Supplementary Information

Benzene-assisted photoionization positive ion mobility spectrometry coupled with a time-resolved introduction for field detecting dimethyl sulfide in seawater

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SI 1. Optimization of dopant and selective analysis

When benzene was used as dopant, the characteristic ions of DMS were identified by a dopant-assisted positive photoionization time of flight spectrometry. And from the mass spectra, we can observed that the m/z of characteristic ion peak for benzene mainly appeared at 78 ($C_6H_6^+$), while two main ion peaks of DMS were achieved at 62 and 124, which is the monomer ($CH_3SCH_3^+$) and dimer (($CH_3SCH_3)_2^+$) ion generated via charge transfer from $C_6H_6^+$, respectively, as seen in Fig. S1.

Table S1 The molecular weight, chemical formula, proton affinity (PA) and ionization

	Substances	Formula	Molecular weight	PA (KJ/mol)	IE (eV)
Analyte	Dimethyl sulfide	c_2H_6S 62.134		830	8.69
	P-xylene	C_8H_{10}	106.167	794.4	8.56
Dopants	Benzene	C_6H_6	78.112	750.4	9.24
	Acetone	C ₃ H ₆ O	58.079	812	9.7
	Dibromomethane	CH_2Br_2	173.835	-	10.24
	Methanethiol	CH ₃ SH	48.1075	773.4	9.44
Potential	Carbon disulfide	CS_2	76.141	681.9	10.073
	Hydrogen sulfide	H_2S	34.0809	168	10.45
interferents	Carbonyl sulfide	COS	60.0751	628.5	11.18
	Sulfur dioxide	SO_2	64.064	672.3	12.35
	Nitrous oxide	N ₂ O	44.0128	549.8	12.889





Fig. S1 Mass spectra of DMS obtained by using benzene-assisted positive



photoionization time of flight spectrometry (BAPI-tof-MS).

Fig. S2 Ionization energy (IE) for dimethyl sulfide, dopants and potential interferents.

SI 2. Two-dimensional identification for eliminating moisture

We compared the Teflon column treated with tape water to that without any treatment, and the results were displayed in Fig. S3. From the signal intensity versus retention time, we could know that DMS and water molecule in gas sample would be resolved by retention time owing to the different retention capacity versus the scale precipitated on the internal surface of PTFE column. Also, the intensity for DMS monomer obtained with PTFE column treated in advance was as twice as that without any treatment.



Fig. S3 Signal intensity for PIPs of DMS and interferent monitored from the ion mobility spectra versus retention time as the PTFE column was (a) treated with tape water in advance and (b) without any treatment.

The ion mobility spectra at retention time of 9 s and 11 s indicated that the PIPs of DMS can be clearly identified from the spectra acquired before 10 s, since none of PIPs of moisture were detected yet, as seen in Fig. S4.



Fig. S4 Ion mobility spectra of 35.84 ppbv DMS gas samples prepared with 90% RH humid air at the introduction time of 9 s and 11 s.



Fig. S5 Signal intensity for PIPs of 35.84 ppbv DMS gas samples versus the moisture contents.

From the curves in Fig. S5, we can obtain that the signal intensity for two PIPs of DMS gathered from the spectra at 9 s just declined slightly with the humidity increasing, declaring that the adverse impact of moisture on sensitivity was basically eliminated. Also, the intensity of dimer peak (DMS 2) didn't enhanced as the moisture increasing, partly verifying the enhancement mechanism of the overlap with other interferents related to moisture.





Fig. S6 PIPs' total intensity curves versus analysis time for one water sample (5 nmol/L DMS) at different bubbling flow rate. Intensity for every point in curves was



introduction analysis.

Fig. S7 Total signal intensity variation of DMS 1 (3.72 ms,) versus analysis time monitored continuously for one water sample (5 nmol/L DMS) at bubbling flow rate of 100 mL/min. The signal intensity was obtained by subtracting background signal. The total analysis time is the sum of bubbling time and retention time. Red dash line represents the signal intensity changes versus the single introduction for IMS analysis,

process.

while the green dash line is the intensity changes during the bubbling stripping



Fig. S8 (a) Ion mobility spectra of 0.5, 1 and 2 nmol/L DMS in artificial seawater at the optimum retention time; (b) the blank signal intensity variation at 3.72 ms versus

analysis time for one artificial seawater sample at bubbling flow rate of 100 mL/min.

The limits of detection (LODs) were calculated based on three times signal-to-noise ratio, as seen in equation S1, wherein s_{bl} is the standard derivation of blank signal of water sample without DMS, S is the slope of calibration curves. For example, the LOD for DMS in artificial seawater was calculated to 0.081 based on the s_{bl} of 0.8177 and S of 30.32, wherein the s_{bl} was obtained from obtained from the ten times blank signal in Fig. S8(b).

$$LOD = 3s_{bl}/S$$
 S1



SI 5. Detection of DMS in the Bohai Sea and North Yellow Sea

Fig. S9 Locations of sampling stations in the Bohai Sea and North Yellow Sea.



Fig. S10 (a) The ion mobility spectra of surface seawater from N14, N20 and B27 stations at the optimum retention time; (b)The DMS in surface seawater from N1、N3、N4 and N6 stations (the North Yellow Sea) obtained by field and lab analysis. Table S2 Data of wind speed, temperature, DMS content and estimation of flux, and

Station	Longitude	Latitude	Wind	Temperatur	Concentration	Flux of DMS
			speed	e (°C)	of DMS	(µmol m ⁻² d ⁻¹)
			(m/s)		(nmol/L)	
B1	120.7256°	38.3361°	5.19	24.60	0.11	0.74
B3	120.1931°	38.3341°	4.44	28.03	23.90	133.96
B4	119.7921°	38.3648°	4.13	27.71	7.82	38.49
B7	119.0084°	38.3183°	4.22	26.90	12.07	60.45
B9	118.9696°	38.6575°	4.66	27.91	11.07	67.33
B11	118.9638°	38.9459°	5.23	27.62	12.31	91.43
B13	119.7106°	39.3112°	4.05	22.80	0.09	0.38
B15	120.3243°	39.1363°	7.38	27.09	0.05	0.74
B17	120.8029°	39.0073°	4.40	27.55	0.07	0.39
B20	120.4426°	39.4861°	4.81	27.10	10.95	69.37
B22	119.8862°	39.0536°	4.53	28.49	19.38	113.84
B24	119.3957°	38.6460°	3.69	28.02	18.72	76.41
B27	119.3881°	38.0027°	2.41	25.20	16.09	30.33
B30	119.9236°	38°	2.84	27.94	12.52	32.79
B31	120.1028°	38.0008°	1.15	29.31	9.86	6.60
N1	123.97°	37.4911°	5.85	26.52	15.74	139.45
N3	123.0386°	37.5004°	4.15	25.20	1.82	8.53
N4	123.2428°	37.7366°	3.02	9.50	0.08	0.15
N6	123.7328°	38.2362°	3.50	26.50	0.05	0.19
N8	123.7512°	39.2439°	6.14	26.46	0.48	4.68
N10	123.2496°	38.7728°	3.32	27.02	15.02	50.00
N12	122.9047°	38.3749°	6.43	27.46	7.62	81.72
N14	122.2527°	37.7581°	6.59	25.87	1.44	15.59
N15	121.7761°	37.7518°	4.21	24.47	0.31	1.46
N17	121.8281°	38.2770°	4.51	25.13	15.05	81.43
N19	122.4928°	38.9936°	4.98	24.57	0.05	0.35
N20	121.8446°	38.5886°	2.65	26.89	3.94	8.97
N22	121.2629°	38.2778°	7.12	22.69	0.11	1.32
N24	121.1728°	37.9382°	4.06	22.08	10.96	46.12

the seawater samples were obtained from 25 July to 2 August, 2019.