

Chromatogram Peak Detection Using a MOS Sensor with MS Validation

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Metal oxide semiconductor (MOS) sensors offer cost-effective gas detection but face challenges due to cross-sensitivity, baseline drift, and long-term aging effects that complicate their use as gas chromatography (GC) detectors. This work presents a mass spectrometry (MS) guided validation framework for GC-MOS systems. Using a 59-compound EPA mixture, a smoothed-derivative peak detection algorithm was developed to identify and validate MOS response regions against MS-confirmed chromatographic peaks. Analysis showed that 79% of detected MOS peaks aligned with MS-validated retention windows, while 21% were instrumental artifacts. The framework also quantified systematic retention time drift (~2 s over 20 injections) and sensor degradation effects, providing a practical path for laboratory validation.

Keywords: signal processing, metal oxide semiconductor sensor, gas chromatography, mass spectrometry validation.

I. INTRODUCTION

Multi-sensor arrays based on metal oxide semiconductor (MOS) sensors have demonstrated strong potential for application in medical diagnostics and food analysis [1]. MOS sensors exhibit high sensitivity while maintaining low size, power consumption, and cost. However, their selectivity is limited due to cross-sensitivity; integrating gas chromatography separation addresses this key limitation. Recent portable GC-MOS devices provide non-invasive and cost-effective solutions for applications such as breath analysis for cancer screening and food safety and quality monitoring. These approaches rely on the detection of volatile organic compounds (VOC), which serve as biomarkers of metabolic alterations in humans and indicators of oxidative degradation and microbial spoilage in food matrices. However, the commercial deployment of GC-MOS systems is still constrained by challenges in data interpretation.

Among all the difficulties, separating genuine analyte-driven responses from confounding effects such as baseline drift, sensor aging, and other sources of instrumental variability is particularly challenging.

In this work, chromatogram processing algorithms are proposed for MOS-based detection and result validation against mass spectrometry as a reference method. The paper first outlines the methodology (Section II), followed by the results, and finally discusses the implications and key findings.

II. EXPERIMENTAL SETUP

The validation system consisted of a Single Quadrupole GC-MS (ISQ 7000, Thermo Fisher Scientific, USA) coupled to

a MOS sensor (ASMLV-P2, ScioSens, The Netherlands). The analyte was a standard EPA mixture containing 59 volatile organic compounds (VOCs). As in [2], the column outlet flow was split between the MOS sensor and the mass spectrometer. Twenty splitless injections (0.20 μ L) were performed using a carrier gas flow of 3 mL/min. The GC oven temperature was ramped from 50 $^{\circ}$ C to 200 $^{\circ}$ C.

Two MOS sensors were tested:

- Old sensor: in the first 14 injections (3 each at 200 $^{\circ}$ C, 300 $^{\circ}$ C, 500 $^{\circ}$ C, and 5 at 400 $^{\circ}$ C MOS static operation temperature)
- New sensor: in the last 6 injections (3 each at 200 $^{\circ}$ C and 400 $^{\circ}$ C)

Data acquisition rates: MS at 5 Hz, MOS at 250 Hz.

A. MS-Guided Validation Pipeline

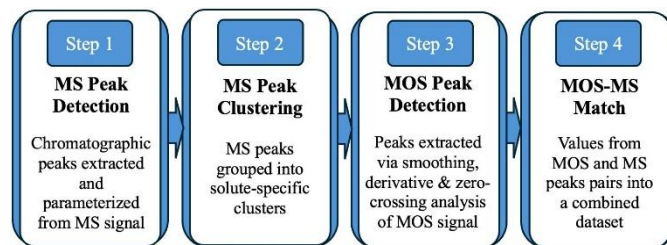


Fig. 1. Feature extraction workflow.

Step 1 – MS peak detection: Following signal smoothing, chromatographic peaks were identified in the MS signals using the `find_peaks` function from SciPy, a Python signal processing library. Each peak was characterized by peak height, left boundary (t_{left}), peak time (t_{peak}), and right boundary (t_{right}). Peak net area was computed via trapezoidal integration.

Step 2 –MS Peak clustering: To identify recurring solutes across injections, peaks were clustered using DBSCAN (Density-Based Spatial Clustering of Applications with Noise) based on retention time similarity (Fig. 2). The temporal tolerance used here was 2.34 s, corresponding to half the minimum observed inter-peak separation across all injections. This yielded 64 solute-specific clusters, consistent with the 59-compound mixture plus potential column residue.

Step 3 – MOS peak detection: Unlike MS, MOS signals exhibit broader, less-defined peaks where right boundaries and baseline are ambiguous. A smoothed-derivative approach was applied:

1. Savitzky-Golay filtering.
2. First derivative computation.
3. Zero-crossing detection: Negative-positive: band start (t_{left}); Positive-negative: peak (t_{peak}) to catch local maximums.

Extensive analysis revealed optimal Savitzky-Golay smoothing with window size=2000 samples (8 s at 250 Hz acquisition rate), matching approximately twice the minimum gap between MS peaks (4.68 s). This window captures signal variance while preserving peak features.

Peak Time Clustering

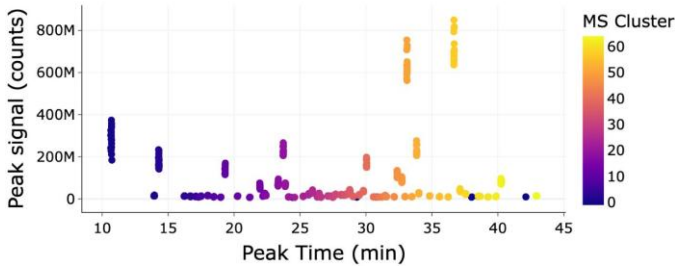


Fig. 2. DBSCAN clustering algorithm of MS collected peaks from raw signal, combining all the 20 injections. The x-axis represents the retention time, while the y-axis corresponds to the MS peak intensity.

Step 4 – MS-MOS match: MOS peaks were matched to MS clusters using a probabilistic approach based on Gaussian peak modeling. For each MS-detected solute, the Bhattacharyya coefficient was computed with all MOS peaks from the same injection and temperature setting. The MOS band yielding the highest overlap score was assigned to that cluster. When a single MOS peak matched multiple MS clusters, only the highest-scoring match was retained, resulting in 689 validated MOS detections (79 % of 873 initially detected peaks).

III. RESULTS

Figure 3 shows representative combined MS and MOS chromatograms. The sharp MS peaks contrast with broader MOS responses, motivating the need for MS-guided validation.

Combined MS and MOS chromatograms

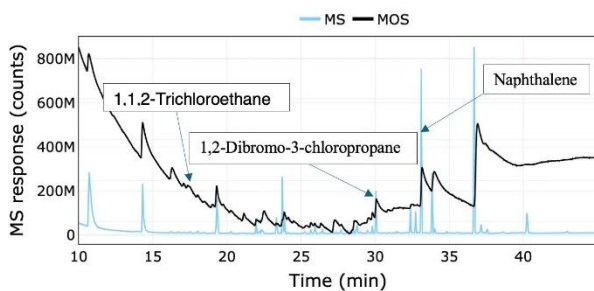


Fig. 3. Combined MS and MOS (Ω^{-1}) chromatograms showing retention time alignment for selected compounds from the EPA mixture. Some of the identified compounds are highlighted.

Among the results obtained, some are presented here:

A. MS-MOS Alignment Performance

The MS detector identified 1,275 chromatographic peaks across 20 injections, which clustered into 64 distinct solutes

using DBSCAN (Fig. 2). The MOS sensor initially detected 873 peaks, of which 79 % aligned with MS-validated retention windows and were retained for analysis. The remaining 21 % of peaks showed no MS correspondence and were classified as potential artifacts from baseline drift, noise, or interference. However, MOS sensors can detect compounds below MS limits [3]. Consistent MOS responses across injections and temperatures may represent genuine low-concentration analytes rather than artifacts, as MOS sensors exhibit superior sensitivity for certain volatile classes.

Notably, octamethylcyclotetrasiloxane (OMCTS, RT 23:21 min) was detected in all injections despite not being present in the EPA mixture. OMCTS probably originates from septum bleeding. Prolonged siloxane exposure causes MOS sensor poisoning [4], as observed in the aged sensor used initially (see Section III-C).

B. Systematic Retention Time Drift

Visual inspection of MS solute clusters revealed that injections with the lowest retention times often corresponded to the latest injection numbers, suggesting systematic temporal drift. Formally, for each solute s , retention times RT were referenced to the first injection, and the relative shift was defined as

$$\Delta RT_{s,i} = RT_{s,i} - RT_{s,1} \quad (1)$$

Where i denotes the injection index. For each injection i , the set $\{\Delta RT_{s,i}\}$ was summarized by its mean across solutes, and the associated uncertainty was quantified via the 95 % confidence interval of the mean. This formulation isolates temporal effects while removing solute-specific retention time offsets.

Mean Difference in Retention Time (vs. Injection 1) with 95% Confidence Interval

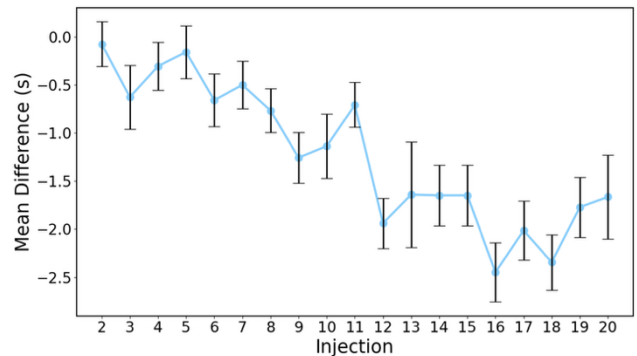


Fig. 4. Mean retention time shift relative to injection 1 across injections. Retention times were normalized per solute to the first injection; points show the mean across solutes and error bars the 95 % confidence interval, evidencing systematic temporal drift.

This quantitative analysis showed mean retention time reduction of ~ 2 seconds between injection 1 and injection 20, with within-cluster variability (IQR) of ~ 0.5 seconds. A clear step change is observed between injections 11 and 12, consistent with the experimental schedule, as injections up to

11 were conducted on the same day, while injection 12 and subsequent runs were performed on the following day.

This drift highlights the need for dynamic retention time correction in long-term GC deployments, particularly for miniaturized or portable systems where column maintenance is infrequent.

C. Sensor Degradation Detection

Comparison between old and new MOS sensors (Tab. 1) revealed performance differences attributable to sensor poisoning:

TABLE 1. COMPARISON OF SOLUTE DETECTION FREQUENCY ACROSS DIFFERENT OPERATING TEMPERATURES FOR AGED AND NEW MOS SENSORS. THE DATA HIGHLIGHTS A SIGNIFICANT LOSS OF SENSITIVITY IN THE AGED SENSOR, ESPECIALLY AT 200 °C.

Temperature (°C)	Number of Detected Solutes	Percentage (over the 59 injected solutes)
200°C	31	52 %
400°C	39	71 %
500°C	55	93 %
200°C, new sensor	47	80 %
400°C, new sensor	54	92 %

IV. DISCUSSION

A. Retention Time Drift Correction Strategies

The observed systematic drift (~2 s over 20 injections) may seem small but is significant relative to typical compound separation windows (4-5 s minimum gap in the data analysed). For robust identification, the following are recommended:

1. Retention index normalization: Use standard, known compounds in each batch to compute relative retention indices rather than absolute times.
2. Adaptive time windows: Expand matching tolerances for later injections based on estimated drift rate.
3. Column maintenance scheduling: Monitor drift velocity; accelerated drift could indicate column degradation requiring replacement.

B. Limitations

The current study presents some limitations. First, only a single type of MOS sensor was tested, specifically the SnO₂-based ASMLV sensor. Second, the experiments were conducted under controlled laboratory conditions using EPA standard gas mixtures, which may not fully represent real-world scenarios. Finally, data processing was performed offline, meaning that real-time analysis was not implemented.

V. CONCLUSIONS

This work demonstrates a mass spectrometry-guided validation framework for MOS sensors in GC systems, addressing the critical challenge of distinguishing genuine chemical responses from instrumental artifacts in electronic nose applications.

Analysis of a 59-compound EPA mixture showed that 79 % of detected MOS peaks aligned with MS-validated retention

windows. The system identified systematic retention time drift (~2 seconds over 20 injections) and quantified sensor degradation effects.

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