Electronic Supplementary Material (ESI) for Analytical Methods.

Synthesis and application of new silver and sulfur decorated S-doped reduced graphene oxide in ultra-trace analysis of pesticides by ion mobility spectrometry

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Optimization of other parameters

Effect of type and volume of buffer

Acetate, citrate, and Britton-Robinson buffers (pH=5.0) were used to evaluate the effect of buffer type. According to results in Fig. S6 the acetate buffer was selected as best buffer. Subsequent experiments were carried out on the volume of the optimum buffer within the range of 0.5–3 mL, and the best results were attained with 1 mL of acetate buffer with the total concentration of 0.1M in pH=5.0.

Effect of the sorbent amount

The amount of adsorbent should not be so small that the extraction is not complete and not so high that it causes high solvent consumption. Therefore, the amount of adsorbent was changed from 8 to 20 mg. Based on the results in Fig. S7, the value of 8 mg was selected as the optimum amount.

Effect of the volume of desorption solvent

The volume of desorbed solvent should be optimized to the minimum possible amount due to the adverse effects of the solvent organic on the environment. Accordingly, the volume of methanol was changed from 80 to 250 μL. The results of Fig. S8 show that a volume of 80 μL is not sufficient to extract the analytes from the adsorbent. On the other hand, by increasing the volume of solvent by more than 100 μL, the extraction efficiency decreases. Therefore, 100 μL was selected as the optimum volume.

Effect of sorption and desorption time

To obtain a satisfactory adsorption equilibrium, adequate contact time between the adsorbent and analytes is required. Due to the specific surface area of the adsorbent (Ag/S/S-RGO), the adsorption process occurred rapidly and 1 min was selected as the best sorption time (Fig. S9). To ensure complete desorption of pesticides from the sorbent determining suitable desorption time is critical. Based on the experiments, 2 minutes was also optimized as the best desorption time.

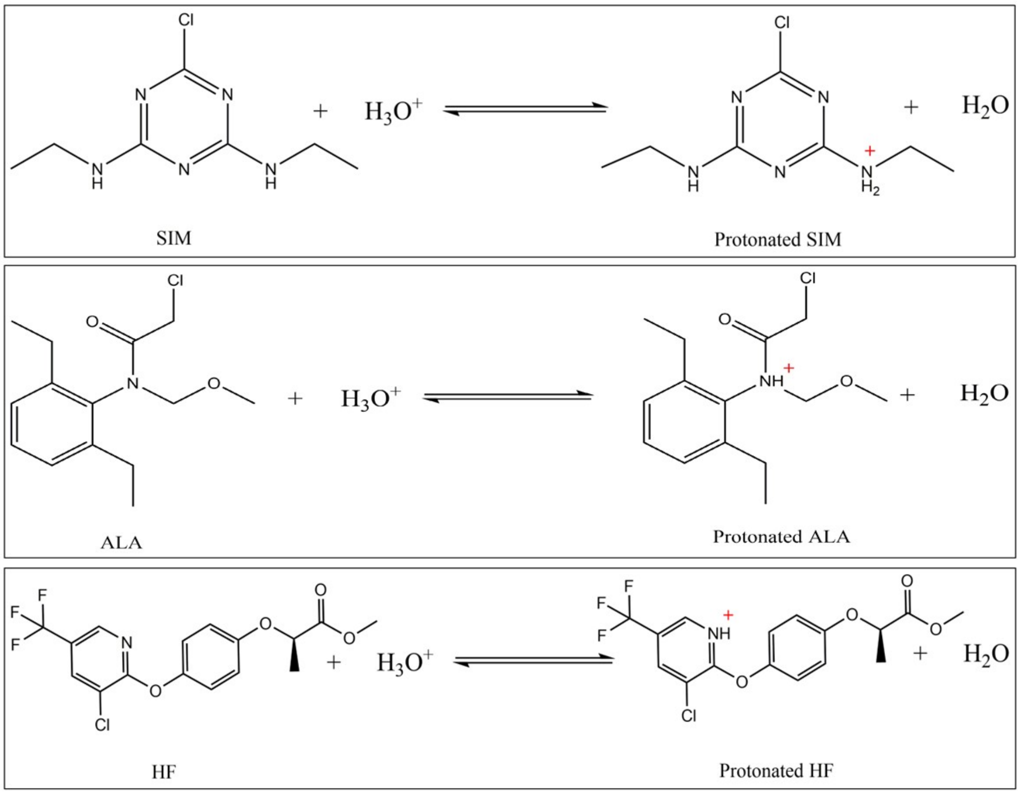
Adsorption capability of Ag/S/S-RGO

To investigate the adsorption capability of Ag/S/S-RGO nanocomposite for various types of pesticides a series of experiments were done and the absorption capacity of nanocomposite for different pesticides was determined. Based on the results, adsorption capacity for herbicides (fenoxaprop: 462, butachlor: 475, hexaflumuron: 731, bensulfuron: 825, and acetochlor: 475 mg g^{-1}), insecticides (amitraz: 950, diazinon: 860 and clofentezine: 350 mg g^{-1}), and fungicides (carbendazim: 643 mg g^{-1}) were obtained. It should be mentioned that sulfur-containing pesticides (bensulfuron and diazinon), due to strong interaction with silver nanoparticles are not easily desorbed from the adsorbent surface.

Reduced ion mobility

Since the mobility and drift time of the analytes in ion mobility spectrometry are affected by the instrument's drift region temperature (T) and ambient pressure (P) the comparisons are facilitated by reporting a quantity as nearly independent of these variables as possible. In theory, reduced ion mobility (K_0) is a constant which is independent of temperature and pressure for a given compound in a given buffer gas and is a qualitative indicator of the ion's identity. The K_0 value in IMS is fundamentally related to the ion's collision cross-section. The reduced ion mobility constant can be calculated by $K_0 = K\frac{P}{760}\frac{273}{T}$. where P is the pressure in the drift region in Torr, T is the buffer gas temperature in Kelvin and K is the ion mobility constant ($cm^2\ V^{-1}\ s^{-1}$). The ion mobility constant is calculated by $K = \frac{L^2}{Vt_d}$. where L is the length of the drift region in cm, V is the total voltage drop in volts across the drift region, and t_d is the time the ion spends traveling the distance L in seconds [1]. The reduced ion mobility of the SIM, ALA, and HF are calculated and reported in Table S1.

Supplementary Figures and Scheme:



Scheme S1. Protonation reaction of simazine, alachlor, and haloxyfop in corona discharge ionization source

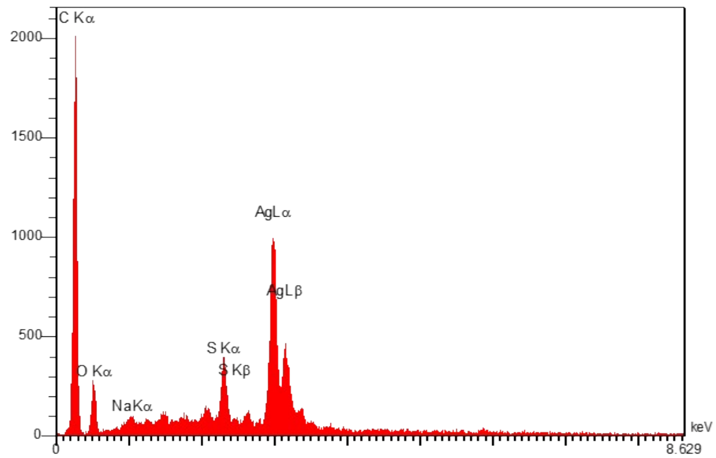


Fig. S1. The EDX spectrum for Ag/S/S-RGO nanocomposite.

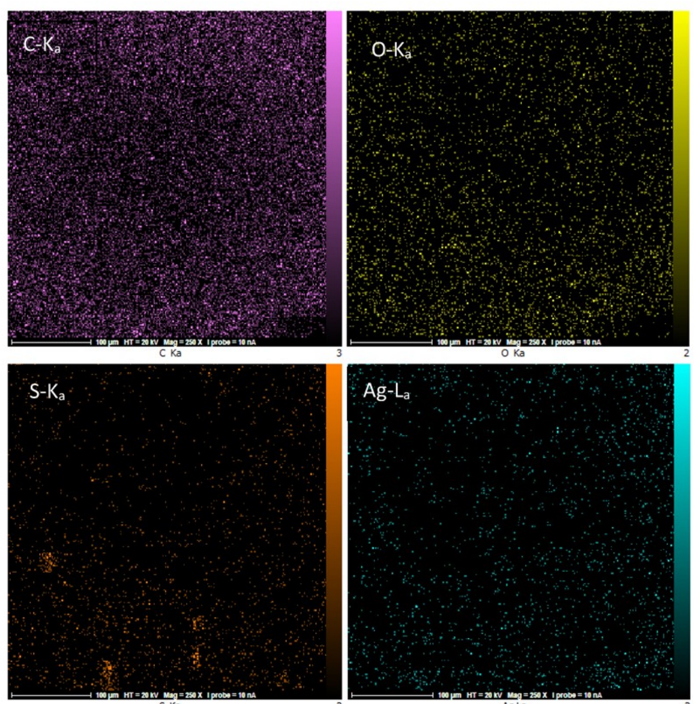


Fig. S2. The EDX map for Ag/S/S-RGO nanocomposite.

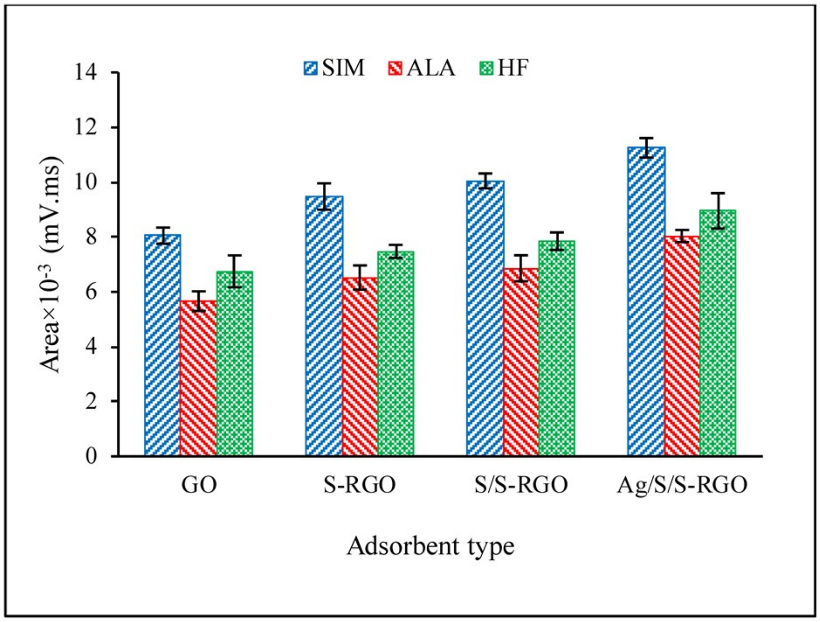


Fig. S3. Adsorption efficiency study of single and multi-component adsorbents.

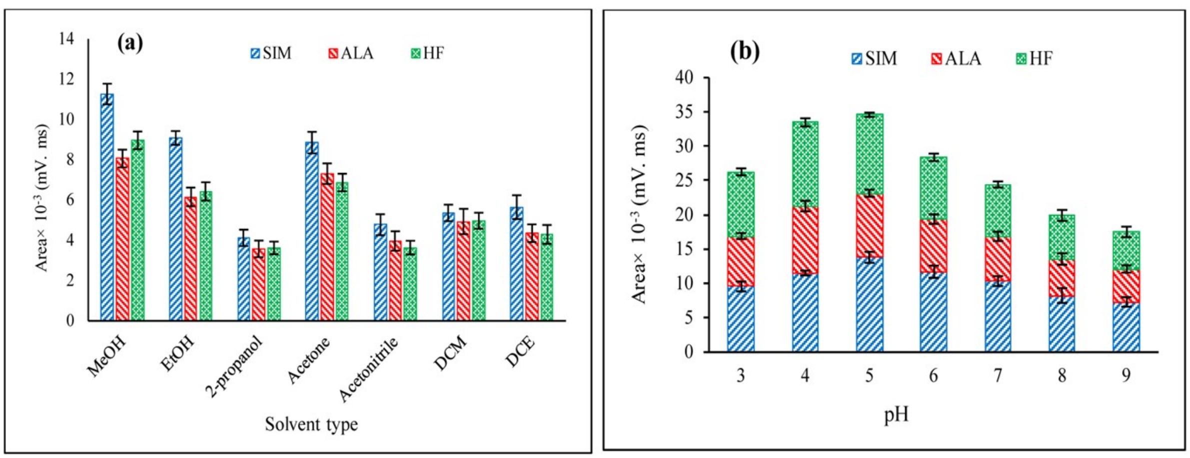


Fig. S4 Effect of **a)** Type of desorption solvent, and **b)** pH on the DSPME method.

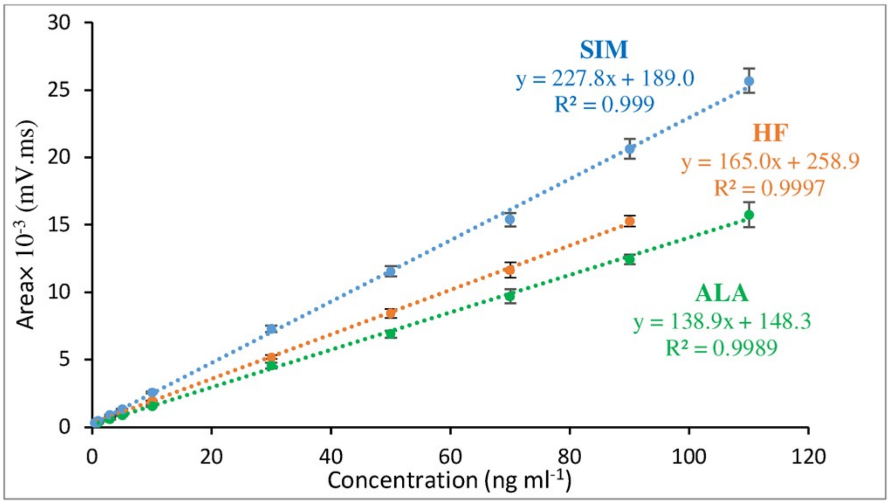


Fig. S5. The calibration plot of simazine, alachlor, and haloxyfop

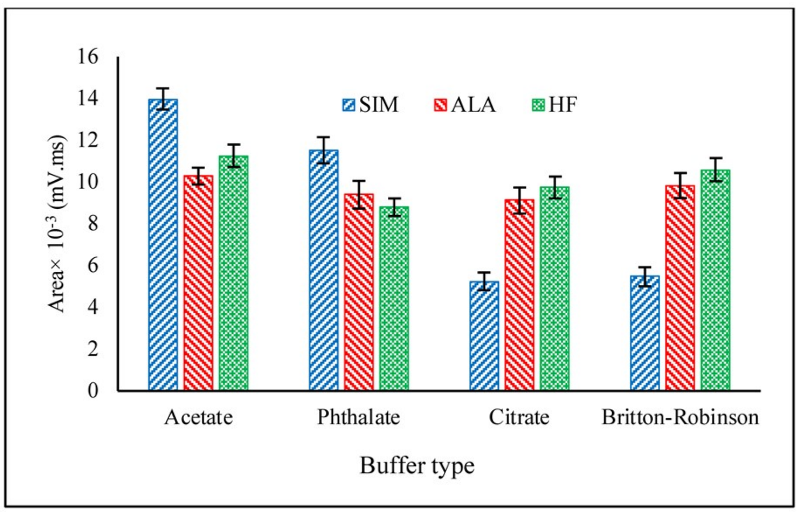


Fig. S6. The effect of buffer type on the extraction efficiency of the DSPME method.

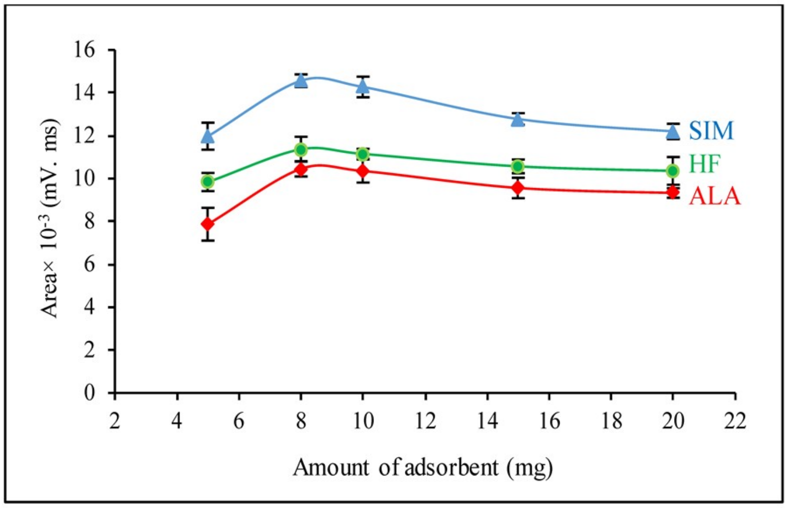


Fig. S7. Effect of the sorbent amount on the simazine, alachlor and haloxyfop extraction.

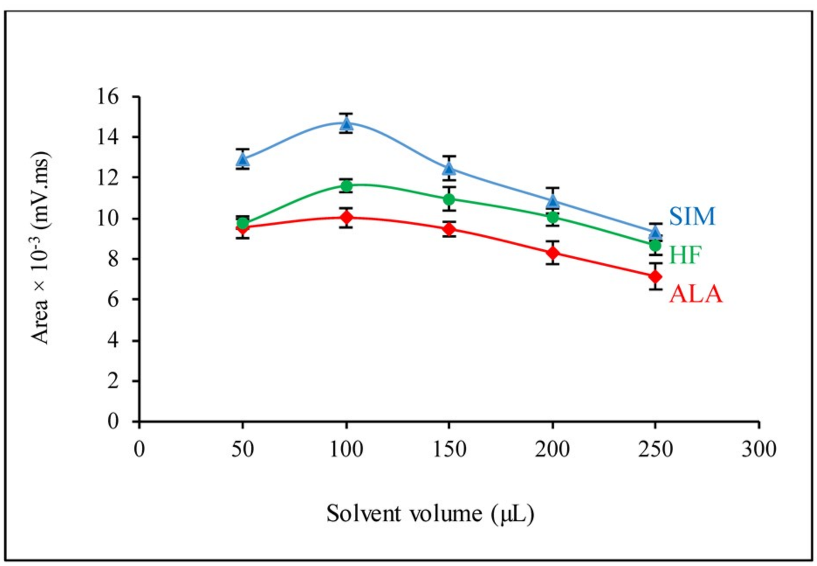


Fig. S8. The effect of desorption solvent volume on the extraction efficiency of the DSPME method.

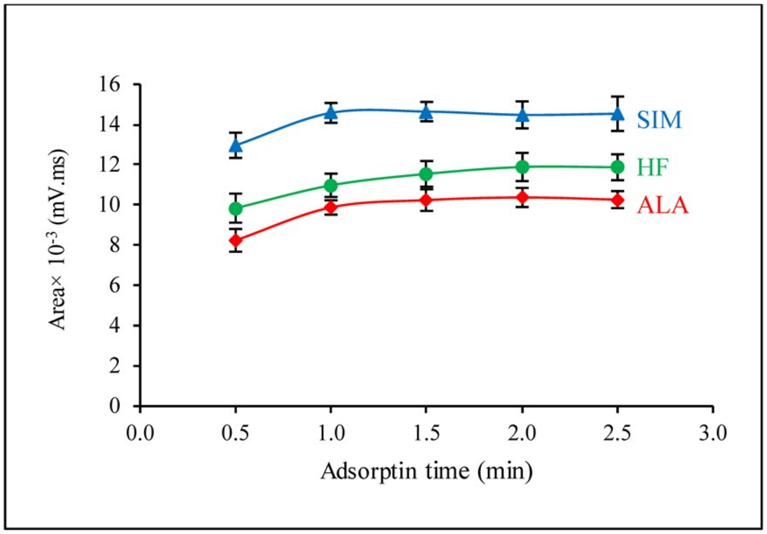
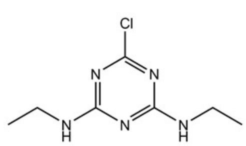
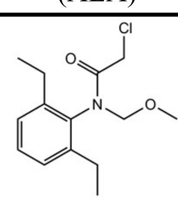
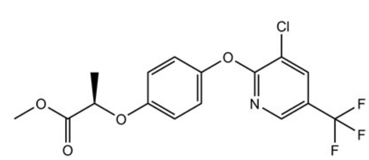


Fig. S9. The effect of sorption time on the extraction efficiency of the DSPME method.

Supplementary Tables:

Table S1: Physicochemical properties of simazine, alachlor, and haloxyfop

Properties	Simazine (SIM)	Alachlor (ALA)	Haloxyfop (HF)
Chemical structure			
Empirical formula	$C_7H_{12}ClN_5$	$C_{14}H_{20}ClNO_2$	$C_{15}H_{11}ClF_3NO_4$
Molecular weight (g mol^{-1})	201.66	269.77	375.73
pK_a	1.62	1.2	2.9
Boiling point (^oC)	365.8	399	390

Flashpoint (°C)	175	137	190
Collision cross section [M+H]$^+$ (Å^2)	143.0[2]	156.4[2]	179.9[3]
(K_0)[a]	7.98	7.32	5.72

[a]Reduced mobility constant of ion mobility spectrometry

Table S2. Optimum instrumental parameters for IMS

optimum instrumental parameters	
Injection port temperature	260 °C
Cell temperature	200 °C
Drift voltage	8000 V
Corona voltage	2500 V
Carrier gas flow rate	400 mL min^{-1}
Drift gas flow rate	800 mL min^{-1}
Shutter grid pulse width	130 µs

Table S3. The BET results for Ag/S/S-RGO nanocomposites

Parameter	Value
V_m [a](STP)	1.6711 cm^3 g^{-1}
$a_{s,BET}$[b]	7.2736 m^2 g^{-1}
C[c]	113.67
Total pore volume (p/p0=0.990)	0.027149 cm^3 g^{-1}
Mean pore diameter	14.93 nm

[a]The volume of gas absorbed to form a layer on the surface of the nanocomposite
[b]Specific surface area of the nanocomposite
[c] constant depends on the gas absorption enthalpy

References:

1 R. Fernández-Maestre, C. S. Harden, R. G. Ewing, C. L. Crawford and H. H. Hill, *Analyst*, 2010, **135**, 1433.

2 A. Celma, D. Fabregat-Safont, M. Ibàñez, L. Bijlsma, F. Hernandez and J. V. Sancho, *Zenodo*, , DOI:10.5281/ZENODO.3966751.

3 L. Bijlsma, R. Bade, A. Celma, L. Mullin, G. Cleland, S. Stead, F. Hernandez and J. V. Sancho, *Anal. Chem.*, 2017, **89**, 6583–6589.