APPLICATION NOTE

How the GasMix™ Enhances Ultra-Low-Level Sulfur and Ammonia Analysis

with the PAC SeNSe² Detector

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INTRODUCTION

The rapid development of hydrogen as an energy carrier has significantly increased the demand for reliable impurity monitoring at extremely low concentration levels. Trace contaminants such as sulfur compounds and ammonia are of particular concern, as even concentrations in the single-ppb range can poison catalysts, damage fuel cells, and reduce process efficiency. International specifications for hydrogen quality (such as **ISO 14687**) therefore impose stringent limits on these species, requiring analytical techniques capable of high selectivity, sensitivity, and long-term stability.

While modern detectors are capable of reaching single-ppb detection limits, calibration at such concentrations remains a major challenge. Commercially available calibration gases in this range are often difficult to source, expensive, and limited in certified lifetime. In addition, reactive compounds such as sulfur species and ammonia may suffer from stability issues when stored in static cylinders at ultra-low concentrations.

To address these challenges, PAC combines its SeNSe² sulfur and nitrogen chemiluminescence detector with the AlyTech **GasMix™** dynamic gas dilution system. Together, these technologies form an integrated analytical platform capable of generating calibration gases on demand and delivering reliable ultra-trace measurements in hydrogen matrices.

Figure 1 – Chemiluminescence reaction mechanism of the PAC SeNSe² detector

PRINCIPLE OF CHEMILUMINESCENCE DETECTION WITH SENSE²

The PAC SeNSe² (SCD/NCD) enables selective detection of sulfur and nitrogen species, independent of the sample matrix. It offers excellent performance in terms of sensitivity, selectivity, equimolar response, and linearity (see Figures page 3).

Following chromatographic separation, sulfur compounds are converted to sulfur monoxide (SO), which reacts with ozone to form an excited sulfur dioxide species that emits light as it relaxes back to its ground state. Similarly, nitrogen compounds are converted to nitric oxide (NO), which reacts with ozone to form excited nitrogen dioxide that emits light upon returning to the ground state. The emitted light intensity is directly proportional to the analyte mass entering the detector, enabling highly sensitive and selective quantification.

- Detection of sulfur components at single-ppbM (nmol/mol) concentration levels.
- Ammonia detection below **100 ppbM.**
- Wide linear dynamic range for reliable quantification across several orders of magnitude.

These characteristics make the SeNSe² particularly well suited for regulatory hydrogen quality control and process monitoring.

DYNAMIC GAS DILUTION AND TRACEABLE CALIBRATION

To support the sensitivity of the SeNSe² detector, a robust calibration strategy is essential. The AlyTech **GasMix™** system applies dynamic dilution in accordance with **ISO 6145-7**, generating calibration gases through controlled mixing of a certified source gas with a diluent gas.

In dynamic dilution, the final concentration is determined by the ratio of the respective gas flow rates. Calibrated mass flow controllers regulate the flow of both the concentrated standard and the diluent, ensuring precise and reproducible mixing. The generated concentration is mathematically defined by the known concentration of the source gas and the controlled flow ratio, enabling **direct traceability to certified reference materials**.

An important advantage of dynamic dilution is that mixtures are generated continuously and consumed immediately, significantly reducing the stability issues commonly observed with static ultra-low concentration cylinders — particularly for reactive species such as ammonia and sulfur compounds. Because the concentration is calculated from traceable input parameters, including the mother gas , the associated uncertainty can be defined and propagated, strengthening metrological confidence in both calibration and analytical results.

APPLICATION EXAMPLE AND METHODOLOGY

The turn-key PAC solution configured with the SeNSe² SCD/NCD and combined with the AlyTech **GasMix™** dynamic dilution system was evaluated for the determination of trace sulfur compounds and ammonia in hydrogen. Calibration gases were generated on demand by dynamically diluting certified source gases with hydrogen following ISO 6145-7 principles and introduced directly into a PAC GC analyser equipped with the SeNSe² detector.

RESULTS

Sensitivity

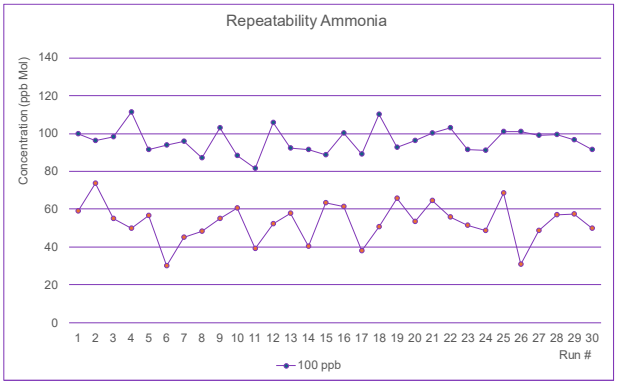

Figure 2 – Sensitivity: NH_3

High sensitivity is essential to detect sulfur compounds and ammonia at concentration levels relevant for hydrogen quality control. Using the SeNSe^2 detector, sulfur species such as H_2S, COS, and SO_2 were reliably detected at single-ppbM levels, while ammonia was detected below 100 ppbM (Figure 2).

Stability

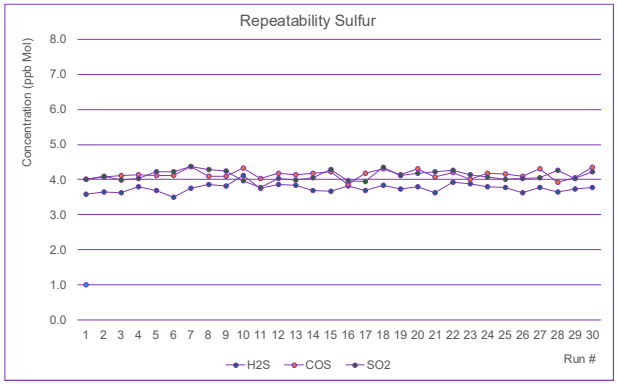

Figure 3 – Stability of sulfur components at 4ppb

Repeat injections of dynamically generated calibration levels showed stable detector response over time, indicating reproducible gas generation by the **GasMix™** system and consistent SeNSe^2 detector performance (Figure 3). This stability is particularly important for reactive sulfur species and ammonia, which are prone to adsorption effect at ultra-low concentration levels.

Linearity

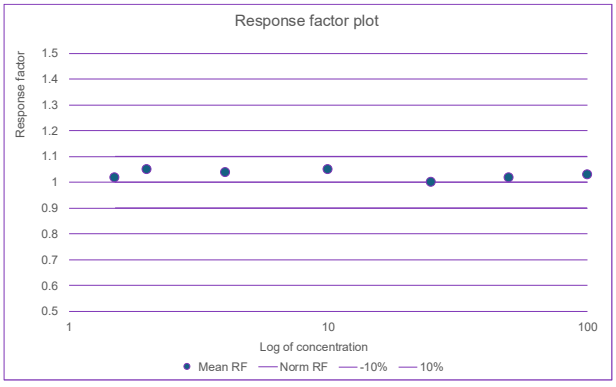

Figure 4 – Linearity: detector response vs. concentration

Linearity was evaluated by generating multiple concentration levels through dynamic dilution from a single certified source gas using the **GasMix™** system. The SeNSe^2 detector showed consistent proportional response across the tested low-ppb range for all sulfur species (Figure 4), confirming that dynamic dilution does not introduce observable bias at ultra-trace concentrations.

Equimolarity

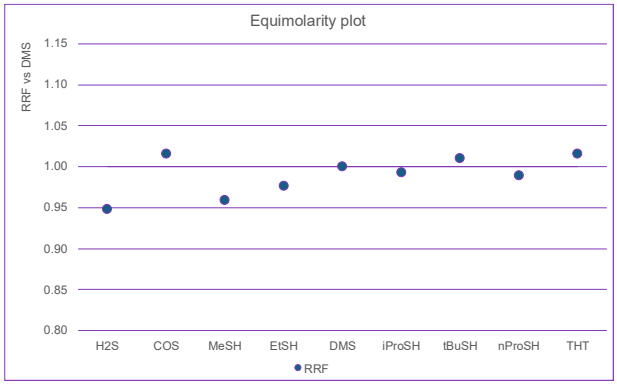

Figure 5 – Equimolarity: response for H_2S, COS, SO_2

The SeNSe^2 detector exhibited an equimolar response for different sulfur species, including H_2S, COS, and SO_2, generated at comparable sulfur concentrations using the **GasMix™** system (Figure 5). This behaviour confirms that detector response depends on total sulfur mass rather than molecular structure, allowing a single sulfur standard to be used for calibration of multiple sulfur compounds.

Selectivity

Following chromatographic separation, the SeNSe^2 detector responds selectively to sulfur- and nitrogen-containing compounds, enabling accurate measurement of the components of interest without interference from the hydrogen sample matrix.

Summary Statistics — Bias and Repeatability

	H_2S	COS	SO_2	NH_3	Total S
Mean	3.76	4.14	4.11	96.30	12.02
Target	3.59	4.00	4.00	100.00	11.59
Bias	0.17	0.14	0.11	-3.70	0.43
Bias%	4.71	3.62	2.87	-3.70	3.70
RSD%	3.2	2.9	3.4	7.1	1.0

Table 1 – Mean measured values, target concentrations, bias, and RSD% across all tested components

The results show low bias (typically below 5%) and good repeatability across all components, confirming both the accuracy of the dynamic dilution process and the stability of the SeNSe^2 detector response.

RESULTS AND DISCUSSION

The combined PAC SeNSe^2 detector and AlyTech **GasMix™** dynamic dilution system demonstrated excellent performance for the determination of sulfur compounds and ammonia in hydrogen at ultra-low concentration levels.

Dynamic dilution using the **GasMix™** enabled on-demand generation of calibration mixtures in the low-ppb range from certified, higher-concentration source gases, avoiding stability and adsorption challenges typically associated with static ultra-low-concentration cylinders. Because the generated concentration is defined by traceable input parameters — namely the source gas concentration and the controlled flow ratios — the resulting calibration levels are directly traceable and associated with a defined measurement uncertainty.

For ammonia analysis, the system demonstrated reliable detection below 100 ppbM in hydrogen. Despite the well-known challenges associated with ammonia adsorption and surface interactions, the SeNSe^2 detector provided clear, well-defined peaks with reproducible response when combined with dynamically generated calibration gases.

Overall, the results show that reliable quantification at single-ppb levels requires more than detector sensitivity alone. While the SeNSe^2 chemiluminescence detector provides the necessary element-specific sensitivity and selectivity, the **GasMix™** system is essential to generate calibration gases with known composition, defined uncertainty, and sufficient short-term stability at these concentration levels.

CONCLUSION

Measuring sulfur compounds and ammonia at ultra-trace levels in hydrogen demands both advanced detection and precise calibration. The combination of PAC's SeNSe^2 detector and AlyTech **GasMix™** delivers an efficient, reliable and traceable solution:

- SeNSe^2 provides sensitive, element-specific detection for sulfur (single-ppb) and ammonia (sub-100-ppb)
- **GasMix™** generates traceable calibration gases on demand for accurate, reproducible calibration
- Dynamic dilution ensures stability and avoids adsorption issues common in static cylinders
- Excellent linearity and repeatability keep detector response and calibration consistent
- Together, SeNSe^2 and **GasMix™** set a benchmark for ultra-trace gas analysis across diverse applications