Electronic Supplementary Material (ESI) for Analytical Methods.
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Journal: Analytical Methods

Supplementary material of the article:

Evaluation and optimization of influence of silver cluster ions into MALDI-TOF-MS analysis of polystyrene nanoplastic polymer

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Supplementary Table S1. List of chemical reagents.

CAS No	Chemical name	Chemical formula	Molecular characteristic		Manufacturer's name	Supplier
			Weight (g mol^{-1})	Density (g cm^{-3})		
1143-38-0	Dithranol	$C_{14}H_{10}O_3$	226.23	1.40	Dithranol	Sigma-Aldrich, USA
490-79-9	2,5-Dihydroxybenzoic acid (DHB),	$C_7H_6O_4$	154.12	1.37	2,5-Dihydroxybenzoic acid (DHB),	Sigma-Aldrich, USA
	Sinapic acid	$C_{11}H_{12}O_5$	224.21		Sinapic acid	
7761-88-8	Silver nitrate	$AgNO_3$	169.87	4.35	Silver nitrate	Sigma-Aldrich, USA
1634-82-8	2-(4-hydroxyphenylazo) benzoic acid	$C_{13}H_{10}O_3$	214.22	1.30	2-(4-hydroxyphenylazo) benzoic acid	Sigma-Aldrich, USA
29953-71-7	Trans-3-Indoleacrylic acid (IAA),	$C_{11}H_9NO_2$	187.19	1.4	trans-3-Indoleacrylic acid (IAA),	Sigma-Aldrich, USA
120-12-7	Anthracene	$C_{14}H_{10}$	178.22	1.1	Anthracene	Sigma-Aldrich, USA
83-32-9	Acenaphthene	$C_{12}H_{10}$	154.20	1.06	Acenaphthene	Sigma-Aldrich, USA
129-00-0	Pyrene	$C_{16}H_{10}$	203.25	1.27	Pyrene	Sigma-Aldrich, USA
2966-50-9	Silver trifluoroacetate	CF_3COOAg	220.88	N/A	Silver trifluoroacetate	Sigma-Aldrich, USA
10125-13-0	Copper (II) chloride	$CuCl_2$	134.45	3.39	copper (II) Chloride	Sigma-Aldrich, USA
109-99-9	Tetrahydrofuran	$(CH_2)_3CH_2O$	72.11	0.89	Tetrahydrofuran	Sigma-Aldrich, USA
75-05-8	Acetonitrile	CH_3CN	41.05	0.79	Acetonitrile	Sigma-Aldrich, USA

Optimization of PSN sample mixture for the MALDI analysis

PSN sample was prepared by mixing silver trifluoroacetate, pyrene and polystyrene and the ratio of this mixture was chosen and optimized, where different volumes were varied. The intensities of different mass spectra results were compared one to another to confirm the proper ratio to use for the PSN analysis. The mass spectra obtained to investigate PSN with pyrene, anthracene and silver trifluoroacetate were almost the same. Therefore, the ratio variation was done to see whether both matrices could produce distinguished mass spectra (Fig. 1).

Solutions were prepared by mixing matrix, analyte and cation while varying the relative proportions of the components such that nine unique samples mixtures are made. For example, keeping the amount of added pyrene stock solution constant (e.g., 10 µL), vary the amount of PSN solution by a factor of two (e.g., 4, 2, and 1 µL), while also varying the amount of AgTFA solution by a factor of two (e.g., 20, 10, and 5 µL). These samples effectively produced a 3 x 3 grid of samples with the two different concentration variables on the x and y axes.

Analyte →

Counter Ion ↑

	1µL	2µL	4µL
20µL	20:20:1	20:20:2	20:20:4
10µL	10:20:1	10:20:2	10:20:4
5µL	5:20:1	5:20:2	5:20:4

Fig. 1 Variation of silver trifluoroacetate and polystyrene nanoplastics ratio for optimization

The 3x3 grid for sample ratio determination was done using a 3x3 grid of samples, the relative concentrations of cationization agent-analyte-matrix were systematically varied to empirically determine an optimized sample preparation. This was typically done by holding one of the three variables constant (20 μL of matrix solution) while increasing the amount of the other two (cationization agent (y-axis) and analyte (x-axis) components) by a set multiple (2-fold in the example depicted).

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