



An overview of the Speed of Sound sensor; theory and application

S. Molisso, M. Naderi, M. Acharya, M. Guo, C. Hewson, D. Burnett, A.R. Garcia, S. Wang, D. Bruere, R. Price and D.R. Williams
Surface Measurement Systems Ltd

This Application note will focus on the principles behind the Dynamic Vapour Sorption (DVS) Speed of Sound (SoS) sensor. It will also detail which solvents are currently calibrated in the DVS systems and demonstrate the ability of the SoS sensor to accurately determine the concentration of organic vapor in the DVS experiment.

Introduction

There are many techniques available to measure online gas composition such as near-infrared spectroscopy (NIR), Fourier transform infrared spectroscopy (FTIR), flame ionization detectors (FID), thermal conductivity detectors (TCD) and dew point analysers (DPA).

While these techniques can be used in industrial processes to measure gas composition, common drawbacks of these methods include the lack of calibration transferability, high cost, long method development and lengthy measurement times, which are undesirable for online gas composition measurements.¹⁻³

The speed of sound (SoS) of a gas system can be used as an acoustic measurement of a gas composition and has become popular in recent years due to its well-established theory and high accuracy.

This application note will give a basic introduction into SoS theory, and how it is applied to Dynamic Vapour Sorption (DVS) systems to determine vapour concentration.

Speed of Sound - basics

The speed of sound (SoS) of a gas is an acoustic measurement which is a fundamental property of a gas system. The SoS is dependent on gas composition, temperature, pressure, and acoustic frequency. The SoS in a gas system, W , can be described by the following equation:

$$W^2 = (W^{id})^2(1 + K_{corr}) = \frac{C_p^{id}RT}{C_v^{id}M}(1 + K_{corr}) \quad (1)$$

where W^{id} is the SoS of the ideal gas, K_{corr} the correction factor to account for the non-ideality of the gas system, R the universal gas constant, T the temperature, M the molecular weight of the gas and finally the ideal gas specific heat capacities at constant pressure (C_p^{id}) and volume (C_v^{id}).

If the temperature, pressure, and acoustic frequency of the gas composition are known, the gas composition itself can therefore be correlated to the SoS as shown in Equation 1. It is by these principles that the SoS can be used to determine the concentration of vapour in a DVS experiment.



Time Of Flight (ToF) Measurements

Ultrasonic transducers can act as both ultrasound transmitters and receivers. The design of the Surface Measurement Systems developed SoS sensor has a double transducer configuration, with an ultrasound transmitter and receiver transducer to measure the ToF.⁴ The SMS SoS design was awarded US Patent Number 10,983,094.

ToF measurements use acoustic pulses: a single pulse of constant frequency travelling over a fixed distance has the following relation to the SoS:

$$W_m = \frac{L}{t_m} (1 + K'_{corr}) \quad (2)$$

Where W_m is the measured SoS, L is the pathlength and t_m is the measured ToF. Due to diffraction of the ultrasonic wave off the physical boundaries that exist in the sensor, K'_{corr} is used as a correction.

This measurement process is simple, has high precision and allows for fast online SoS measurements.

In the sensor, the SoS is determined by the time difference between the first signal received on the transmitter, and the second signal which has reflected off the transmitter (Figure 1).

To obtain the ToF, the time (Δt) between two points (t_1 and t_2) on the received wave pulses must be calculated (Figure 2).

The points are determined when the amplitude of the wave pulses reach a preset threshold. This gives an approximate Δt , which is further refined.

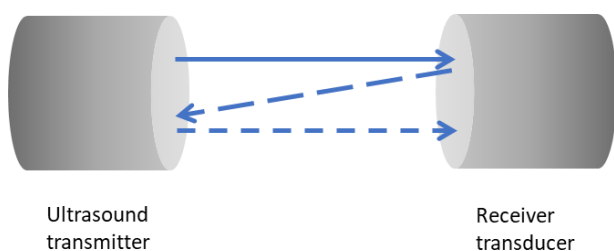


Figure 1. The path travelled by an ultrasound wave in the SoS sensor to measure ToF.

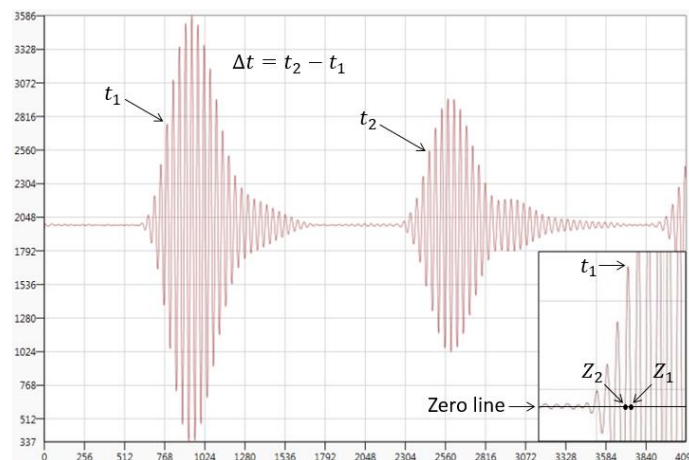


Figure 2. A received signal waveform showing the t_1 and t_2 of the two pulses, inset showing the Z_1 and Z_2 of the first pulse. (x-axis: time, y-axis: amplitude)⁴

The algorithm used in the SoS sensor calculates two zero crossing points before and after each t for these waveforms (Z_2 and Z_1 for waveform one, Z'_2 and Z'_1 for waveform two.), The time between each corresponding Z pair is averaged to give a true Δt . These calculations are repeated at 100Hz, and 100 single measurements are averaged to give a resolution for the ToF of ± 1 ns.

SoS Experimental Procedure

A Dynamic Vapor Sorption (DVS) Advantage instrument was used to generate binary gas mixtures of heptane and dry air. The system was configured to allow gas composition measurement using both gas density and SoS. The speed of sound sensor (Figure 3) measured the SoS of the binary mixture, while the outlet flow entering the test chamber of the DVS allowed gas density measurements using the Archimedes principle [Application Note 47].

In the microbalance of the DVS system, a closed hollow glass sphere was suspended on one side of the balance, with a counterweight of similar mass but smaller volume on the other side. This setup was used to measure the gas density. Further details of this method can be found in the literature.⁴

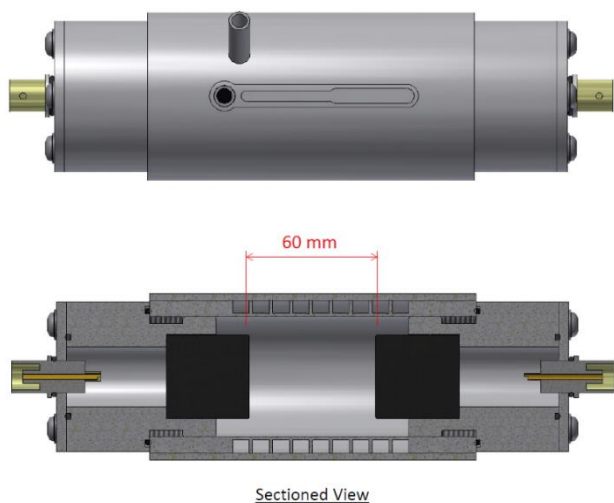


Figure 3. A cross-section view of the SoS sensor.

Figure 4 shows the experimental procedure for measuring the heptane/dry air binary gas mixtures. The volume difference on the two sides of the balance was calculated, allowing pure gas with a known density, and a gas mixture with an unknown density to be passed through. From this, the density of the unknown gas mixture can be calculated.

The raw data for an experiment is shown in Figure 5. When the target mole fraction of the heptane/dry air binary gas mixture increases, the increased gas density in the testing chamber of the DVS results in a decrease of the mass readings. This corresponds to a ToF increase in the denser vapor, which results to a shorter SoS measurement, as per Equation 2.

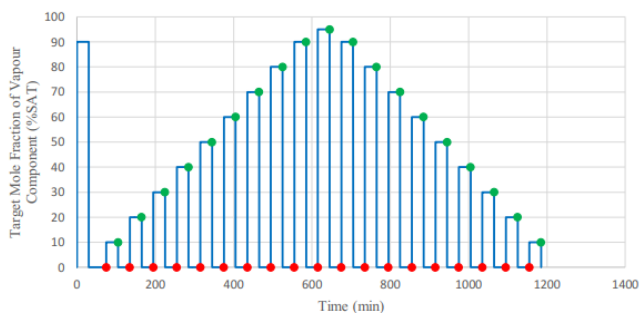


Figure 4. A typical experimental procedure for the measurements on heptane/dry air binary gas mixtures.⁴

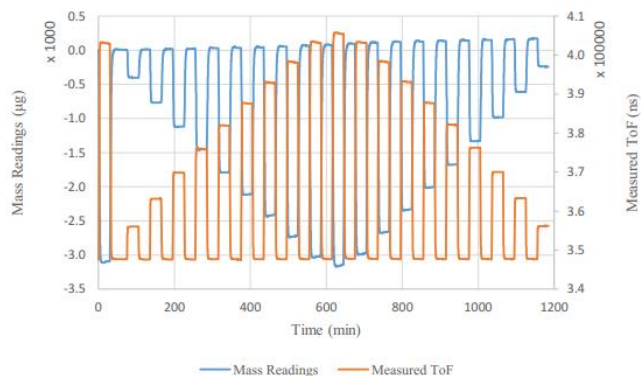


Figure 5. Raw experimental data for mass reading and measured ToF (heptane/dry air at 35 °C)⁴

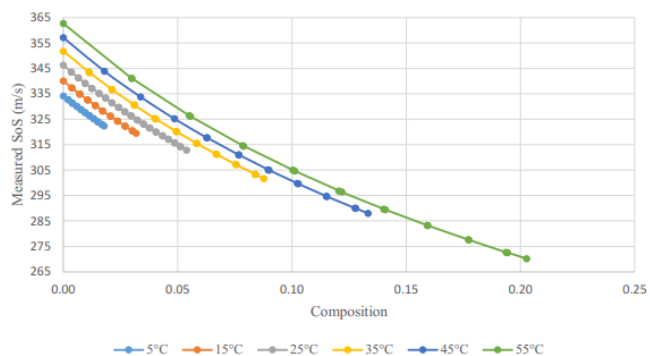


Figure 6. SoS measurements for different mole fraction compositions for heptane/dry air binary gas mixtures at different temperatures.⁴

Different gas compositions of heptane/dry air mixtures were examined which showed a nearly linear relationship with the SoS measurements (Figure 6.) The SoS measurements were found to be particularly sensitive to the temperature of the system.

Solvents Currently Calibrated using SoS sensor

The SoS measurement experiments have been applied to a range of solvents to calibrate vapour partial pressure readings in DVS instruments.

The following table shows which solvents are currently calibrated for the SoS sensor, including the carrier gas and temperature range used for the calibration.

Table 1: The solvents calibrated using the SoS Sensor and their associated parameters (* A more detailed breakdown of the calibrated temperature ranges can be found in the literature)

Carrier Gas	T min	T max	Solvent	
Air/N ₂	15 °C	15-50 °C*	DCM	Hexane
			Acetone	Methanol
			Chloroform	THF
	15 °C	50-85 °C*	Cyclohexane	Heptane
			Ethanol	Isopropanol
			Ethyl Acetate	1-Propanol
	15 °C	85 °C	1-Butanol	Nonane
			Benzyl Acetate	Octane
			Decane	o-Xylene
			d-Limonene	Phenol
DMSO			Toluene	
		m-Xylene	Water	
N ₂ only	15 °C	58 °C	Acetonitrile	
	15 °C	60 °C	Dioxane	
	15 °C	85 °C	Ethylbenzene	
	15 °C	16 °C	Pentane	

Speed of Sound Sensor Normalization

The SoS sensor can be easily and quickly normalized when a carrier gas and solvent combination is used, or if the temperature of the experiment is changed since its last calibration.

The P/P₀ in the system must be at zero before the SoS sensor is normalized. The SoS sensor can be found in the instrument control panel in the DVS Control Software.

This panel will display when the last time the sensor was zeroed at, and what temperature the system was at the time of zeroing (Figure 7). It is recommended that the system is left to reach the full equilibrium temperature before zeroing the sensor.

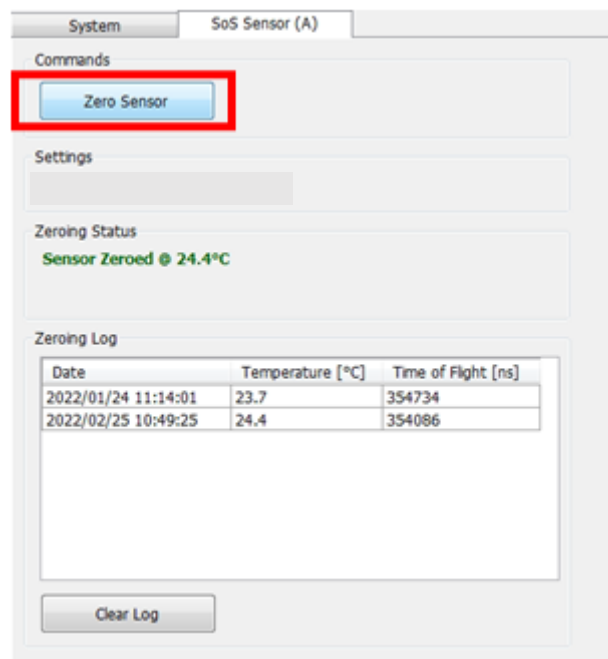


Figure 7. The SoS sensor panel, where the sensor can be zeroed for calibration before DVS experiments.

SoS Performance in the DVS

To examine the performance of the SoS sensor in the DVS, several experiments were performed with different solvents and temperatures. This section will detail some of these experiments, and the conclusions that can be drawn from the data. All data was collected using a DVS-Resolution.

i) SoS sensor accuracy with Acetone

Figure 8 shows the generation of acetone vapour using the SoS sensor. This was performed in a closed loop configuration, where the SoS constantly provides feedback to the Mass Flow Controllers of the DVS to ensure the Target P/P₀ is accurate. As can be seen in this figure, the generation of acetone vapour using this method is within $\pm 0.3\%$ of the target acetone partial pressure.

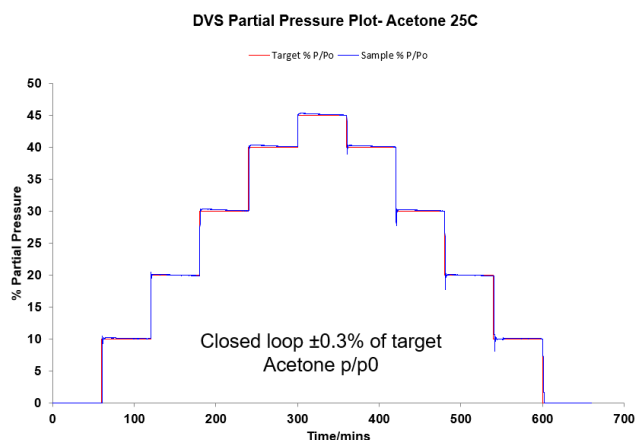


Figure 8. DVS plot for the generation of acetone partial pressure using the SoS sensor in a closed loop configuration.

This demonstrates the ability of this sensor to provide high accuracy partial pressure generation with organic solvents.

ii) Comparison of SoS Sensor to Rotronic probe

Figure 9 demonstrates the comparison between the SoS sensor for measuring and generating %RH in a closed loop configuration, and the Rotronic humidity probe which is used in other DVS instruments. These humidity sensors are based on a small capacitor consisting of a hygroscopic dielectric polymer placed between a pair of electrodes. These probes have been well-established for reliable humidity measurements over a broad range of industries, applications, and conditions (accuracy +/- 0.8%RH at 25C).

The use of the SoS sensor closely matches that of the Rotronic probe, further validating the use of the SoS sensor in DVS measurements.

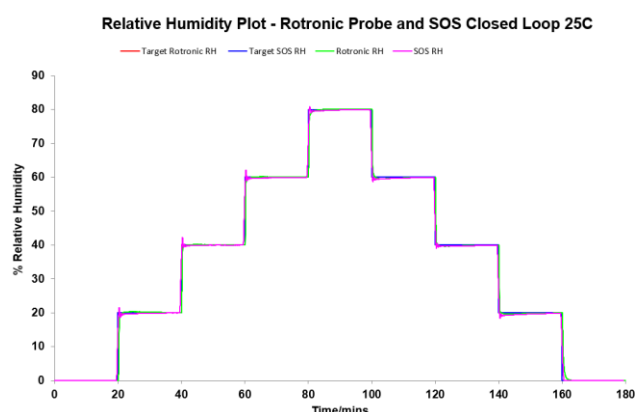


Figure 9. DVS plot showing %RH generation using both the rotronic probe and the SoS sensor, showing good agreements between the two methods at 25°C.

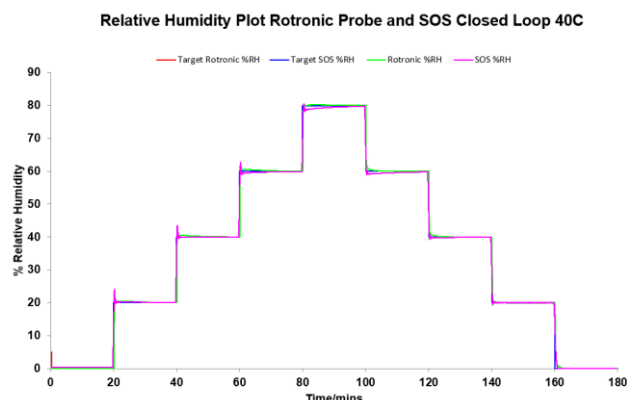


Figure 10. DVS plot showing %RH generation using both the Rotronic probe and the SoS sensor, showing good agreements between the two methods at 40°C.

At higher temperatures the same matching is also seen in Figure 10. This verifies the similarity in readings for the Rotronic probe and the newly developed SoS sensor.

iii) Dual SoS sensors

The DVS Resolution Advanced is equipped with two SoS sensors, allowing generation and control of two vapor streams using the SoS. Although the SoS can measure and control relative humidity, SMS recommends using the Rotronic sensor for humidity-based experiments. The Rotronic sensor can outperform the SoS in terms of accuracy over certain temperature ranges (i.e. at and below 25 C). For this reason, the DVS Resolution Advanced is supplied with both a Rotronic probe and SoS on side A. Combined with a switching valve, this allows for the greatest flexibility in vapor generation and control over a wide temperature range.

Figure 11 demonstrates this capability with a sorption experiment measuring the uptake of octane whilst at the same time changing the %RH using the SoS detection method.

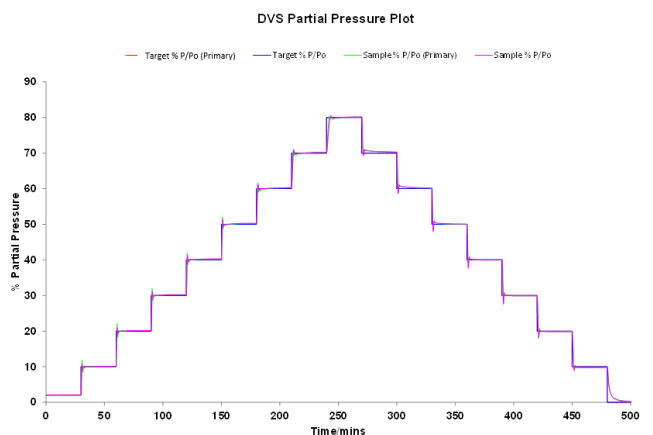


Figure 11. DVS plot for the generation of octane and water partial pressure using two SoS sensors in a closed loop configuration.

From the figure the target partial pressures and actual partial pressures generated are a good match, further supporting the use of the SoS sensor in DVS systems.

Co-adsorption of o-Xylene and p-Xylene

A dual channel SoS configuration allows co-adsorption of two different organic vapours to be measured. Figure 12 and 13 shows the partial pressure plot of o-Xylene and p-Xylene sorption on a zeolite sample at 50°C using the DVS Resolution Advanced.

Figure 12 shows a large increase in mass for o-Xylene sorption at 10% P/Po correlating to the pore filling of the zeolite. Above these partial pressures, there is little uptake until 95% P/Po where a large increase indicates either intermolecular condensation of o-Xylene,⁵ or occupancy at new sites within the zeolite structure such as a pore channel.⁶

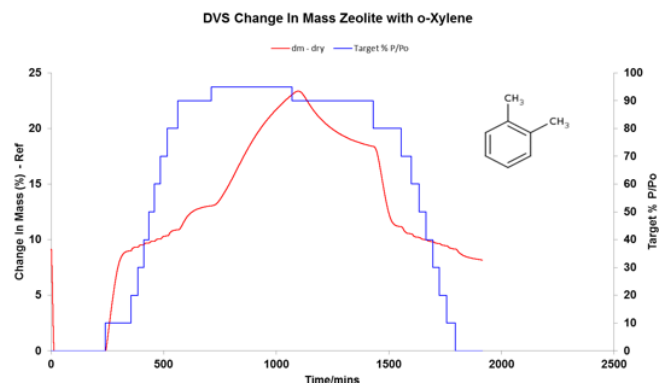


Figure 12. The DVS change in mass plot for o-Xylene sorption on Zeolite at 50°C.

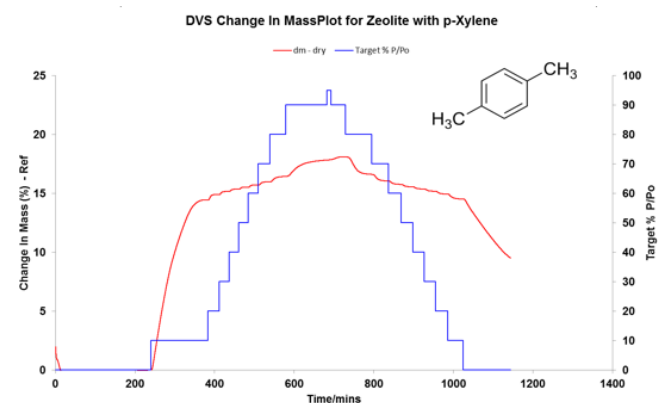


Figure 13. The DVS change in mass plot for p-Xylene sorption on Zeolite at 50°C.

The sorption of p-Xylene shows a similar uptake behaviour, with reduced condensation at high partial pressures. The greater initial uptake suggests the zeolite has a better selectivity for p-Xylene over o-Xylene in its porous structure. There is no significant increase in sorption at high P/Po in comparison to the sorption of p-Xylene.

For the co-adsorption experiment, Figure 14 shows the partial pressure plot for both p-Xylene and o-Xylene.

Figure 15 shows the kinetic data for mass uptake for the zeolite sample in the co-sorption experiment. There is a reduced uptake of both vapours at low P/Po in comparison to sorption of the vapours separately.

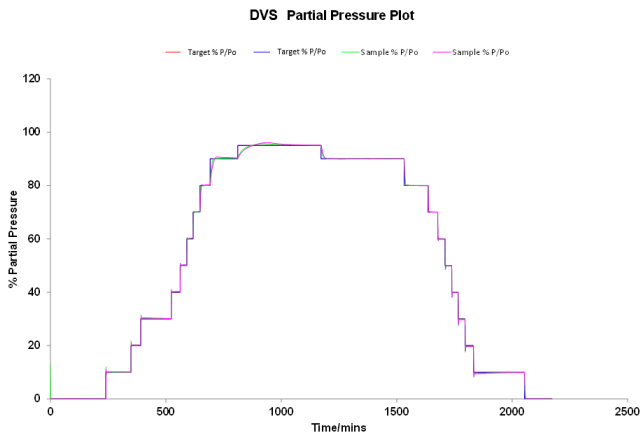


Figure 14. DVS partial pressure plot of *o*-Xylene and *p*-Xylene measured by dual channel SOS at 50°C.

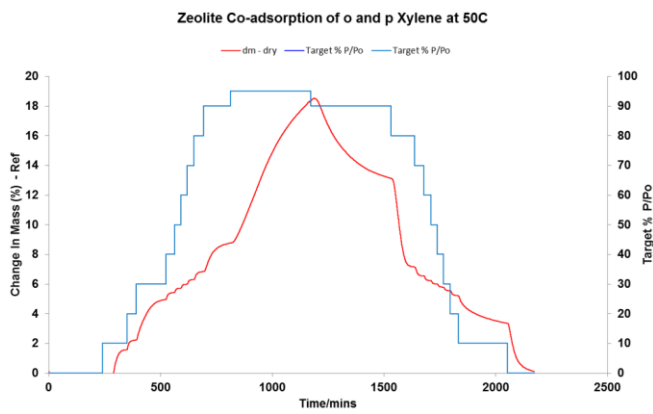


Figure 15. Zeolite co-adsorption of *o*-Xylene and *p*-Xylene at 50°C.



The zeolite sample absorbs more o-Xylene than p-Xylene in the separate sorption experiments, while the dual sorption experiment shows a reduced sorption capacity for both. This is especially evident at low P/Po, where the zeolite absorbs high amounts of each Xylene, but a reduced amount of both at the same time. At 95% P/Po the sorption is comparable to that of o-Xylene, suggesting that at higher P/Po, o-Xylene can better compete for sites than p-Xylene.

This experiment demonstrates the complex behaviour of vapour sorption on zeolites, showing that co-adsorption is measurable by using dual channel SoS sensors in a DVS instrument.

Conclusion

The SoS sensor is a novel method of measuring the composition of vapours and gases. With additional benefits over traditional gas composition measurement techniques, the SoS sensor is compatible with a wide range of solvents over varying temperatures. As an accurate and rapid online measurement of gas composition it allows the measurement of co-adsorption, and with feedback mechanisms to ensure target partial pressures with high precision.

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Head Office:

Surface Measurement Systems, Ltd
5 Wharfside, Rosemont Road
London HA0 4PE, UK
Tel: +44 (0)20 8795 9400
Fax: +44 (0)20 8795 9401
Email: science@surfacemeasurementsystems.com

United States Office:

Surface Measurement Systems, Ltd, NA
2125 28th Street SW, Suite I
Allentown PA, 18103, USA
Tel: +1 610 798 8299
Fax: +1 610 798 0334

