Surface Measurement Systems
World Leader in Sorption Science

BTA Technical Note 1001

BTA Frontier: A versatile breakthrough analysis instrument for realistic gas and vapor sorption applications

Surface Measurement Systems Ltd.

Introduction

Surface Measurement System's Breakthrough Analyzer (BTA) Frontier is a vital tool in laboratory environments, offering precise and reliable measurements across a range of scientific and industrial applications such as energy storage, carbon capture, and filtration technologies by enabling precise gas/vapor measurement under real-world conditions. This advanced instrument is designed to streamline the analysis of material properties, particularly in the context of capture and separation processes. Its high sensitivity and accuracy allow researchers to gain deeper insights into gas-solid interactions. This technical note explores the key features of the BTA, emphasizing its importance as a versatile, high-performance instrument for various analytical tasks.

Breakthrough Analysis Method

The breakthrough analysis method (BTA) is a chromatographic technique which operates on a packed cylindrical bed (or column) of sample open at two ends. It introduces a regulated gas or vapor mixture into one side of the column, that interacts with the packed bed, and monitors the effluent, or outlet gas concentrations and flowrate. A schematic is shown in Figure 1.

In the BTA Frontier, an advanced gas mixing system generates an accurate composition of up to 5 gases, including a balance of inert gas that does not adsorb or interact with the sample, referred to as carrier gas. Humidity and organic vapours can be generated through the bubbling method, passing the flow through reservoirs filled with liquid, and whose concentrations are adjusted by precisely blending with dry gases in a specific ratio. Pressure indicators (PI) before and after the column monitor the pressure drop across the sample, while various detectors including Relative Humidity (RH), NDIR (CO_2), Photoionization Detectors (PID), and Thermal Conductivity Detector (TCD), continuously measure the concentration and characteristics of the feed and exhaust gas from the column. The outlet gas flowrate is also precisely measured by a mass flow meter (MFM). All gas mixing, vapor generation, tubing, columns, and detectors are housed within an incubator, where the temperature is carefully controlled to avoid condensation. The columns are surrounded by a dedicated resistive oven, which is independently controlled and enables studying high-temperature processes including activation, regeneration, reaction, etc.

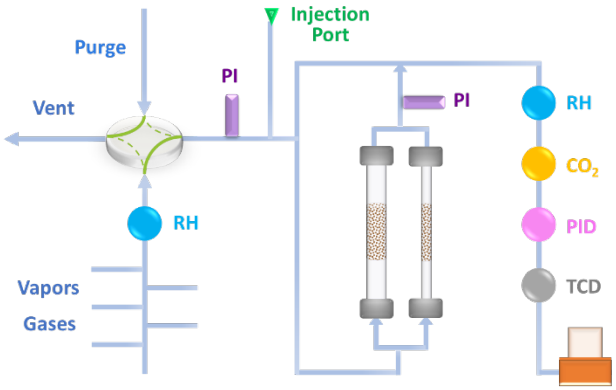

Fig 1. Schematic of the breakthrough analyzer.

Information Obtained From BTA

A typical breakthrough curve obtained from the BTA Frontier is shown in Figure 2 which illustrates the probe molecule gas phase concentration front passing through a packed bed of sorbent material and its measurement of front at the outlet.

Initially, as the gas flows through the sorbent, the material fully captures the probe molecules, resulting in an outlet gas concentration (C/C0, where C0 represents the inlet concentration) of zero. Over time, the sorbent material becomes saturated, and the front reaches the outlet, leading to the "breakthrough" point, denoted by tb. The curve then steepens, as the sample approaches full saturation. Finally, the equilibrium time, te, marks the point where the sorbent is fully saturated, and the gas concentration at the outlet matches the inlet concentration (C/C0 equals 1).

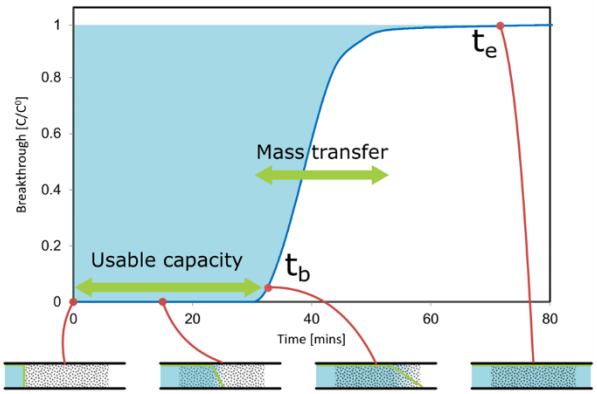

Fig 2. Breakthrough curve for CO_2 adsorption in a sorbent material, illustrating the progression from initial gas exposure to full saturation. Key parameters include the breakthrough time (tb) where CO_2 begins to emerge, and equilibrium time (te) where the material is fully saturated.

The resulting experiment produces a wealth of critical information on the sorption process. Firstly, by performing a mass balance over the known inlet and outlet molar flowrates, the uptake for the sample of the probe molecule can be obtained. As there are dedicated sensors for multiple components of the gas phase, uptakes of each component from a mixture can be determined, and true multicomponent selectivity can be calculated. The shape of the breakthrough curve is closely related to the mass transfer of molecules from the gas phase to the sorbent active sites. As the column can also include a thermocouple for monitoring the sample temperature, several kinetic and heat transfer parameters can be determined through careful BTA experiments. By purging the saturated column with an inert gas, it is possible to measure what is evacuated from the column.

Broadly, the data from the BTA also provides critical information to simulate real-world processes, including usable capacity, selectivity, heat and mass transfer parameters, all of which are essential for evaluating the performance of sorbent materials in gas capture and separation applications.

Evaluating the gas adsorption/separation performance under realistic conditions is essential, and a key benefit of using the BTA is its ability to perform analyses under both dry and humid conditions. It can provide comprehensive insights into the material's performance across different environmental scenarios. By conducting BTA experiments under dry conditions, researchers can assess the optimal uptake without interference of water. Under humid conditions, the BTA can reveal how moisture affects the sorbent's capacity, kinetics, and durability. This dual analysis is crucial for understanding the real-world applicability of materials particularly where atmospheric humidity is a factor, ensuring that the material's performance is robust and reliable under practical operating conditions.

BTA Frontier Key Features

The BTA Frontier offers several key features that make it an exceptional tool for researchers. It provides a fully integrated, cost-effective solution for accurate, high throughput testing optimised for small sample sizes. The BTA Frontier is a small, bench-top, self-contained instrument – it can even be placed in a fume cupboard. It features an integrated design, with its sensor train including detection for water, CO_2, VOCs, and a generic TCD detector allowing for most experiments to be

performed without the need for the optional Mass Spectrometer (MS), lowering the barrier of entry to accurate sorbent testing while still maintaining full automation of experiments, optimised accuracy and ease of use.

The BTA Frontier's gas generation and mixing system is designed for flexibility and accuracy. It features up to 5 high turn-down mass flow controllers (MFCs), plus a 6th inlet dedicated to an inert purge. The MFCs full scale can be selected as per user requirements, and their calibration can be selected in the software depending on the inlet connected gas. The mixture generation system also includes up to two heated reservoirs for solvent generation. The water/solvent bubblers are located inside the temperature-controlled chamber and are internally heated to mitigate evaporative cooling. The mixing of the saturated and dry gas streams takes place in a custom manifold located in the reservoir cover, with automated shut-off valves. These features ensure a reliable, uniform and condensation-free vapour introduction over long experiments and a TrueDry stream when needed.

The gas flow path can be routed differently to achieve for dead volume minimisation, sample purging and sharp concentration front generation. A bypass can be used to isolate the column section while routing the generated gas to the sensor section. This feature allows for baseline concentration generation to be calibrated and followed. An upstream switching manifold allows for the inlet to the column to be switched between the inert gas stream and the mixed stream. This feature allows for simultaneous gas generation stabilisation and sensor/sample purging and activation, particularly useful during the initial target vapour generation. The gas routing feature ensures the most accurate measurements with challenging mixtures, even on small samples below 100 mg.

The BTA supports a variety of packed bed column sizes – the small column platform with 2 mm, 3 mm, and 4 mm in internal diameter (ID) and the large columns with 10 mm (ID), and of various materials – silanized glass, stainless steel, or quartz. All sizes can be interchanged using the BTA Frontier quick-connect system without the need for any tooling. This flexibility allows for optimized bed packing, ensuring the best sensitivity for a wide range of materials and experimental setups, accommodating a variety of samples, including powders, granules, pellets, fibres, and more. The columns can be used with or without a thermocouple inserted in the packed bed. The thermocouple monitors the sample temperature and highlights any thermal effects during adsorption, desorption or reaction. Pressure transducers are located before and after the column, monitoring the drop in pressure alongside the bed, important information not only for an accurate mole balance, but also for determining whether blockages have occurred during packing.

The two-column system allows for the simultaneous loading of two samples, greatly enhancing workflow efficiency. This capability enables parallel activation and sequential analysis without downtime between tests, optimizing time management in the lab. By scheduling experiments more efficiently, researchers can maximize productivity, making the dual-column system a significant advantage for laboratories requiring high throughput or conducting multiple tests in rapid succession.

After the columns, a wide array of in-built dedicated sensors are used to determine the concentrations of the gas phase as it passes through the sample. Here we can find dedicated sensors for humidity (capacitive), CO_2 (NDIR), and most ionizable organics (PIDs), and a general-purpose thermal conductivity detector (TCD) capable of monitoring most binary mixtures. The advantage of the integrated sensor train is that many experiments can be performed without the use of a mass spectrometer (MS), although one is available as an option for the system if more flexibility is desired. Also, an optional mass flow meter (MFM) can be used here to measure the change in flowrate after the column, a crucial measurement for accurate mole balance over the packed bed, but also a handy tool to monitor for any potential leaks.

The entire gas generation, packed bed and sensor system is housed in the temperature-controlled incubator, which plays an important role in maintaining stable organic and water vapor

generation. This control prevents unwanted condensation, ensuring that experimental conditions remain stable throughout the measurement.

Case Study

The following case study involves several experiments to analyze the carbon capture capability of zeolite 13X and the impact of humidity. BTA analysis is important in the carbon capture field as it provides detailed insights into the adsorption properties of sorbents under real-world conditions. By simulating gas flow, temperature, CO_2 concentrations, and moisture levels, the BTA Frontier allows researchers to evaluate how well sorbents like zeolite 13X can capture carbon dioxide in various applications. This information is useful for improving sorbent performance and ensuring efficiency in industrial carbon capture processes.

First, single component water vapor sorption experiments were conducted to evaluate the material's hydrophilicity, by measuring its adsorption capacity at different temperatures (25 °C and 40 °C) and varying relative humidity (from 10% to 70%). Then, co-adsorption experiments with a wet CO_2 stream were conducted under simulated post-combustion carbon capture conditions (15% CO_2, 60% RH, 25 °C). Regeneration experiments demonstrated the temperature dependency of water and CO_2 as dependency the temperature increased from ambient to 200 °C. Finally, two more cycles of adsorption-desorption were carried out to assess the material's long-term stability.

About 200mg binderless shaped zeolite 13X pellets (0.4 mm diameter) were packed into a 4 mm ID silanized glass column. The sample was activated at 300 °C for 10 hours under a 200 sccm nitrogen flow, followed by cooling to ambient conditions (25 °C). The integrated BTA sensors are used in these experiments, therefore foregoing the need for complex calibration of a mass spectrometer.

Figure 3 shows breakthrough curves for the sorption of water vapor at 50% RH on the zeolite 13X pellets. The results are shown for two temperatures: 25 °C and 40 °C. At 40 °C, the breakthrough occurs earlier when compared to 25 °C. By integrating the breakthrough data, it is found that the uptakes are not significantly different at the two temperatures (14.9 mmol/g vs 15.1 mmol/g at 40 °C and 25°C, respectively). The earlier breakthrough at higher temperatures can then be understood in terms of the difference in absolute water content of the inlet stream, which is about 40% higher at 40°C than at 25°C.

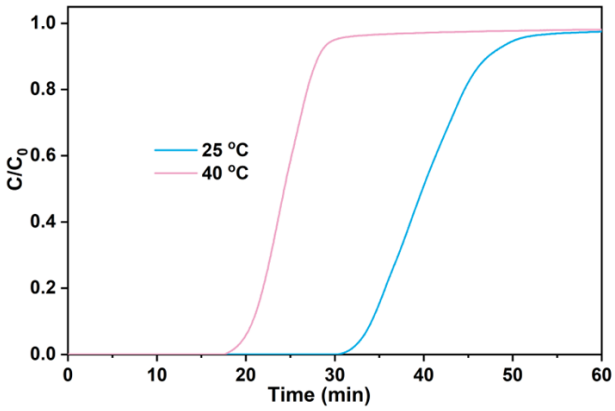

Fig 3. Water (50%RH) breakthrough on zeolite 13X at two different temperatures

Water vapor adsorption on zeolite 13X at 25 °C across different RH levels, ranging from 10% to 70% is shown in Figure 4. As the relative humidity increases, the breakthrough time shortens significantly. At lower humidity levels (e.g., 10%), the breakthrough occurs much later, after approximately 900 minutes, whereas at higher humidity levels (e.g., 70%), it occurs much earlier, around 200 minutes. Calculating the uptake through integration we find that amount of water adsorbed is relatively constant at 14-15 mmol/g throughout the humidity range. This result highlights the hydrophilic feature of zeolite 13X which induces high water vapor uptake even at low relative humidity. The delayed breakthrough time at low humidity is due to the lower molar flowrate of water in the inlet stream leading to a delayed

propagation of the concentration front through the bed.

This behavior analysis is important in applications where the presence of moisture can influence the

overall efficiency of sorbents. The results highlight the importance of considering humidity levels and hydrophilicity of sorbents in designing and optimizing capture processes for industrial applications, as process performance varies significantly with changing environmental conditions.

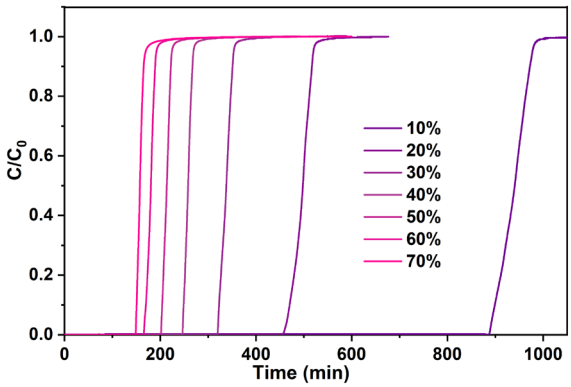

Fig 4. Water adsorption on zeolite 13X at varying levels of relative humidity at 25 °C

Multicomponent adsorption data is crucial for developing effective carbon capture technologies because real-world conditions rarely involve single gases in isolation. The breakthrough analysis shown in Figure 5 demonstrates the significant competitive adsorption between CO_2 and water vapor on zeolite 13X. While zeolite 13X typically exhibits an excellent CO_2 adsorption capacity of around 3.6 mmol/g at 25 °C under dry conditions, the presence of humidity dramatically reduces this performance. At 30% relative humidity, the CO2 capacity drops substantially to just 0.19 mmol/g and decreases further to 0.10 mmol/g at 60% RH. This occurs because water molecules preferentially occupy the adsorption sites on zeolite 13X, effectively blocking CO_2 uptake. The water uptake remains high (14.3-15.5 mmol/g) regardless of humidity level, confirming zeolite 13X's strong hydrophilicity. This competitive behavior cannot be accurately predicted from single-component isotherms alone, highlighting why true co-adsorption measurements are essential for evaluating sorbent materials under realistic capture conditions.

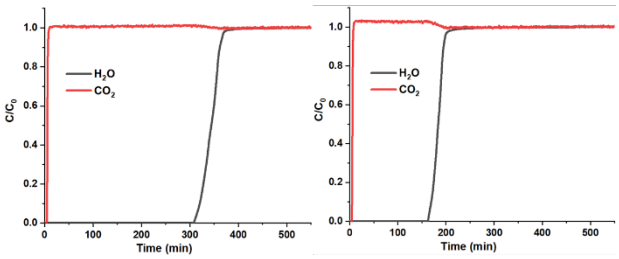

Fig 5. Multicomponent CO_2 / H_2O water breakthrough on zeolite 13X at a 15 vol% CO_2 concentration and varying levels of relative humidity (30 and 60% RH) at 25 °C

The ease of regeneration is another essential factor to evaluate the cost of use of sorbents. Figure 5 shows the regeneration profile of zeolite 13X while heating from the previous saturated conditions after the co-sorption of water and CO2 (15% CO2, 60% RH, 25 °C). Water and CO2 show very different desorption behaviour. Water desorbed over a broad temperature range (ambient to 200 °C), with distinct peaks observed at approximately 30 °C and 120 °C, indicating the presence of adsorption sites with varying strengths in zeolite 13X. A single sharp CO_2 desorption peak appears at 25 °C, indicating a low amount of CO_2 adsorbed in a population with a low guest-host affinity. The results suggest that during CO_2 and water co-adsorption, water binds more strongly to the zeolite and requires sustained heating for complete desorption.

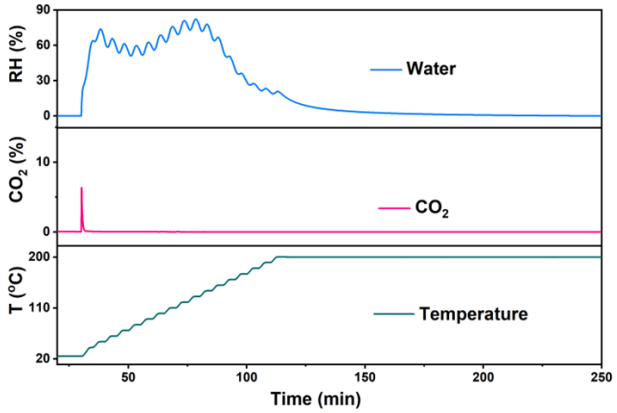

Fig 6. Regeneration of zeolite 13X from sorption of water (top) and CO_2 (middle) using elevated temperatures (bottom)

Cyclic testing is crucial for evaluating the durability and long-term performance of materials under repeated use, ensuring their reliability in practical

applications. Figure 6 shows the cyclic adsorption behavior of water and carbon dioxide on zeolite 13X over time. The adsorption and desorption processes remain highly consistent across the three cycles, with no significant decrease in adsorption capacity. These results demonstrate that at these conditions zeolite 13X is stable during both adsorption and desorption, even when exposed to water and high temperatures.

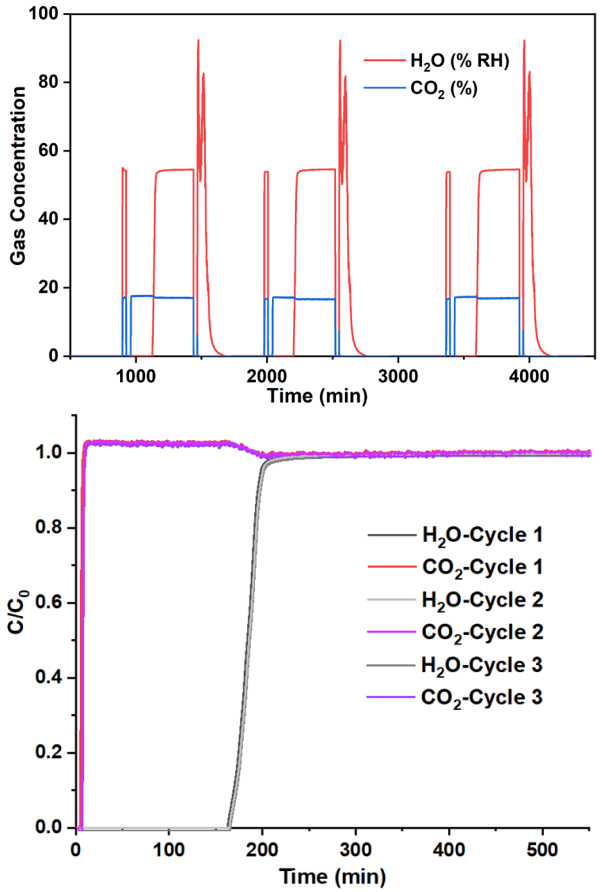

Fig 7. CO_2 and H_2O sorption cycles on zeolite 13X – raw data (left) and processed, overlapped data (right)

Conclusions

The BTA Frontier is an essential tool in the laboratory for studying the gas capture and separation efficiency of materials. Its fully integrated and cost-effective design make it accessible to a broad range of researchers. Optimized for small sample sizes it can accommodate for a wide range of sample types. The two-column system allows simultaneous loading of two columns. This enables sequential analyses, significantly enhancing workflow efficiency and maximizing productivity in the lab. The system is particularly suited for two applications: carbon dioxide and VOC capture under dry and wet conditions. These applications are important in areas such as environmental science and industrial air purification, where understanding gas-solid interactions is essential.

To demonstrate the capabilities of the BTA, breakthrough analyses were performed using zeolite 13X. Breakthrough curves were observed using water and CO_2 reflecting real world conditions. The breakthrough profiles revealed the sorbents adsorption capacities at different relative humidities. The BTA was also used to study the regeneration of zeolite 13X after saturation with water and CO_2. These differences revealed the stronger binding of water to zeolite compared to CO_2 and emphasizes the need for precise temperature control during regeneration.