}$	2.24	y = 5616 x 0.9999 + 163	89.0	8.1	2.24	NPEO$_{16}$	0.86	y = 8816 x 0.9993 + 1169	100.1	8.0	0.86
	22.43		72.6	3.8			8.55		78.4	12.8	
	44.85		82.9	14.5			17.10		90.4	11.9	
OPEO$_{17}$	1.27	y = 12949 0.9999 x + 552	83.2	9.3	1.27	NPEO$_{17}$	0.61	y = 8572 x 0.9978 + 1370	90.9	16.9	0.61
	12.75		78.5	7.1			6.05		84.1	11.9	
	25.49		88.8	2.1			12.10		83.3	11.6	
OPEO$_{18}$	0.56	y = 32169 0.9999 x - 1062	77.8	6.7	0.56	NPEO$_{18}$	0.43	y = 5821 x 0.9997 + 293	105.2	15.4	0.43
	5.56		78.9	2.4			4.25		87.5	3.7	
	11.12		81.6	7.2			8.50		91.0	7.3	
OPEO$_{19}$	0.63	y = 23701 0.9995 x + 1129	76.6	12.5	0.63	NPEO$_{19}$	0.27	y = 9757 x 0.9998 + 228	75.6	7.9	0.27
	6.33		70.3	4.8			2.65		81.5	2.4	
	12.66		77.9	3.6			5.30		87.2	2.0	
OPEO$_{20}$	0.17	y = 23593 0.9988 x + 611	66.9	1.5	0.17	NPEO$_{20}$	0.16	y=23166 x 0.9999 + 375	74.2	13.3	0.16
	1.70		61.8	7.5			1.62		66.9	13.6	
	3.40		72.1	3.1			3.24		62.9	16.9	

Figure S1. Full-scan mass spectra of (A) OPEO (9-10) (n_{EO} = 3-15), (B) OPEO (16) (n_{EO} = 9-20), (C) NPEO (4) (n_{EO} = 9-11), (D) NPEO (9-10) (n_{EO} = 3-15), and (E) NPEO (14) (n_{EO} = 6-20) in 5 mg/kg standards.
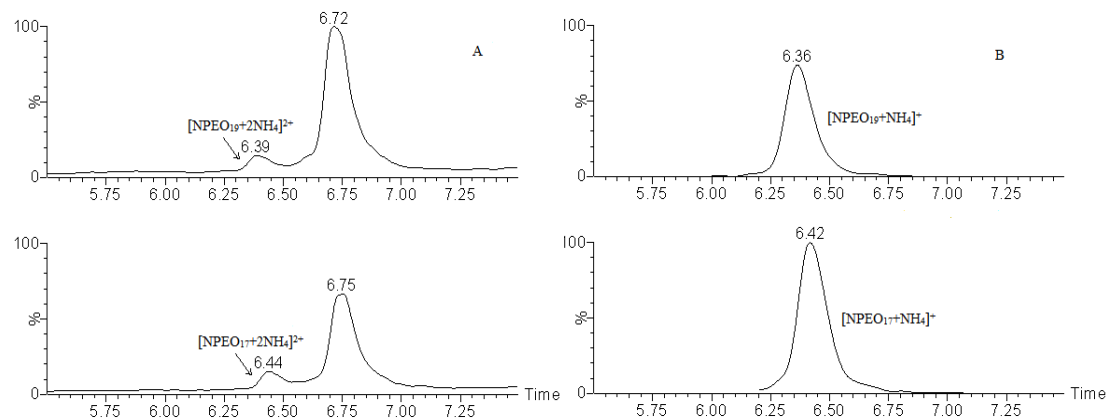

Figure S2. Chromatograms of (A) NPEO$_{17}$ and NPEO$_{19}$ combined two ammonium ions, and (B) NPEO$_{17}$ and NPEO$_{19}$ combined one ammonium ion.
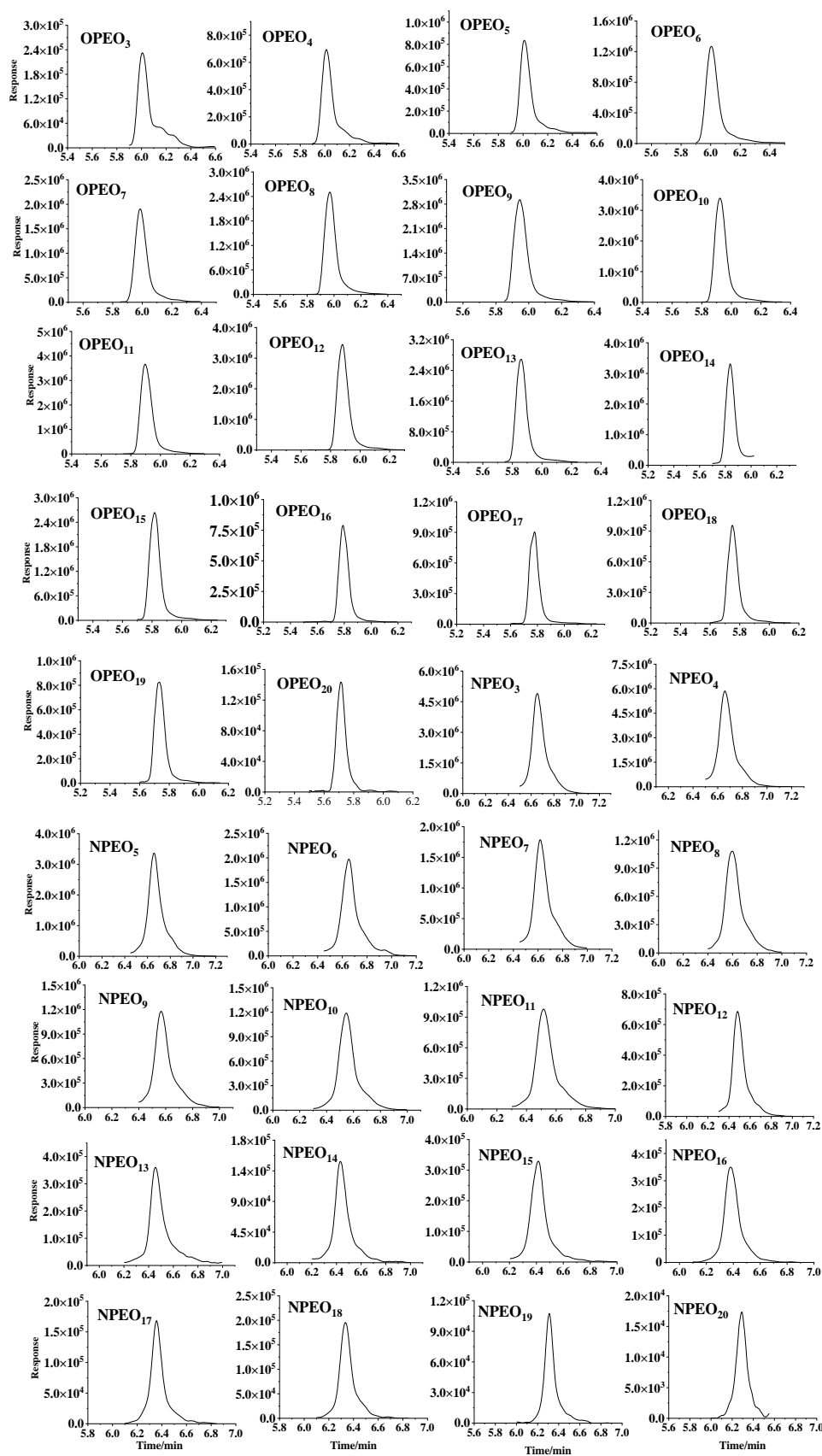
Figure S3. Multiple reaction-monitoring chromatograms of HPLC-MS/MS for blank tea samples spiked at the middle concentration of OPEOs and NPEOs.